Interatomic potentials of metal dimers: probing agreement between experiment and advanced ab initio calculations for van der Waals dimer Cd$_2$

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Interatomic potentials of metal dimers: probing agreement between experiment and advanced \textit{ab initio} calculations for van der Waals dimer Cd$_2$

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\textbf{ABSTRACT}

A critical review of experimental studies and \textit{ab initio} calculations of the low-lying ungerade excited and ground state interatomic potentials of Cd$_2$ van der Waals dimer is presented. Consistency as well as discrepancies between experimental results and \textit{ab initio} calculations are probed. In order to obtain better agreement with existing experimental data, fill in gaps in current knowledge and provide a unifying framework, advanced all-electron \textit{ab initio} calculations were performed and simulations of the reported spectra were executed. From simulations of laser-induced fluorescence excitation and dispersed emission spectra, analytical and/or point-wise representations of the A$^10_u$ (5$^1P_1$), B$^11_u$(5$^1P_1$), a$^31_u$ (5$^3P_1$), b$^30^+_u$ (5$^3P_1$) and c$^31_u$(5$^3P_2$) excited-, and the X$^10^+_g$ (5$^1S_0$) ground-state Cd$_2$ interatomic potentials were obtained. The comparison of the \textit{ab initio} calculated potentials with results of the analyses allows to illustrate a current state-of-the-art of theory-and-experiment correspondence for such a demanding system. Results are presented in the context of an importance of the group 2 and group 12 metal dimer interatomic potentials especially, in ultra-cold physics and chemistry, and in fundamental tests of quantum mechanics.

\textbf{KEYWORDS}

Cadmium dimers (Cd$_2$); \textit{ab initio} calculations; van der Waals (vdW) complexes; laser-induced fluorescence (LIF) excitation spectra; LIF dispersed emission spectra; interatomic potentials; potential energy curves (PEC); bond lengths; vibrational energy structures; rotational energy structures; molecular isotopic composition; supersonic expansion beams

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5.3. Future directions
1. Introduction

1.1. Importance of group 12 dimer Cd₂

In different branches of chemical physics, physical chemistry, condensed-matter physics and chemistry, quantum chemistry and physics, atomic and molecular physics (cold and ultra-cold including), and in the chemistry of cold reactions, there is rapidly growing interest in the forces acting between neutral closed-shell atoms at different interatomic distances. It concerns the s² full valence orbit group 12 transition metal (M) atoms (M = Zn, Cd, Hg) as well as group 2 alkaline earth M atoms (M = Be, Mg, Ca, Sr, Ba, Ra) along with rare earth M atoms (M = Yb, Er, Dy).

Group 12 cold and ultra-cold atoms may interact in a variety of traps for Zn [1], Cd [2] or Hg [3–9]. Experiments of current interest that involve Hg₂ include matter-wave interferometry, photo-association of cold molecules [10], optical lattice clocks [3,4,6], quantum degeneracy, quantum entanglement created via dissociation of diatomic Hg₂ molecules [11] and internal vibrational cooling of molecules [12]. Recently, the interest in higher-excited molecular electronic states has been revived in the context of two- and three-step photo-association (PA) processes in magneto-optical traps (MOT); for Hg₂ (as discussed by Villwock et al. [7]), the cooling process is made highly efficient and leads to the generation of ultra-cold Hg₂ from Hg in a MOT.

Similarly as Hg₂, van der Waals (vdW) dimer Cd₂ has been a subject of numerous experimental and theoretical ab initio studies [13,14]. Due to its very shallow predominantly vdW ground state and several low-lying strongly bound excited states, there has been an interest in Cd₂ due to the possibility of laser applications [15–17] (in analogy with the homo- and hetero-atomic noble gas excimers and exciplexes). Creation of quantum entanglement via dissociation of diatomic Cd₂ [18] molecules has been proposed and is in an early stage of realisation [19–21]. Knowledge on Cd₂ interatomic potentials is highly desirable. Methods of investigating experiment-to-theory correspondence as well as programme, tests and procedures developed for Cd₂ studies can be employed for other neutral–neutral M₂ dimers mentioned above.

1.2. Electronic structure of homoatomic dimer: the case of angular momenta couplings in Cd₂

Figure 1 presents a schematic diagram showing correlation of the 5s² ¹S₀, 5s5p ³P₁ and 5s5p ¹P₁ (where J = 0, 1, 2 is a total atomic angular momentum) Cd atomic levels with Cd₂ molecular energy states. Upper part of Figure 1 presents also vector diagrams for the Hund’s coupling cases (c) and (a) on the left- and right-hand-sides, respectively. In this figure, the following vectors are depicted: the angular momentum of nuclear rotation N, total electronic orbital angular momentum L, total electronic spin S. The ordering of coupling of these angular momenta that results in total angular momentum J depends on the hierarchy of the interactions within the molecule.
Figure 1. (Colour online) A schematic diagram showing correlation of the $5s^21S_0, 5s5p^2P_1$, and $5s5p^1P_1$ (where $J = 0, 1, 2$ is a total atomic angular momentum) Cd atomic levels with Cd$_2$ molecular $s$–$o$ electronic states of Hund’s case (c) i.e. strong $s$–$o$ interaction (shown on the left) and Hund’s case (a) i.e. very weak $s$–$o$ coupling interaction (shown on the right). Thick horizontal lines indicate molecular Hund’s case (c) ungerade states studied experimentally via a direct electric-dipole excitation from the ground state. To facilitate the Hund’s cases (c)–(a) correspondence, a colour code was used. Allowed (wavelengths in nm) and forbidden transitions in Cd atom are also shown. Interatomic potentials and allowed transitions in Cd$_2$ are shown in Figure 2. Upper part shows vector diagrams for the Hund’s coupling cases (c) and (a). Cones of precessions are also shown with dotted lines.
First, let us consider Hund’s case (a) [22] where the spin–orbit (s–o) interaction is neglected in the first approximation. Cylindrical symmetry of cadmium dimer implies that only projections of \( \mathbf{L} \) and \( \mathbf{S} \) on the internuclear axis are conserved; their magnitudes along the internuclear axis are denoted by \( h\Lambda \) and \( h\Sigma \), respectively. Obviously, the sum \( h\Omega = h(\Lambda + \Sigma) \) is also conserved. The total angular momentum \( \mathbf{J} \) is formed from rotational angular momentum \( \mathbf{N} \) perpendicular to the internuclear axis \( \hat{z} \) and sum of projections \( h(\Lambda + \Sigma) \hat{z} \) i.e. \( \mathbf{J} = h(\Lambda + \Sigma) \hat{z} + \mathbf{N} \). The notation of electronic terms for Hund’s case (a) follows the general scheme: \( ^{2S+1}(\Lambda)\Omega \), where \( \Lambda = \Sigma, \Pi, \Delta, \ldots \) for \( \Lambda = 0, 1, 2, \ldots \), respectively or, in short, \( ^{2S+1}(\Lambda) \). Note: \( \Sigma \) states (for which \( \Lambda = 0 \)) should not be confused with a projection of \( \mathbf{S} \) on the internuclear axis, the \( \Sigma \). As the homonuclear diatomic molecule possesses centre of symmetry, states of such molecule are of gerade (even-parity) or ungerade (odd-parity) symmetry; consequently, additional ‘g’ or ‘u’ subscript, respectively, appear as follows \( ^{2S+1}\Sigma^g \) or \( ^{2S+1}\Sigma^u \). Finally, the electronic \( ^{2S+1}\Sigma \) states may change sign upon a reflection with respect to the plane containing internuclear axis i.e. \( \sigma \left| ^{2S+1}\Sigma^{\pm} \right> = \pm \left| ^{2S+1}\Sigma^{\pm} \right> \).

For relatively heavy molecules, like e.g. \( \text{Cd}_2 \), the s–o interaction has to be taken into account. In this case, called Hund’s case (c), \( \Lambda \) and \( \Sigma \) cease to be good quantum numbers. \( \mathbf{L} \) and \( \mathbf{S} \) are coupled to the total electronic angular momentum \( \mathbf{J} \) by the s–o interaction. Due to cylindrical symmetry of the molecule, the good quantum number \( \Omega \) is associated with the projection of \( \mathbf{J} \) on the internuclear axis with eigenvalue \( h\Omega \) (see the left upper part of Figure 1). Finally, the projection of total electronic angular momentum and the angular momentum of nuclear rotation form the resulting total angular momentum i.e. \( \mathbf{J} = h\Omega \hat{z} + \mathbf{N} \), just as in Hund’s case (a). In Hund’s case (c), the notation of electronic terms follows the scheme: \( ^{2S+1}\Omega_g \) or \( ^{2S+1}\Omega_u \). As in the Hund’s case (a), \( ^{2S+1}0 \) states are additionally denoted by superscripts ‘+’ or ‘−’ corresponding to the reflection symmetry [see Hund’s case (a)].

For detailed explanation of the Hund’s cases, the reader is referred to textbooks and articles on molecular spectroscopy (e.g. [23–25]).

In Figure 1, the molecular electronic energy states of \( \text{Cd}_2 \) are depicted using notation described above. The ground state \( \text{X} \ ({}^10^+ \text{ or } ^1\Sigma^+ \text{ Hund’s case (c) or (a), respectively}) \), and excited states: a (\(^3\Pi_u \text{ or } ^3\Sigma^u \)), \( \text{b} \ ({}^1\Pi_u \text{ or } ^1\Pi_g) \), c \( ({}^1\Pi_g \text{ or } ^3\Pi_g) \), A \( ({}^1\Pi_u \text{ or } ^1\Pi_g) \) and B \( ({}^1\Pi_g \text{ or } ^3\Pi_g) \) are among them. All of them correlate with the \( 5^3\Sigma^0 \) state i.e. transitions to the \( \text{a}^3\Pi_u(5^3\Pi_1) \), \( \text{b}^1\Pi_u(5^3\Pi_1) \) or \( \text{c}^1\Pi_g(5^3\Pi_1) \) atomic asymptotes. In the review, the rigorous Hund’s case (c) notation, as the only appropriate case of \( \text{Cd}_2 \) is used. However, although in relatively heavy \( \text{Cd}_2 \) dimer the Hund’s case (c) coupling is in effect, it is justified to quote the respective Hund’s case (a) parent (e.g. in Table 4).

There is also a number of other excited molecular states with ‘g’ symmetry that correlate with the \( 5^3\Pi_1 \) atomic asymptote as well as those with ‘u’ symmetry that correlate with the \( 5^3\Pi_1 \) and other asymtotes belonging to the \( 5^3\Pi \) manifold. The states are denoted (Hund’s case (a) in parentheses): \( {}^3\Pi_g(\Sigma^g\Pi_g) \) and \( {}^3\Pi_u(\Sigma^u\Pi_u) \) [correlated with the \( 5^3\Pi_1 \)], \( {}^3\Pi_u(\pi\Pi_u), {}^3\Pi_u(\pi\Pi_u), {}^3\Pi_u(\pi\Pi_u) \), \( {}^1\Pi_g(\Sigma^g+\Pi_g \text{ mixing}) \), and \( {}^3\Pi_u(\Sigma^u\Pi_u, \Delta^u\Pi_u) \) [correlated with the \( 5^3\Pi_2 \)], as well as \( {}^3\Pi_g(\Sigma^g) \) and \( {}^3\Pi_u(\Sigma^u) \) [correlated with the \( 5^3\Pi_0 \)]. States, which correlate with the \( 5^3\Pi \) asymptote are: \( {}^1\Pi_u(\Pi_u, \Sigma_u \Pi_u) \), \( {}^1\Pi_u(\Sigma_u \Pi_u, \Pi_u \Pi_u) \), and \( {}^1\Pi_u(\Pi_u) \).

The remaining group 12 dimers: \( \text{Zn}_2 \) [14,26] and \( \text{Hg}_2 \) [27] have similar structure of the electronic energy states as also has group 2 dimers: \( \text{Be}_2 \) [28], \( \text{Mg}_2 \) [29], \( \text{Ca}_2 \) [30,31], \( \text{Sr}_2 \) [32], \( \text{Ba}_2 \) [33], \( \text{Ra}_2 \) [34,35], and lanthanide \( \text{Yb}_2 \) [36]. Taking into account the discussion presented above, the fact of varying magnitude of s–o coupling determines that Hund’s case (a) is applicable for \( \text{Zn}_2, \text{Be}_2, \text{Mg}_2, \text{Ca}_2 \) and \( \text{Sr}_2 \), while Hund’s case (c) for \( \text{Hg}_2, \text{Ba}_2 \) and \( \text{Yb}_2 \).

Figure 2 presents five transitions of excitation in \( \text{Cd}_2 \) originating as an effect of the direct electric dipole excitation from the \( \text{X}^10^+(5^3\Sigma_0^0) \) state i.e. transitions to the \( \text{a}^3\Pi^+ \).
b^3O_u(^5P_1), c^31_u(^5P_2), A^1O_u(^5P_1) and B^11_u(^5P_1) states (inset on the left side shows corresponding LIF excitation spectra drawn in the energy scale). Two emission transitions, from the A^1O_u and B^11_u to the X^10_g state, are shown as well. The upper part of Figure 2 presents transition dipole moments (TDM), in fact their lengths i.e. |TDM|, calculated within ab initio approach for the transitions reviewed here.

**Figure 2.** (Colour online) Interatomic potentials of Cd_2 showing the a^31_u(^5P_1), b^30_u(^5P_1), c^31_u(^5P_2), A^10_u(^5P_1) and B^11_u(^5P_1) low-lying ungerade excited states as well as the X^10_g(^5S_0) ground state. Upward arrows and energies (in cm\(^{-1}\)) are shown; they correspond to the centres of the b^30_u \rightarrow X^10_g, c^31_u \rightarrow X^10_g, A^10_u \rightarrow X^10_g and B^11_u \rightarrow X^10_g LIF excitation spectra. Also shown are the 222–290 nm (45,105–34,460 cm\(^{-1}\)) and 258–313 nm (38,786–31,940 cm\(^{-1}\)) spectral ranges corresponding to the B^11_u \rightarrow X^10_g and A^10_u, \(\nu' = 38 \rightarrow X^10_g\) LIF dispersed emission bands, respectively. The excitation spectra and emission bands were reported in Refs. [19,115–120] and additionally analysed here. The allowed a^31_u \rightarrow X^10_g transition centred, according to ab initio calculations, at 364.8 nm (27,400 cm\(^{-1}\)) was never recorded [128] but it is re-analysed in this review. Upper part: The TDM determined for the purpose of this review (three separate vertical scales are used to distinguish between its magnitudes for different transitions). The position of the \(R_e = 3.76\) Å is indicated with dashed vertical line.
1.3. Studies of group 2, Yb and group 12 atoms and dimers

Atomic and molecular energy structure of group 2 and group 12 atoms and dimers has a number of correspondences. Most of the transitions between the ground and low-lying excited levels (in atoms) and electronic energy states (in dimers) occur mostly in VIS and UV in the former and later, respectively. Figure 3 presents a comparison between atomic energy levels structure for the $nsnp^1P_1$ and $nsnp^3P_1$ multiplets drawn for group 2 [Be ($n = 2$), Mg($n = 3$), Ca ($n = 4$), Sr ($n = 5$), Ba ($n = 6$), Ra ($n = 7$)], lanthanide Yb ($n = 6$), and group 12 [Zn ($n = 4$), Cd($n = 5$), Hg ($n = 6$)] atoms. For the sake of brevity, even-parity states of $ns(n-1)d$ configuration of Ca, Sr, Ba, Ra and Yb are omitted in Figure 3; in case of Yb, also the low-lying levels of $4f^{13}5d6s^2$ configuration are not displayed. The electric-dipole transitions from the ground states of the considered atoms to the omitted excited states are forbidden due to Laporte selection rule and/or due to the $\Delta J \leq 1$ condition. At the same time, all of the $nsnp^1P_1 \leftrightarrow ns^21S_0$ and $nsnp^3P_1 \leftrightarrow ns^21S_0$ transitions shown in Figure 3 are accessible using conventional lasers using fundamental frequency or conversion of the fundamental to the second or third frequency harmonics (except that of $6^1P_1 \leftrightarrow 6^1S_0$ in Hg, which occurs in VUV). Therefore, laser spectroscopy of M$_2$ molecular energy states (including isotopic, vibrational, and rotational structure) that correlate asymptotically with the n$^1P_1$ and n$^3P_1$ excited M-atom states has been feasible.

One of the phenomena that links the interest in group 12 and group 2 atoms is due to the fact that the group 12 atoms may be cooled and trapped, and may interact in a variety of traps arranged in different configurations (i.e. MOTs, optical dipole or magnetic traps,

![Figure 3](image-url)

Figure 3. (Colour online) Energies of the $nsnp^1P_1$ (highest levels) and $nsnp^3P_1 (J = 0,1,2)$ (lower levels) multiplets of group 2 [Be ($n = 2$), Mg ($n = 3$), Ca ($n = 4$), Sr ($n = 5$), Ba ($n = 6$), Ra ($n = 7$)], lanthanide Yb ($n = 6$), and group 12 [Zn ($n = 4$), Cd ($n = 5$), Hg ($n = 6$)] atoms. The transitions from the ground to the n$^3P_1$ and n$^1P_1$ energy levels are indicated with arrows and expressed in cm$^{-1}$ and nm. Diagram shows also a comparison between magnitudes of the s–o splitting in the n$^3P_1$ multiplets (in Be, Mg and Ca the splittings are small – insets show them in magnification). According to Ref. [203]. For the sake of brevity, the even-parity states of ns(n-1)d configuration of Ca, Sr, Ba, Ra and Yb are omitted; in the case of Yb, also the low-lying levels of 4f$^{13}5d6s^2$ configuration are not displayed. The omitted states are not accessible via the electric-dipole transitions from the ground state.
as well as in optical lattices). Experience gained in studies with group 2 atoms and dimers can be transferred to these of group 12. There is a limited theoretical and experimental evidence of laser-cooling and trapping in MOTs of Zn, Cd or Hg [1–9]. In contrast, there are comprehensive theoretical and experimental studies on cooling and trapping of all but one (i.e. the lightest Be) alkaline earth metal group 2 atoms Mg [37–39], Ca [40–43], Sr [43], Ba [44] and Ra [45,46]. Moreover, an extensive experimental evidence of cooling and trapping of Yb [47–51] has been reported. The picture would not be completed without mentioning cooling and trapping of isotopes of two other rare earth metal atoms – Er and Dy, [52,53] for which MOTs have been constructed and reported paving the way for obtaining their quantum degeneracy. In contrast to group 12, for group 2 atoms and several lanthanides metals production of Bose–Einstein condensates (BEC) or quantum degenerate Fermi gases has been reported. They have been obtained for Ca [54,55], Sr [56–62] and Yb [63–69]. For Er and Dy, realisations of BECs and Fermi quantum degeneracies have also been reported [70–73].

There is another application that joins studies of group 2, Yb and group 12 atoms and dimers. Alkaline earth metal atoms along with the rare earth Yb, and Zn and Hg have attracted broad attention due to their narrow intercombination transitions with various possible applications in physics, chemistry and technology. These include utilisation in optical atomic clocks [74] based on Mg [75], Sr [76–80], Yb [81], Zn [1] or Hg [3], application of optical atomic clocks for testing gravitational and temporal changes of fundamental constants (i.e. variations of $\alpha$ fine structure constant and $m_e/m_p$ electron–proton mass ratio) [74,78,79,82], quantum computation e.g. using Yb [83], precision measurements e.g. employing Sr$_2$ [82], that require development of sensitive techniques to produce and interrogate the dimers. Also, great attention has been paid to parity violation studies [84], determination of molecular potentials with high accuracy [85], investigation of scattering processes e.g. for Ca [86], and the production of ultra-cold molecules e.g. Sr$_2$ [87], in the excited or ground state using one-, two- or three-step (-colour) PA processes. Thus, prospects of studying ultra-cold chemistry e.g. with Sr$_2$ and ultra-cold chemical reactions [88] performed employing e.g. decelerated supersonic beams [89] have become possible. The precise determination of interatomic potentials including the long-range interaction between atoms in the corresponding ground or excited states e.g. by PA spectroscopy is a prerequisite for many applications.

Precise knowledge of sometime complex shape of the interatomic potentials greatly facilitates an optimum design of the PA schemes that have been realised for a number of transitions in group 2 and Yb atoms to produce their ultra-cold dimers. Also, theoretical studies of PA configurations have been performed to determine favourable conditions for their realisation in laboratory or facilitate analysis of the experiments.

The most abundant $^{40}$Ca were photo-associated to ($^{40}$Ca)$_2$ via one-step process [90,91]. The process was realised close to the $4^1\Pi_1$ [90] or $4^3\Pi_1$ [91] asymptotes allowing for long-range characterisation of the $A^1\Sigma_u^+(4^1\Pi_1)$ [90], and $e^3\Pi_u(4^3\Pi_1)$ and $a^3\Sigma_u^+(4^1\Pi_1)$ [91] electronic states, as well as determination of the ground-state s-wave scattering length [90] and studies of molecular Zeeman splitting [91]. Theoretically, one-step PA of Ca was studied by three groups [92–94], leading to a determination of, among others, $C_3$, long-range dipole–dipole, and $C_6$, $C_8$ and $C_{10}$ vdW coefficients for the investigated molecular states. As far as Sr is concerned, the $^{88}$Sr and $^{86}$Sr were photo-associated via one-step process close to the $5^1\Pi_1$ [95,96] or $5^3\Pi_1$ [97–99] asymptote. It allowed for long-range ($C_3$ and $C_6$) characterisation of
the $^1\Sigma_u^+(4^1P_1)$ [96], and $^3\Sigma_u^+(4^3P_1)$ and $^3\Sigma_u^+(4^3P_1)$ [97–99] electronic states, determination of the atomic lifetime in the $^5\Sigma_u^+$ state [96], and studies of linear and quadratic molecular Zeeman effect [98]. Also a corrected description of a mass scaling (it is a model that would reproduce the bound-state energies for all isotopes) was facilitated taking into account perturbation of the positions of the series of levels observed in PA spectroscopy near the $^3\Pi_u-^5\Sigma_0^+$ intercombination line due to the short-range avoided crossing between the $^3\Pi_u(5^3P_1)$ and $^1\Sigma_u^+(4^1D_2)$ electronic states [99].

A two-step PA for $^{88}\text{Sr}$ and $^{84}\text{Sr}$ has been applied via energies close to the $^5\Sigma_1^+$ asymptote (with the $^3\Sigma_0^+$ state as an intermediate) [87,100,101]. The two-step (two-colour) process, often called stimulated Raman adiabatic passage (STIRAP), transfers coherently an initial two-atom state (e.g. two Sr atoms in BEC or occupying the ground state of an optical lattice well) into a diatom by optical transitions [e.g. Sr$_2$ in one of the $\chi_1^1\Sigma^+_g$-state ($\nu'', J''$) levels]. Using the approach, positions of the $\nu'' = 62, J'' = 0, 2$ levels were measured and $s$-wave scattering length was determined for $^{88}\text{Sr}_2$ [100]. This paved the way for immediate applications of ground-state $^{88}\text{Sr}_2$ in precise time and frequency metrology, studies of fundamental constants variations, and investigation of chemical reactions at ultralow kinetic energies [87].

PA spectroscopy applied for Yb resulted in numerous outcomes. A number of ytterbium isotopes, were photo-associated to corresponding dimers via one-step process using transitions close to the $^6\Sigma_1^+$ [102,104,108] or $^6\Pi_1$ [103,105–107,109] asymptotes allowing for long-range (C$_3$, C$_6$) characterisation of the $^1\Sigma_u^+(6^1P_1)$ [102], and $^3\Sigma_g^+(6^3P_1)$ [105] and $^3\Sigma_g^+(6^3P_1)$ [103,105,106] electronic states. Also, determination of $s$-wave scattering length [104], control of the scattering wave function by an optical Feshbach resonance [107] and nuclear spin exchange entangling interactions due to a $s$- and $p$-wave phase shifts difference [108,109] were performed. Also, heteronuclear $^{170}\text{Yb}^{174}\text{Yb}$ and $^{174}\text{Yb}^{176}\text{Yb}$ isotopologues of Yb$_2$ were photo-associated [110]. It allowed for determination of C$_3$, C$_6$ and C$_8$ long-range characteristics for the $^1\Sigma_g^+$, $^3\Sigma_u^+$ and $^3\Sigma_g^+$ electronic states correlating with the $^6\Pi_1$ asymptote. Finally, a two-step STIRAP process was applied for all Yb isotopes by employing PA of homonuclear dimers via $^6\Pi_1$ [111] or $^6\Pi_1$ [111–113]. As a result, the $\chi_1^1\Sigma^+_g$-state $s$-wave scattering lengths and C$_6$ coefficients were determined [113], ground-state long-lived (with 8.0 s lifetime) ultra-cold vdW molecules were created in 3D optical lattice [111] and limits on non-Newtonian gravity were proposed [112].

To date, there are no reports on realisation of PA schemes for ultra-cold group 12 M$_2$ dimers. Development in laser cooling and trapping of atoms such as Zn [1], Cd [2] and Hg [3–9] will hopefully allow PA investigations of these systems in the future. Cd and Hg, like Yb, are good candidates for mass tuning of the scattering length because of their numerous isotopes. In addition, Hg is seen as a very promising candidate for future optical frequency standards. The clock frequency shift induced by black body radiation is especially small in Hg [3], compared with group 2 elements [114]. Undoubtedly, studies of group 2 and lanthanides atoms and dimers greatly facilitate increase of success while using the group 12 analogues.

1.4. The goal of the review

State-of-the-art knowledge on experimentally determined interatomic potentials of group 12, some of the lanthanides (e.g. Yb) and group 2 metal dimers is assessed against the results of ab initio calculations. This article constitutes a critical review of experimental
studies and *ab initio* calculations of the low-lying *ungerade* excited and ground state interatomic potentials of Cd₂ – one of the group 12 weakly bound homoatomic vdW dimer. Consistency as well as discrepancies between experimental results and *ab initio* calculations are probed here to illustrate available approaches for the comparison. In order to obtain better agreement with existing experimental data, fill in gaps in current knowledge and provide a unifying framework, one of the objectives is a confrontation of the interatomic potentials from *ab initio* calculation for the Cd₂ low-lying *ungerade* excited and the ground states, and supplementary simulations of the LIF excitation and dispersed emission spectra reported in Refs. [19,115–120].

It is necessary to emphasise that some of the analyses reported in the literature to date were performed using limited resources. They were executed only for low $\nu'$ and $\nu''$, and with only a Morse representation of interatomic potentials in their bound region, also without systematic consideration of the isotopic composition and rotational energy structures that otherwise can completely change results of the simulation (e.g. intensity of the vibrational bands and their shape). Therefore, the purpose of the re-analyses is to help rationalise and draw together the literature reviewed here. Thus, after reviewing *ab initio* calculations (Section 2) and experimental studies of Cd₂ interatomic potentials (Section 3), the following agenda is realised (Section 4):

- Supplemental re-analysis of LIF excitation and dispersed emission spectra reported in Refs. [19,115–120] and analysis of additionally recorded LIF excitation spectra in order to refine the simulations applying programmes and procedures that were originally omitted or unavailable e.g. LeRoy’s LEVEL [121], BCONT [122] and RPOT [123,124] as well as Western’s PGOPHER [125];
- Although a number of *ab initio* potentials for Cd₂ system has been previously published, we challenged them by more thorough all-electron (AE) calculations performed for excited states; furthermore, the state-of-art ground state potential was obtained in order to improve the theory-to-experiment agreement;
- Implementation of analytical and/or point-wise representations for the lowest *ungerade*- and ground-state potentials of Cd₂, and subsequent comparison of *ab initio* calculated potentials with results of additional analyses as well as with results of other *ab initio* calculations and experiments.

Precise data on interatomic potentials and energy structure of, among others, group 12 metal dimers can be crucial to propose and realise fundamental tests of quantum mechanics based on PA of diatomic molecule. Very recently, Urbańczyk et al. [18], and Urbańczyk and Koperski [21] made preparations for an experimental realisation (based on proposals of Lo and Shimony [126], and Fry et al. [11] for Na and Hg, respectively) of Bohm’s 1/2-spin particle version of the Einstein–Podolsky–Rosen (E–P–R) experiment that is based on the production of entangled atoms by PA of the $^{(111)}$Cd₂ isotopologue in a supersonic expansion beam using the spectroscopically selective STIRAP. Also, using the so-called Walther scheme proposed for internal vibrational cooling of Hg₂ in the ground electronic state [127], an analogous scheme is suggested here for Cd₂ and entirely based on interatomic potentials being the result of analyses presented in this review.

The results reviewed here concern Cd₂ dimers that are produced and ro-vibrationally cooled in a free-jet expansion beams and their molecular energy structure is investigated using methods of laser spectroscopy [13,14 and references therein]. The method has been applied, among others, in experimental studies of the $a^1_u(5^3P_1)$ [128], $b^3O_u(5^3P_1)$
2. Ab initio calculations for group 2 and group 12 atoms: the case of Cd$_2$ system

2.1. General overview

Ground-state electron configuration of Cd atom is [Kr] 4d$^{10}$ 5s$^2$, where [Kr] denotes (closed shell) electron configuration of Kr. The ground-state s$^2$ closed shell is a characteristic property of group 2 atoms, i.e. Be ([He] 2s$^2$), Mg ([Ne] 3s$^2$), Ca ([Ar] 4s$^2$), Sr ([Kr] 5s$^2$), Ba ([Xe] 6s$^2$), Ra ([Rn] 7s$^2$) and group 12 atoms i.e. Zn ([Ar] 3d$^{10}$4s$^2$), Cd and Hg ([Xe] 4f$^{14}$5d$^{10}$6s$^2$).

Lowest excited states of Cd atom correspond to a single excitations to 5p orbitals (see Figure 3). Main qualitative difference between group 2 and group 12 atoms is the lack of closed shell (n−1)d$^{10}$ in alkaline earth metals. It is manifested in the relatively low-lying excited states of ns$^1$ (n−1)d$^l$ configuration, where n = 4, 5, 6, 7 for Ca, Sr, Ba and Ra, respectively (these energy levels are not presented in Figure 3). Obviously, these states are missing in spectra of group 12 atoms as they possess fully occupied (n−1)d shell, were n = 4, 5, 6 for Zn, Cd and Hg, respectively.

As it can be seen in Table 1, levels of the [Kr]5s5p configuration of Cd atom are well separated on energy scale from the rest of Cd atom energy spectrum. Furthermore, these levels are of the valence character; this is manifested by relatively small expectation values of the electron radial coordinate ($\langle r \rangle_5s \sim 2.8$ a.u. and $\langle r \rangle_5p \sim 4.3$ a.u.). At the same time, the higher energy levels of Cd atom are not well separated (in the energy scale) and they correspond to the excitations to orbitals of Rydberg character ($\langle r \rangle_6s \sim 7.5$ a.u., $\langle r \rangle_5d \sim 8.3$ a.u., $\langle r \rangle_6p \sim 11.1$ a.u., $\langle r \rangle_7s \sim 18.2$ a.u., etc.). The expectation values of the electron radial coordinate were obtained with newly devised atomic basis set of Cd (for details see footnotes in Table 1 and Supplementing data). From the computational point of view, the radial behaviour of the considered orbitals determines the necessary spatial extent of the atomic basis set. In this review, we focus our attention mainly on the ground and the excited (valence) states of Cd$_2$, correlating to the 5s$^2$ and 5s5p atomic configurations. This means that in such a case, the spatial requirements on the atomic basis set are rather limited.

The majority of Cd$_2$ excited electronic states calculations found in the literature (see Table 3) was performed with the use of effective core potentials (ECP). In this approach, the effect of the inner-core electrons is represented by the pseudopotential, whereas the valence states are explicitly treated with appropriately devised basis set of atomic (pseudo)orbitals [133,134]. The ECPs also allow to take into account the scalar (and s–o) relativistic effects [134] within standard non-relativistic framework of quantum chemistry methods. This is an economic way of treatment of systems containing heavy atoms, where the relativistic and electron correlation effects have to be taken into account simultaneously. For example, the inclusion of correlation and relativistic effects leads to a substantial decrease of the values of polarisabilities of group 12 atoms [135]. In particular, the so-called direct relativistic effect of the spatial shrinkage of orbitals of s and p symmetry leads to the decrease of the ‘volume’ of the atom and, as a consequence, the atomic polarisability is lowered. Furthermore, nowadays computational resources make the all electron theoretical treatment of heavy-element systems feasible, where the inner-core orbitals are described with a minimal basis and
Table 1. Experimental and theoretical values of Cd atomic energy levels.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Term</th>
<th>J</th>
<th>$E_{\text{expt}}$</th>
<th>$E_{\text{theor}}$</th>
<th>$E_{\text{theor}} - E_{\text{expt}}$</th>
<th>$E_{\text{theor}} - E_{\text{expt}}$</th>
<th>$E_{\text{theor}} - E_{\text{expt}}$</th>
<th>$E_{\text{theor}} - E_{\text{expt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Kr] 4d$^{10}$ 5s$^2$</td>
<td>1$^S$</td>
<td>0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Kr] 4d$^{10}$ 5s5p</td>
<td>3$^p$</td>
<td>0</td>
<td>30,113.990</td>
<td>30,220</td>
<td>106</td>
<td>−716</td>
<td>30,459.675</td>
<td>346</td>
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<tr>
<td></td>
<td></td>
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<td>30,685</td>
<td>29</td>
<td>−804</td>
<td>30,905.616</td>
<td>250</td>
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<td></td>
<td></td>
<td>2</td>
<td>31,826.952</td>
<td>31,634</td>
<td>−193</td>
<td>−1029</td>
<td>31,835.512</td>
<td>9</td>
</tr>
<tr>
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<td>1$^p$</td>
<td>1</td>
<td>43,692.384</td>
<td>44,784</td>
<td>1092</td>
<td>43,657.292</td>
<td>−35</td>
<td>43,288.458</td>
</tr>
<tr>
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<td>51,863</td>
<td>379</td>
<td>51,195.597</td>
<td>−288</td>
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<td>52,759</td>
<td>−551</td>
<td>53,477.884</td>
<td>168</td>
<td></td>
</tr>
<tr>
<td>[Kr] 4d$^{10}$ 5s6p</td>
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<td>0</td>
<td>58,390.9</td>
<td>57,996.297</td>
<td>−395</td>
<td></td>
<td>58,055.597</td>
<td>−406</td>
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<td>1</td>
<td>58,461.6</td>
<td>58,635.7</td>
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<td></td>
<td>58,188.814</td>
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<td>59,101.925</td>
<td>−118</td>
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<td>−358</td>
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<td>59,128.138</td>
<td>−358</td>
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<td>2</td>
<td>59,497.868</td>
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<td>[Kr] 4d$^{10}$ 5s6p</td>
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<td>59,902.724</td>
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<td></td>
<td>59,902.724</td>
<td>−5</td>
</tr>
<tr>
<td>[Kr] 4d$^{10}$ 5s7s</td>
<td>1$^S$</td>
<td>1</td>
<td>62,563.435</td>
<td>62,265.014</td>
<td>−298</td>
<td></td>
<td>62,265.014</td>
<td>−298</td>
</tr>
<tr>
<td>[Kr] 4d$^{10}$ 5s7s</td>
<td>1$^S$</td>
<td>0</td>
<td>63,086.896</td>
<td>63,104.014</td>
<td>17</td>
<td></td>
<td>63,104.014</td>
<td>17</td>
</tr>
<tr>
<td>Std. deviation</td>
<td></td>
<td></td>
<td>559</td>
<td>428</td>
<td>262</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Ref. [203,227].
$^b$Ref. [133]; sa-CASSCF/CASPT2 + SO, CAS = (5s5p6s6p)$^2$, Cd$^{50+}$ relativistic basis set (9s8p7d4f2g)/(8s7p6d4f2g).
$^c$This review; sa-CASSCF/MS-CASPT2/RASSI-SO, CAS = (5s5p6s6p)$^2$, DKH-2, basis set AE ANO-RCC (21s19p13d6f4g2h)/[10s8p8d5f4g2h] from Ref. [140].
$^d$This review; sa-CASSCF/MS-CASPT2/RASSI-SO, CAS = (5s5p6s6p7s)$^2$, DKH-2, basis set AE ANO-RCC (27s24p19d8f4g2h)/[18s16p16d8f4g2h].
they are not correlated [136]. In this way, the implicit frozen-core approximation of ECP approach is partially relaxed.

The proper description of the potential energy curves (PECs) of the excited states of diatomic molecules requires as accurate as possible reproduction of the atomic asymptotes. In particular, it is crucial for the correct localisation of the avoided crossings of adiabatic PECs corresponding to states of the same symmetry. In Table 1 we present comparison of experimental and theoretical values of Cd atomic energy levels. Theoretical atomic energies are obtained with basis sets used in diatomic molecules calculations performed by Czuchaj et al. (columnb [133]) and in this review (columna). Czuchaj et al. used relativistic ECP [137] accompanied with 9s8p7d4f2g Gaussians contracted to 8s7p6d4f2g valence basis set (notation: (9s8p7d4f2g)/[8s7p6d4f2g]); this means that, for example, there are eight atomic orbitals of s symmetry being linear combinations of nine primitive Gaussian functions i.e. 

\[ f_i(\vec{r}) = \sum_{k=1}^{9} c_{ik} \exp \left( -a_k r^2 \right), \]

where \( i = 1, 2, \ldots, 8 \). In order to make the presentation more complete we provide results of AE quasi-relativistic calculations (by means of second order Douglas–Kroll–Hess (DKH-2) Hamiltonian [138,139]) performed with Atomic Natural Orbitals (ANO-RCC) basis set (21s19p13d6f4g2h)/[10s8p8d5f4g2h] [140] (see columnc in Table 1). It can be seen that the overall performance of both approaches is comparable. However, the lack of the energy levels of 5s6s electron configuration in columnc of Table 1 is due to the fact that ANO-RCC basis from Ref. [140] is unable to describe spatial extent of the 6s Rydberg orbital of Cd. Namely, this basis set was devised for description of the states of 5s2 and 5s5p electron configurations. The remaining atomic orbitals of ANO-RCC i.e. 6s, 5d, 6p, 7s, etc., do not correspond to consecutive excitations to higher energy states. Since they are responsible for the proper description of the electron correction of semi-core and valence orbitals, they have a compact spatial characteristic. Therefore, for the purpose of this review, the extended ANO-RCC basis set (27s24p19d8f4g2h)/[18s16p16d8f4g2h] was devised in order to show the capabilities of the AE approach (see Supplementing data for details of the basis set). Columnd of Table 1 presents theoretical atomic energies levels corresponding to the excitations up to 7s orbital obtained with the extended ANO-RCC basis set. The deviations of the corresponding theoretical energies from the experimental ones (columna) are also shown, and for the result of this review they do not exceed 450 cm\(^{-1}\). The new ANO-RCC basis set includes very diffuse Gaussian-type orbitals which allow the description of the low-lying Rydberg states (recall that \( \langle r \rangle_{21} \sim 18.2 \) a.u.).

The most important part of the calculations is the proper description of the electron correlation. In particular, the multi-reference character of the excited states demands the relevant (multi-reference) methods of quantum chemistry. Taking into account the accuracy and the computational cost, the complete active space (CAS) based methods are suitable for the task, providing the CAS is adequately chosen for the considered system. Complete active space self-consistent field (CASSCF) method [141–143] allows the description of the non-dynamical electron correlation effects originating from the multi-reference character of the considered states. Assuming that at the CASSCF level the considered system is quite accurately described, the remaining (dynamical correlation) effects can be treated perturbatively; this is achieved within CAS perturbation theory (CASPT2) [144–147], where up to the second-order corrections to energy are taken into account. Finally, the matrix of the s–o interaction operator is calculated for the CASSCF states with the diagonal matrix elements corrected by means of CASPT2. Such a treatment of the s–o interaction can be performed within restricted active space state interaction method (RASSI-SO) [148]. All the theoretical
energies of Cd atom presented in Table 1 were obtained within CASSCF/CASPT2 approach completed with s–o effect; the details of the calculation are listed in footnotes of Table 1.

It should be pointed out that the atomic transition probabilities $A_{\text{expt}}$ in Cd atom are reasonably well described within the theoretical approach described above, as it can be seen in Table 2, where the experimental relative intensities, transition probabilities $A_{\text{expt}}$ and theoretical (absorption) oscillator strengths and (emission) transition probabilities $A_{\text{theor}}$ are collected. At the same time, the experimental values of relative intensities should be treated with caution as they may depend on the experimental settings [149]. Nevertheless, one can conclude a qualitative agreement between experimental relative intensities and theoretical oscillator strengths, by means of the fact that the observed intense transitions possess relatively large theoretical oscillator strengths, etc. In the case of the $5s^2 1S_0 \leftrightarrow 5s5p \ 1P_1$ and $5s^2 1S_0 \leftrightarrow 5s5p \ 3P_1$ transitions, the comparison of various theoretical approaches (e.g. AE vs. ECP) can be performed; it can be concluded from Table 2 that the all of these approaches

Table 2. Experimental values of relative intensities and transition probabilities $A_{\text{expt}}$ and theoretical values of oscillator strengths and transition probabilities $A_{\text{theor}}$ in Cd atom. All the theoretical values are obtained in this work within AE and ECP approaches (see footnotes below the table for details).

<table>
<thead>
<tr>
<th>Lower level</th>
<th>Upper level</th>
<th>$A_{\text{expt}}$ (s$^{-1}$)</th>
<th>Oscillator strength $A_{\text{theor}}$ (s$^{-1}$)</th>
<th>($A_{\text{theor}} - A_{\text{expt}}$)/$A_{\text{expt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5s2 1S_0$</td>
<td>$5s5p \ 1P_1$</td>
<td>1500</td>
<td>$5.30 \times 10^8$</td>
<td>1.8218</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1600</td>
<td></td>
<td>1.9485</td>
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<td>2.2965</td>
</tr>
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<td>$5s5p \ 1P_1$</td>
<td>$5s7s \ 1S_0$</td>
<td>150</td>
<td>0.0158</td>
<td>3.55 $\times 10^6$</td>
</tr>
<tr>
<td>$5s5p \ 1P_1$</td>
<td>$5s7s \ 1S_0$</td>
<td>30</td>
<td>0.0003</td>
<td>5.93 $\times 10^4$</td>
</tr>
<tr>
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<td>$5s7s \ 1S_0$</td>
<td>200</td>
<td>0.0133</td>
<td>8.76 $\times 10^4$</td>
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<tr>
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<td>$5s7s \ 1S_0$</td>
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<td>0.0088</td>
<td>9.08 $\times 10^4$</td>
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<td>$4.06 \times 10^8$</td>
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<td>0.0012</td>
</tr>
<tr>
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<td>$5s5d \ 1D_2$</td>
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<td>$7.70 \times 10^7$</td>
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<tr>
<td>$5s5p \ 1P_1$</td>
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<td>$5s5p \ 2P_1$</td>
<td>$5s6s \ 3S_0$</td>
<td>300</td>
<td>$4.10 \times 10^7$</td>
<td>0.1465</td>
</tr>
<tr>
<td>$5s5p \ 2P_1$</td>
<td>$5s6s \ 3S_0$</td>
<td>1000</td>
<td>$5.60 \times 10^7$</td>
<td>0.1510</td>
</tr>
<tr>
<td>$5s5p \ 1P_1$</td>
<td>$5s7s \ 1S_0$</td>
<td>6</td>
<td>0.0000</td>
<td>2.37 $\times 10^3$</td>
</tr>
<tr>
<td>$5s5p \ 1P_1$</td>
<td>$5s5d \ 3D_2$</td>
<td>100</td>
<td>0.0359</td>
<td>3.61 $\times 10^6$</td>
</tr>
<tr>
<td>$5s5p \ 1P_1$</td>
<td>$5s5d \ 3D_2$</td>
<td>30</td>
<td>0.0003</td>
<td>5.10 $\times 10^4$</td>
</tr>
<tr>
<td>$5s5p \ 1P_1$</td>
<td>$5s5d \ 3D_2$</td>
<td>2000</td>
<td>$5.90 \times 10^7$</td>
<td>0.6141</td>
</tr>
</tbody>
</table>

*Ref. [203].
*Ref. [231].
*Ref. [149].

All values of relative intensities listed in Ref. [149] are two times smaller than the counterparts listed above and in Refs. [203,231] with the exception of $5s^2 1S_0 \leftrightarrow 5s5p \ 1P_1$ transition, where the value 800 of relative intensity is reported [149].

This review; using MOLCAS programme [179–181]; if it is not stated explicitly, theoretical values of $A_{\text{theor}}$ and oscillator strengths are obtained within the following approach: sa-CASSCF/MS-CASPT2/RASSI-SO, CAS = $(5s5p5d6s6p7s)^2$, DKh-2, basis set AE ANO-RCC (27s24p19d8f4g2h)\(18s16p16d8f4g2h\).

This review; using MOLCAS programme [179–181]; sa-CASSCF/MS-CASPT2/RASSI-SO, CAS = $(5s5p6s)^2$, DKh-2, basis set AE ANO-RCC (21s19p13d6f4g2h)\(10s8p8d5f4g2h\) [140].

This review; using MOLPRO programme [172,173]; sa-CASSCF, CAS = $(5s5p6s)^2$, relativistic ECP [134], valence basis set aug-cc-pV5Z [174].
provide qualitatively similar results. Furthermore, the value of atomic polarisability \( \alpha_d \) of the ground state of Cd (46.9 a.u.) obtained by Roos et al. [140] with original ANO-RCC is close to its experimental value (49.7 ± 1.6 a.u. [150]). This shows the potential ability of the presented theoretical approach to account for a dispersive interactions between Cd atoms that are crucial from the point of view of the stability of vdW dimers.

2.2. Review of \textit{ab initio} calculations of Cd\(_2\) interatomic potentials

\textit{Ab initio} calculations of Cd\(_2\) ground- and excited-state interatomic potentials were carried out by a number of researchers using a variety of computational methods at different levels of theory. Table 3 summarises the majority of the reports by overviewing methods and types of calculation that have been performed since 1979 up-to-date. As one can see, the development and degree of sophistication of the computational approaches is evident. It has led to increasingly better results. However, at the same time it should be pointed out that the ordering in Table 3 does not reflect strictly the improvement of the theoretical description of the Cd\(_2\) electronic energy states.

Interatomic potentials of excited electronic energy states were calculated among others by Stevens [17], Bender et al. [151], Czuchaj et al. [152], Garcia de la Vega and Miguel [153], as well as Łukomski et al. [118,128], Strojecki et al. [116] where calculations of Czuchaj [154], and Czuchaj and Krośnicki [155] (those including s–o coupling effect) were incorporated. Figgen et al. [134] and Koperski et al. [19] reported \textit{ab initio} calculated interatomic potentials also for Rydberg electronic states. The most recent calculations were performed by Kullie [156,157]. \textit{Ab-initio} calculated ground-state interatomic potentials were reported by all of the above (except by those from Ref. [19]) and also, among other, by Yu and Dolg [135], Schautz et al. [158], Flad et al. [159], Lukeš et al. [160], Bučinský et al. [161] and Pahl et al. [162,163]. Up to the present, one of the best calculated Cd\(_2\) ground-state potential is that of Pahl et al. [162].

2.3. Ground state

As the Cd atoms have \( s^2 \) electronic configuration, their interaction is analogue to the interactions of group 2 alkaline earth metal and group 12 dimers, and Cd\(_2\) molecules exhibit same similarities in the interaction mechanisms. Thus, Cd\(_2\) can be considered as a representative for such systems. The most important feature of interaction of two \( s^2 \) atoms is non-bonding character, which originates from the fact that spin exchange between doubly occupied outermost shells prevents them from binding. On the other hand, two interacting \( s^2 \)-type atoms experience very large dispersion interaction which is always attractive.

In general case, the dispersion energy can be written in terms of atomic wave functions, through the second-order expansion in terms of interatomic potential operator \( V \), which represents electron–electron interactions between atoms A and B:

\[
E^{(2)}_{\text{disp}} = -\sum \frac{\left| \langle \psi^A_{n} \psi^B_{k} | V | \psi^A_{0} \psi^B_{0} \rangle \right|^2}{\Delta E_{n0} + \Delta E_{k0}}
\]  \hspace{1cm} (1)

In Equation (1), the summation runs over the excited states of atoms A and B, respectively, the quantities in the denominator \( \Delta E_{n0} \) and \( \Delta E_{k0} \) are the excitation energies between ground
<table>
<thead>
<tr>
<th>Type of calculation employed</th>
<th>Calculated electronic energy state potentials</th>
<th>Author(s) year [Reference]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PECs computed using AE full configuration-interaction (FCI) for 4 valence electrons; s–o coupling included</td>
<td>excited ((S^1P, S^1P^1)) and (X^1O^1_g)</td>
<td>Bender et al. (1979) [151]</td>
</tr>
<tr>
<td>PECs computed using multiconfiguration self-consistent-field (MCSCF) method; (\text{Cd}_2) treated as 4-electron system, core electrons replaced by non-relativistic ECP; s–o coupling not investigated</td>
<td>excited ((S^1P, S^1P^1, 6^1S, 6^1S^1)) and (X^1O^1_g)</td>
<td>Stevens (1979) [17]</td>
</tr>
<tr>
<td>PECs and TDMs computed using multi-reference configuration-interaction MRCI(SD) method for 4 valence electrons; core electrons ([\text{Kr}]4d^{10}) represented by semi-empirical (\zeta)-dependent pseudopotentials; s–o coupling not investigated</td>
<td>excited ((S^1P, S^1P^1, 6^1S, 6^1S^1)) and (X^1\Sigma^+_g)</td>
<td>Czuchaj et al. (1994) [152]</td>
</tr>
<tr>
<td>Spectroscopic constants ((R^0, D^0, \alpha^0)) computed using relativistic energy-consistent small-core pseudopotentials, large valence basis sets and CC calculations including single and double excitations and noniteractive triple corrections ([\text{CCSD(T)}]) applied for 40 electrons; averaged coupled-pair functional (ACPF) treatments; (\text{Möller-Plesset perturbation theory with single, doubles, triples and quadruples [MP4(SDTQ)] calculations; s–o coupling neglected; covalent bonding contributions to van der Waals (vdW) interaction analysed in terms of atom-based local occupation number operators and associated interatomic charge fluctuations obtained within CASSCF method}</td>
<td>(X^1\Sigma^+_g)</td>
<td>Yu and Dolg (1997) [135]</td>
</tr>
<tr>
<td>PECs and spectroscopic constants ((R^0, D^0, \alpha^0)) computed using pure diffusion quantum Monte Carlo (PDQM–C) and (\text{CCSD(T)}) with relativistic energy-consistent large-core ([\text{Kr}]4d^{10}) pseudopotentials and corresponding core-polarisation potentials (CPP); covalent bonding contributions to vdW interaction analysed in terms of local occupation number operators and the associated inter-atomic charge fluctuations</td>
<td>(X^1\Sigma^+_g)</td>
<td>Schautz et al. (1998) [158]</td>
</tr>
<tr>
<td>Properties of ground-state bonding (ionisation potentials, electron affinities, (R^0, D^0, \alpha^0)) of (\text{Cd}_n) ((n = 2, 3, 4, 5, 6)) clusters investigated by quantum chemical (ab) (\text{initio}) methods: relativistic large-core ([\text{Kr}]4d^{10}) pseudopotentials, CPP; correlation taken into account within (\text{CCSD(T)}) method for 2n electrons; s–o coupling neglected; electron localisation function (ELF) calculated for qualitative picture of covalent contributions to bonding</td>
<td>(X^1\Sigma^+_g)</td>
<td>Flad et al. (1999) [159]</td>
</tr>
<tr>
<td>PECs and spectroscopic constants computed using AE multireference doubles excitation CI MRDCI method for 40 electrons using Slater-type functions (STF) optimised at SCF level; s–o coupling not investigated</td>
<td>excited ((S^1P, S^1P^1)) and (X^1\Sigma^+_g)</td>
<td>García de la Vega and Miguel (2000) [153]</td>
</tr>
<tr>
<td>PECs and TDMs computed using quasirelativistic valence (ab) (\text{initio}) calculations using CASSCF/CASPT2 method; (\text{Cd}) atom considered as 20-valence electron system, the (\text{Cd}^{10+}) core replaced by energy consistent pseudopotential which accounted for scalar-relativistic effects; s–o interaction accounted for within the valence shell</td>
<td>excited ((S^1P, S^1P^1)) and (X^1O^1_g)</td>
<td>Łukomski et al. (2003) [118], Łukomski et al. (2005) [128], Strojecki et al. (2010) [116], Czuchajczuchaj and Krośnicki (2004, 2005) [154,155]</td>
</tr>
</tbody>
</table>
State average CASCCF calculation for active space consisted of 5s and 5p orbitals followed by multi-reference averaged coupled pair functional (MRACPF) with single and double excitations from 4d, 5s and 5p; core electrons of Cd\(^{20+}\) represented by newly developed (in Ref. [134]) energy consisted relativistic pseudopotentials, s–o effect included; separate CCSD(T) calculations for ground state with the same pseudopotentials where BSSE correction was included

Spectroscopic constants \((R^0, D^0, \omega^0)\) computed using state-of-the-art calculations at the coupled cluster level of theory including the effects of core valence correlation; PEC extrapolated to the complete basis set limit; s–o coupling corrected data represent some of the most accurate and result in new recommendation for the \(R^0_{\text{exc}}\) of the group 12 dimers

PECs computed using CCSD(T); relativistic small core pseudopotentials employed using ST97 [228] and CRENBL [229,230] methods; BSSE determined via the counterpoise method of Boys and Bernardi [170]; physical origin of stability of molecule analysed by symmetry adapted perturbation theory; s–o coupling not included

PECs and spectroscopic constants \((R^0, D^0, \omega^0)\) calculated at different levels of theory: Dirac-Coulomb Hamiltonian (DCH), 4-component spin-free-Hamiltonian, nonrelativistic Lévy-Leblond (NRLL) Hamiltonian and with the simple Coulombic correction to DCH; PECs computed in an AE approach including BSSE correction; electron correlation treated at CCSD(T) level

PEC computed at coupled cluster with CBS/CCSD(T) + SO + ΔT level of theory with small core relativistic pseudopotentials; 40 electrons correlated by means of CCSD(T); full triple corrections ΔT extracted from CCSDT calculations with 24 correlated electrons; s–o coupling contributions taken from four-component Dirac–Fock calculations; extrapolated to the complete basis set (CBS) limit; BSSE correction included

PECs and TDMs computed using quasi-relativistic valence ab initio calculations using CASCCF/CAS at CASPT2 level; Cd atom considered as 20-valence electron system, the Cd\(^{20+}\) core replaced by effective pseudopotential; s–o effect included

PECs from all electrons calculations performed with time-dependent density functional theory (TDDFT) for relativistic DCH (s–o coupling included) and relativistic spin-free-Hamiltonian (s–o coupling not included); various exchange-correlation functionals used (PBE, BPW91, B3LYP, CAMB3LYP – see references in [156])

Excited \(5^3\Pi_r, 5^1\Pi_r, 6^3S_r, 6^1S_r\) \(6^3\Pi_r, 5^1\Pi_r\) and \(X^1\Sigma^+_g\)

Figgen et al. (2005) [134]

Excited \(5^3\Pi_r, 5^1\Pi_r, 6^3S_r, 6^1S_r\) \(6^3\Pi_r, 5^1\Pi_r\) and \(X^1\Sigma^+_g\)

Kullie (2013) [156]
and excited states for both atoms, and the wave functions $\Psi^A_n$ and $\Psi^B_k$ describe the excited states of these atoms. Clearly, the dispersion energy is always negative, hence the corresponding interaction is always attractive. It is also possible to connect Equation (1) with the polarisabilities of the interacting atoms by performing the multipole expansion of the $V$ operator, and introducing well known vdw $C_6$ coefficients, which describe a dominant long-range inverse power expansion of the dispersion energy as $E^{(2)}_{\text{disp}} = -C_6/R^6$,

$$C_6 = \frac{3}{\pi} \int_0^\infty \alpha^A_d(i\omega)\alpha^B_d(i\omega)d\omega,$$

(2)

where $\alpha^{A,B}_d(i\omega)$ is a dipolar polarisability of atom (A or B) at imaginary frequency. The dispersion energy can be also evaluated within simple Drude–London model according to which, the dispersive $E_{\text{disp}}$ interaction (so-called London interaction) between two ground-state atoms is proportional to $-1/R^6$ and can be expressed by a relationship

$$E_{\text{disp}} = \frac{3}{2} \alpha_1 \alpha_2 \frac{I_1 I_2}{(I_1 + I_2)} \frac{1}{R^6},$$

(3)

where $I_{1,2}$ and $\alpha_{1,2}$ are ionisation potentials and static atomic polarisabilities of atom 1 and 2, respectively. Note: Assuming $E_{\text{disp}} = D''_e$, for homoatomic molecule ($1 = 2 = M$) one may calculate $R''_e,\text{vdW}$

$$R''_e,\text{vdW} = \sqrt{\frac{3I_M \alpha^2_M}{4D''_e}},$$

(4)

(see Section 4.4.1 where the covalent admixture to the Cd$_2$ ground state bonding is discussed).

The potential energy minima in dimers with $s^2$ configuration originate from a subtle balance between attractive dispersion and repulsive electron-exchange effects. This helps one to understand the pattern of well depths for all dimers with $s^2$-configuration: in case of Yb$_2$, Sr$_2$ or Ca$_2$ dimers, the well depths are significantly larger as compared to those of group 12 systems, like Zn$_2$, Hg$_2$ or Cd$_2$, since the polarisabilities of the former group of atoms are much larger than in the latter case.

Let one analyse the interaction of the ground-state Cd$_2$ as a prototype system. What is peculiar for neutral closed-shell non-bonded systems of two metal atoms, the Hartree–Fock (H–F) interaction energy is positive for all interatomic distances. It is the energy of the correlation of electron movements that makes the Cd atoms attractive. The most important in this effect is the dispersion interaction which results from the correlation of the electrons between the atoms. The most important effect of the interatomic correlation is the long-range attraction of neutral closed-shell atoms which shows up in the vdW expansion at long range i.e. $E^{(2)}_{\text{disp}} = -C_6/R^6 - C_8/R^8 - C_{10}/R^{10} - \cdots$ [see Equation (14) in Section 5.1.2]. Hence the methods that include the electronic correlation are essential in describing the interactions between atoms with $s^2$ configuration.

While for the excited states the electronic structure methods are by no means black-box, situation is much simpler in case of an interaction of ground-state atoms (or molecules) which have strong single-reference character: this character reveals mostly in large lowest excitation energy. In case of the Cd atoms, the criterion is very well satisfied. For such systems the coupled-cluster (CC) theory is the first-choice method of use.
In CC theory, one assumes that the exact many-electron wavefunction can be obtained by the so-called CC ansatz [164]: \( \Psi = e^T \Phi \), where \( \Phi \) is the H–F reference state (Slater determinant) and \( T = T_1 + T_2 + \cdots \) is the so-called cluster operator which is an excitation operator: acting on the HF reference state it replaces the occupied orbitals by virtual ones. The \( T \) operator can be split into the sum of operators \( T_j \) (see above) corresponding to a number of excitations that it produces in the reference state. A great advantage of the CC method is systematic improvability. In principle, it is possible to improve result by going from \( n \)th to \( (n + 1) \)th order in the excitation operator – nowadays, it is possible for small systems since a general scheme for arbitrary order CC has been developed [165,166]. However, the CC method becomes prohibitively expensive if one adds \( T_3 \) and higher excitations into the \( T \) operator, they must be treated approximately for typical applications. In the field of quantum chemistry, approximate version of CC theory that includes the triple excitations has become particularly popular, as so-called CCSD(T) [167], in which the triply excited configurations are calculated approximately. A test calculations for CCSD(T) performed on large data-set showed that they typically reproduce the interaction energies with about 1.5% accuracy [168]. (Note: for more details regarding the CC method, the reader is referred to a review paper of Bartlett and Musiał [169].) It is also very important to account for the basis set superposition error (BSSE) in the calculation by applying standard counterpoise correction [170,171].

Needless to say, almost all the calculations of the ground state PEC that can be found in the literature (see Table 3) were performed with CC method. Correction due to BSSE was taken into account in the ground-state calculations by Figgen et al. [134], Lukeš et al. [160], Bučinský et al. [161] and Pahl et al. [162].

2.3.1. New calculation of the ground state

In order to improve quality of the calculated \( \text{Cd}_2 \) ground-state interatomic potential, we performed additional \textit{ab initio} calculations. For all such calculations, the MOLPRO programme was employed [172,173].

For most of the atoms with \( s^2 \) electronic configurations, there are well optimised correlation-consistent Gaussian basis sets and for heavy ones (Cd, Hg, Yb, Ba) there are exist well-tailored ECP. The core potentials used here are designed by the Stuttgart group [134]. The basis sets were the same as formerly used by Pahl et al. [162] in their work on \( \text{Zn}_2 \), \( \text{Cd}_2 \) and \( \text{Hg}_2 \) dimers, which were optimised by Peterson and Puzzarini [174]. To better account for the behaviour near vdW minimum and on the repulsive wall, the midbond (mb) functions have been added on the top of that. The mb functions are placed on ghost-atoms (with no charge) in the geometric centre of the dimer and were built from H atom functions [augmented correlation-consistent n-zeta valence basis set pseudopotentials (aug-cc-p\( \text{VnZ-PP} \)] with \( n = 3(T), 4(Q), 5 \) as proposed recently by Bakr et al. [175].

The effect of basis set saturation in the vdW minimum and at the repulsive wall is the following. While the HF interaction energy [in Figure 4(c)(d) denoted as \( E_{\text{HF}} \)] is very well converged for all the basis sets (to about 0.2 cm\(^{-1} \) in the minimum), changes of the \( E_{\text{corr}} \) correlation energy (a part of the total interaction energy \( E \)) are quite significant. In the \( R_e^0 \) the difference between aug-cc-pCVTZ-PP + mb and aug-cc-pCVSZ-PP + mb basis sets (where \( \text{CV – core valence} \) is about 16 cm\(^{-1} \), larger than the magnitude of remaining errors in the potential. The difference between aug-cc-pCVSZ-PP + mb and aug-cc-pCVQZ-PP + mb basis sets is about 3 cm\(^{-1} \). Figure 4(c) shows a decomposition of the interaction energy \( E \)
into $E_{\text{HF}}$ and $E_{\text{corr}}$. The latter includes the intramonomer correlation contribution to the $E$ and the dispersion interaction $E_{\text{disp}}$. At the short range, both terms increase exponentially but have opposite signs. Increasing the basis set from aug-cc-pCVTZ-PP + mb to aug-cc-pCV5Z-PP + mb lowers the $E_{\text{corr}}$ and shifts the position of classical turning point by about 0.026 Å inward [see Figure 4(d)].

### 2.3.2. van der Waals coefficients of $\text{Cd}_2$ system

Since calculation of interaction potentials using the supermolecular method at very long range might be imprecise due to error cancellations, it is recommended to use the perturbation theory to evaluate the long-range coefficients. For the group 2 and 12 atoms, the calculations of vdW coefficients have become the state-of-the-art. In particular, for Sr and...
Yb atoms it was possible to confront them directly with precise spectroscopic measurements obtained from two-colour photo-association. To this end, one might express the $C''_6$ and $C''_8$ coefficient in terms of the $\alpha_d$ dipolar and $\alpha_q$ quadrupole frequency dependent polarisabilities (real for pure imaginary frequencies): $C''_6$ [see Equation (2)] and $C''_8 = \frac{15}{2\pi} \left( \int_0^\infty \alpha_d^2(i\omega)\alpha_q^2(i\omega)d\omega + \int_0^\infty \alpha_d^4(i\omega)\alpha_q^4(i\omega)d\omega \right)$. The most accurate frequency dependent polarisabilities for many-electron systems can be calculated using the CC response theory [176,177]. Using aug-cc-pCV5Z basis set, the $C''_6$ and $C''_8$ coefficients for the Cd ground state were calculated as 436.54 and 20,012 a.u., respectively. [Note: in Table 4, the $C''_6$ and $C''_8$ are expressed in (cm$^{-1}$ Å$^6$), 1 a.u. = 4820.2 cm$^{-1}$ Å$^6$, and compared with those of Czajkowski and Koperski [115], Łukomski et al. [118] and Ruszczak et al. [119].]

Result of our improved ab initio calculation for the $\chi^0_1$ ground state is presented in Figure 4(a, b) (red empty circles/solid line) where it is compared with those performed by other investigators and with those of experimental studies.

### 2.4. All-electron calculations of excited states of Cd$_2$

As it can be seen in Table 3, there have been no new all-electron (AE) ab initio calculations of Cd$_2$ excited-state interatomic potentials. Namely, Czuchaj et al. [152], García de la Vega and Miguel [153], Łukomski et al. [118,128], Strojecki et al. [116], Czuchaj [154], Czuchaj and Krośnicki [155], Figgen et al. [134] and Koperski et al. [19] have performed the ab initio calculations of the excited states of Cd$_2$ within ECP framework. Therefore, in order to complete this review, we performed AE calculations for the $A^+_1$, $B^1_u$, $a^{3_1_u}$, $b^{3_0_u}$ and $c^{3_1_u}$ electronic states.

In this calculations, we used original ANO-RCC basis set of Roos et al. [140]. The Hamiltonian used in electron correlation calculations was the same as in the case of the atomic calculations i.e. spin-free DKH-2 Hamiltonian. In order to account for static correlations, CASSCF calculations were performed. In the CASSCF calculations, molecular orbitals and configuration interaction (CI) coefficients of the wave functions were simultaneously optimised. The active space was formed by distributing four active electrons on molecular counterparts of atomic orbitals Cd-5$s$, Cd-5$p$ and Cd-6$s$. All closed orbitals were optimised. As starting orbitals, canonical H–F orbitals were used. The starting dimension of the small CI matrix in the Davidson procedure for the $X^1\Sigma^+_g$ and $(1)^3\Sigma^+_u$ states was set to two, and for the $(1)^3\Sigma^+_u$ state it was set to three. [Note: (1) denotes first on the energy scale of the electronic energy state with the given symmetry.] This avoided convergence problems for short interatomic distances. The molecular orbitals and wave functions were optimised in CASSCF calculations separately for each molecular excited electronic state of ungerade symmetry that originated from the 5$s5$p atomic configuration, with only one exception in case of $(1)\Pi_u$ state which was optimised simultaneously with second state of this symmetry (having ionic character) due to a strong CI.

In the second step, dynamic electron correlations using restricted active space multi-state CASPT2 (MS-CASPT2) [144–147] were included. In the CASPT2 calculations, 24 electrons (4 active and 20 closed-shell) were fully correlated. The active space was the same as on the level of CASSCF theory. The 10 molecular counterparts of atomic 4$d$ orbitals were correlated through single and double excitations. The rest of (inner) core orbitals were not correlated.

In the last step, s–o coupling effects were included by means of RASSI-SO calculations. In this step, many-electron Hamiltonian with the s–o coupling terms of the DKH-2
Table 4. Characteristics of \textit{ungerade} low-lying excited and ground electronic energy states of Cd$_2$.

<table>
<thead>
<tr>
<th>Energy State</th>
<th>$X^0_1(1\Sigma^+)$ ($5s^21S^0$)</th>
<th>$a^1I_p(1\Sigma^+)$ ($5s5p^1P^0$)</th>
<th>$b^1O_p(1\Pi^0)$ ($5s5p^1P^0$)</th>
<th>$c^1I_p(1\Pi^0)$ ($5s5p^1P^0$)</th>
<th>$A^0_0(0\Sigma^0)$ ($5s5p^1P^0$)</th>
<th>B$^1I_p(1\Pi^0)$ ($5s5p^1P^0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$ (cm$^{-1}$)</td>
<td>317.4 ± 3.0$^{bc}$</td>
<td>–</td>
<td>260.1 ± 7.1$^{bc,1a}$</td>
<td>709.7 ± 1.0$^a$</td>
<td>8490.2 ± 22.0$^c$</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>317.4 ± 3.1$^{3a,b}$</td>
<td>–</td>
<td>250.1 ± 6.1$^{3a,b}$</td>
<td>709.4 ± 2.3$^{3a,b}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>311.7 ± 0.4$^{3a,b}$</td>
<td>–</td>
<td>243.3 ± 0.4$^{3a,b}$</td>
<td>708.0 ± 10.0$^{3a,b}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$D_e$ (cm$^{-1}$)</td>
<td>328 ± 3$^{3a,b}$</td>
<td>8545.7$^{2a}$</td>
<td>258.8 ± 11.1$^{3a,b}$</td>
<td>721.4 ± 1.0$^{2a}$</td>
<td>8539.0 ± 22.0$^{c,d}$</td>
<td>4100 ± 100$^{2g}$</td>
</tr>
<tr>
<td></td>
<td>328 ± 3$^{3a,b}$</td>
<td>8545.7$^{2a}$</td>
<td>258.8 ± 11.1$^{3a,b}$</td>
<td>721.4 ± 1.0$^{2a}$</td>
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<td></td>
<td>328 ± 3$^{3a,b}$</td>
<td>8545.7$^{2a}$</td>
<td>258.8 ± 11.1$^{3a,b}$</td>
<td>721.4 ± 1.0$^{2a}$</td>
<td>8539.0 ± 22.0$^{c,d}$</td>
<td>4100 ± 100$^{2g}$</td>
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<td></td>
<td>328 ± 3$^{3a,b}$</td>
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<td>8539.0 ± 22.0$^{c,d}$</td>
<td>4100 ± 100$^{2g}$</td>
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<td>$E_b$ (cm$^{-1}$)</td>
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<td>1190 ± 20$^{2g}$</td>
<td>1394.6$^{2a}$</td>
<td>1449.5$^{2a}$</td>
<td>2432.4$^{2b}$</td>
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<tr>
<td>$\omega_e$ (cm$^{-1}$)</td>
<td>21.4 ± 0.2$^{3a,b}$</td>
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<td>18.40 ± 0.10$^{1a}$</td>
<td>27.2 ± 0.5$^{3a,b}$</td>
<td>97.74 ± 0.80$^{3a,b}$</td>
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<td>20.9$^{3a,b}$, 23.9$^{3a,b}$</td>
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<td>18.30 ± 0.06$^{1a}$</td>
<td>28.9 ± 0.5$^{3a,b}$</td>
<td>100.50 ± 0.25$^{3a,b}$</td>
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<td>20.0$^{3a,b}$, 23.9$^{3a,b}$</td>
<td>–</td>
<td>18.30 ± 0.06$^{1a}$</td>
<td>28.9 ± 0.5$^{3a,b}$</td>
<td>100.50 ± 0.25$^{3a,b}$</td>
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<td>$\omega_xe$ (cm$^{-1}$)</td>
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<td>0.40 ± 0.01$^{3a,b}$</td>
<td>–</td>
<td>0.311 ± 0.006$^{1a}$</td>
<td>0.26 ± 0.023$^{3a,b}$</td>
<td>0.303 ± 0.010$^{1c}$</td>
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<td>0.40 ± 0.01$^{3a,b}$</td>
<td>–</td>
<td>0.311 ± 0.006$^{1a}$</td>
<td>0.26 ± 0.023$^{3a,b}$</td>
<td>0.303 ± 0.010$^{1c}$</td>
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<tr>
<td>$R_e$ ($\text{Å}$)</td>
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<td>2.785$^{2a}$</td>
<td>4.05 ± 0.006$^{1e}$</td>
<td>3.86 ± 0.02$^{2k}$</td>
<td>2.750 ± 0.015$^{2k}$</td>
<td>2.67 ± 0.05$^{2c}$</td>
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<td>3.76 ± 0.04$^{3a,b}$</td>
<td>2.785$^{2a}$</td>
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<td>3.86 ± 0.02$^{2k}$</td>
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<td>2.750 ± 0.015$^{2k}$</td>
<td>2.67 ± 0.05$^{2c}$</td>
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\[ X_1^{0} + g(1 \Sigma^+ g) \left( \begin{array}{c} 5s^2 1S_0 \end{array} \right) a_3 \left( \begin{array}{c} 3 \Sigma^+ u \end{array} \right) \left( \begin{array}{c} 5s 5p 3P_1 \end{array} \right) \]

\[ b_3 \left( \begin{array}{c} 3 \Pi^+ u \end{array} \right) \left( \begin{array}{c} 5s 5p 3P_1 \end{array} \right) \]

\[ c_3 \left( \begin{array}{c} 3 \Pi^+ u \end{array} \right) \left( \begin{array}{c} 5s 5p 3P_2 \end{array} \right) A_1 \]

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Table 4. (Continued).

<table>
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<th>( \alpha'_{\sigma} ) (a.u.)</th>
<th>X'0(^+\left(\Sigma^+\right)) (Ss(^{1}S))</th>
<th>a(^{1}1(_{\upsilon}\left(\Sigma^+\right)) (SsS(^{3}P))</th>
<th>b(^{1}0(_{\upsilon}\left(\Pi\right)) (SsS(^{3}P))</th>
<th>c(^{1}1(_{\upsilon}\left(\Pi\right)) (SsS(^{3}P))</th>
<th>A(^{0}0(_{\upsilon}\left(\Sigma^+\right)) (SsS(^{3}P))</th>
<th>B(^{1}1(_{\upsilon}\left(\Pi\right)) (SsS(^{3}P))</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.7 ± 1.6(^{16})</td>
<td>46.9(^{15})</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>9.34(^{18\alpha}), 9.2(^{18\beta})</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4.03–5.16(^{17\alpha})</td>
<td>5.44(^{17\alpha})</td>
<td>4.45 ± 0.02(^{17\alpha})</td>
<td>–</td>
<td>–</td>
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</table>

\(^{1}\)This review, refined analysis of experimental data (recommended values in \textbf{bold}). (a) simulation of the \( b^{0}0^{+}_{\upsilon} \rightarrow X'0^{+}\Sigma \) LIF excitation spectrum; (b) simultaneous simulation of the LIF excitation and LIF dispersed emission spectrum; (c) agreement plot and simulation of the \( A^{0}0^{+}_{\upsilon} \rightarrow X'0^{+}\Sigma \) LIF excitation spectrum; (d) simulation of the \( A^{0}0^{+}_{\upsilon} \rightarrow X'0^{+}\Sigma \) LIF dispersed emission spectrum; (e) agreement plot and simulation of the \( b^{0}0^{+}_{\upsilon} \rightarrow X'0^{+}\Sigma \) LIF excitation spectrum, starting data from B–S analysis of Ref. [130]; (f) simulation of the \( b^{0}0^{+}_{\upsilon} \rightarrow X'0^{+}\Sigma \) LIF dispersed emission spectrum, starting data from Ref. [116]; (g) Equation (8); (h) Equation (9); (i) Equation (10); (j) Equation (11); (k) simulation of the \( c^{1}1_{\upsilon} \rightarrow X'0^{+}\Sigma \) LIF excitation spectrum.

\(^{2}\)Experimental results. (a) Ref. [116]: (a) \( c^{1}1_{\upsilon} \rightarrow X'0^{+}\Sigma \) and \( b^{1}0^{+}_{\upsilon} \rightarrow X'0^{+}\Sigma \) LIF excitation spectra, vibrational analysis; (b) \( b^{0}0^{+}_{\upsilon} \rightarrow X'0^{+}\Sigma \), \( b \rightarrow b \) LIF dispersed emission spectrum. (b) Ref. [118]: (a) \( A^{0}0^{+}_{\upsilon} \rightarrow X'0^{+}\Sigma \), \( b \rightarrow b \) LIF dispersed emission spectrum, \( B-S \) plot and isotopic analyses, some analyses for \( \_{\gamma}^{22} \text{Cd} \); (b) \( A^{0}0^{+}_{\upsilon} \rightarrow X'0^{+}\Sigma \), \( b \rightarrow b \) and \( b \rightarrow f \) LIF dispersed emission spectrum. (c) Ref. [131], analysis of rotational profiles \( A^{0}0^{+}_{\upsilon} \) \( (\upsilon' = 26, 27, 42, 46, 48), B_{\upsilon} \) of \( (\_{\gamma}^{\text{Cd}}) \), from for: (a) \( B_{\upsilon} = B_{\upsilon} - B_{\upsilon}(u' + 1/2) + \nu(u' + 1/2)^2; (b) \upsilon = 27; (c) \upsilon' = 0.5; (d) Ref. [120], \( A^{0}0^{+}_{\upsilon} = 45 \) analysis of rotational profile for \( \_{\gamma}^{22} \text{Cd} \), (e) Ref. [115], \( b^{1}0^{+}_{\upsilon} \rightarrow X'0^{+}\Sigma \) LIF excitation spectrum, vibrational analysis; (a) estimated from Liuti-Pirani method of Ref. [232], (f) Ref. [130]. (g) Ref. [119]: (a) \( B^{1}1_{\upsilon} \rightarrow X'0^{+}\Sigma \) LIF excitation spectrum, vibrational analysis; (b) \( B^{1}1_{\upsilon} \rightarrow X'0^{+}\Sigma \), \( b \rightarrow b \) and \( b \rightarrow f \) LIF dispersed emission spectrum. (h) Ref. [132], \( B^{1}1_{\upsilon} \rightarrow X'0^{+}\Sigma \), \( b \rightarrow b \) and \( b \rightarrow f \) LIF dispersed emission spectrum. (i) Ref. [117], \( c^{1}1_{\upsilon} \rightarrow X'0^{+}\Sigma \) LIF excitation spectrum. (j) Born-Mayer potential \( U_{\text{BM}} = Ae^{-B_{\nu}} + C_{\upsilon} \) Morse-vdW potential \( U_{\text{M-vdW}} = D_{\nu} \left(1 - e^{-D/2R} \right)^{2} - \left(1 - e^{-D/2R} \right)^{3} \). (k) Lennard-Jones potential, \( \chi = 6 \) (Ref. [129], (m) Ref. [193]. (o) Ref. [194]. (p) Ref. [150].

\(^{3}\)Results of \textit{ab initio} calculations. (a) Refs. [154,155]. (b) Ref. [19]. (c) Refs. [162,163]. (d) Ref. [158]. (e) Ref. [135]. (f) Ref. [190], (g) Ref. [151]. (h) Ref. [159]. (i) Ref. [174]. (j) Ref. [140].
Hamiltonian were supplemented and the atomic mean-field approximation for their integrals [178] was adopted. In the RASSI code, s–o matrix elements were calculated in a wave function basis which is formed from individually optimised CI expansions in the former CASSCF/CASPT2 calculations. All ungerade triplet and singlet states originating from \((5s5p)^3P\) Cd and \((5s5p)^1P\) Cd configuration, as well as the ground state were included in this step. The TDM were determined within RASSI by calculation the interaction matrix elements between the ground and the excited states. The calculations were performed using the MOLCAS 8.0 package [147,180,181].

Results of \textit{ab initio} calculation performed additionally for the purpose of this review for the \(A^10_u, B^11_u, a^11_u, b^10_u\) and \(c^11_u\) low-lying states are presented in Figures 5–9, while Figure 4(a, b) shows the result obtained for the \(X^10^+\) ground states (red full circles/solid line). The results are compared with those performed by other investigators [19,155–157,162] and with those of experimental studies reported in Refs. [19,115–120].

2.5. Transition dipole moments

The upper part of Figures 2, 5–9 presents the TDM (in fact their lengths i.e. \(|\text{TDM}|\)) determined here within the RASSI calculations (red full circles/solid line). In Figures 5–9, they are compared (after a normalisation) with those of Czuchaj and Krośnicki [155] (blue empty circles/solid line). The magnitude of TDM influences the intensity of the transition from the ground state to the corresponding ungerade excited state. What is especially important, the figures illustrate how the TDM change with \(R\). This behaviour has an influence on the intensity of simulated vibrational components for particular transition and can constitute an additional criterion for verification and adjustment of the TDM in function of \(R\). One can see that general trends in TDM determined here and those of Czuchaj and Krośnicki [155] are similar however, one can note differences in relative shifts of their extrema. Further discussion is presented in detail below.

3. Review of experimental studies of \(\text{Cd}_2\)

3.1. Laser spectroscopy of \(\text{Cd}_2\) in supersonic beams: experimental results

The \(\text{Cd}_2\) dimer has been a subject of experimental studies [14,182 and references therein]. Early investigations of absorption and fluorescence of cadmium vapours were performed at the beginning of the twentieth century [183–185]. Soon after, the molecular absorption and the fluorescence spectra of \(\text{Cd}_2\) were recorded by Kapuściński [186], Mohler and Moore [187], Jabłoński [188], Mrozowski [189], Hamada [190], and Cram [191]. The studies concluded with information on the location of the detected spectra and their origin. Approximate depths and equilibrium internuclear distances for the ground- and low-lying excited-state PECs were also given [191]. Due to its very shallow predominantly vdW ground state and several bound excited states, there was a considerable interest in \(\text{Cd}_2\) (in analogy to \(\text{Hg}_2\)) due to the possibility of laser applications (in comparison with the homo- and hetero-atomic noble gas excimers and exciplexes) [15,16 and references therein].

3.1.1. The \(A^10_u(\Sigma_u^+)\) and \(B^11_u(\Pi_u)\) states correlating with the \(5^1P\) asymptote

The \(A^10_u^+\) singlet ungerade state correlating with the \(5^1P\) asymptote (see Figure 5) has been first-time studied in supersonic beam by Łukomski \textit{et al.} [118]. The \(A^10_u^+ \rightarrow X^10_g^+\)
(laser-induced fluorescence) LIF excitation spectrum which is centred at approx. 258.2 nm (i.e. 38,730 cm$^{-1}$) has been recorded as a long $\nu^\prime \leftarrow \nu^\prime = 0$ vibrational progression with resolved isotopic structure due to the fact that considerably high $\nu^\prime$ (i.e. from 19 to 54) were reached in the excitation. The isotopic shift was analysed providing values for the vibrational characteristics (frequency and anharmonicity) $\omega_{e}^\prime = 100.50$ cm$^{-1}$ and $\omega_{e}^\prime x_{e}^\prime = 0.325$ cm$^{-1}$ for the $^{226}$Cd$_{2}$ isotopologue. The A$^{1}0_{u}^{+}$-state potential has been obtained numerically using an inverse perturbation approach (IPA) methodology [192]. In the simulation of the

![Figure 5. (Colour online) Interatomic potential of the A$^{1}0_{u}^{+}(5P_{1})$ excited electronic state of Cd$_{2}$. The scheme shows ab initio calculated potentials of Czuchaj and Krośnicki [155] (blue empty circles/solid line), Koperski et al. [19] (black empty triangles/solid line), Kullie [156,157] (green empty squares/solid line) and of this review (red full circles/solid line), as well as those obtained experimentally by Lukomska et al. [118] (Morse potential, blue dot-dashed line) and in this review from additional simulation of the LIF excitation and dispersed emission spectra reported in Ref. [118] – Morse potential shifted by $-655.8$ cm$^{-1}$, with $R^e = 2.750$ Å (red solid line) and with $R^e = 2.772$ Å (red dashed line), respectively. Positions of $\nu^\prime = 18$ and $\nu^\prime = 53$ vibrational levels show the energy region between the excitation spectrum was recorded [118]. Upper part: The determined TDM (normalised) of Czuchaj and Krośnicki [155] (blue empty circles/solid line) and of this review (red full circles/solid line). The position of the $R^e = 3.76$ Å is indicated with solid vertical lines. F–C window for excitation from the X$^{1}0_{g}^{+}, \nu^\prime = 0$ is approximately depicted in blue. See text for details.

![Figure 5](image-url)
A$^1\text{O}_u^+ \leftarrow X^1\text{O}_g^+$ LIF excitation spectrum [118], neither an influence of TDM nor rotational structure of the transition has been taken into account. Later on, rotational structure of the transition has been taken into account. Later on, rotational energy structure in several $(\nu', \nu''=0)$ bands, where $\nu' = 26, 27, 42, 45, 46, 48$, in $(^{114}\text{Cd})_2$ was investigated [120,131]. It has led to a determination of the A$^1\text{O}_u^+$-state rotational constants $B_\nu$, and bond length $R'_e (\text{A}^1\text{O}_u^+) = 2.71$ Å [131]. In the work of Rodriguez and Eden [193] or Tran and Eden [194], where the A$^1\text{O}_u^+ \rightarrow X^1\text{O}_g^+$ emission or A$^1\text{O}_u^+ \leftarrow a^3\Pi_g$ excitation spectra (called there...
the $B^1\Sigma_u^+ \rightarrow X^1\Sigma_u^+$ or $B^1\Sigma_u^+ \leftarrow a^3\Pi_g$ transitions, respectively) have been observed by photo-associating pairs of Cd ground state atoms in a high-temperature (800–1000 K) cell and exciting the $A^1\Pi_u^+$ state at several discrete wavelengths (for observation of the $A^1\Pi_u^+ \rightarrow X^1\Pi_g$ emission) or using pump-and-probe approach to excite the $A^1\Pi_u^+$ state via the $a^3\Pi_g$ intermediate (for observation of the $A^1\Pi_u^+ \leftarrow a^3\Pi_g$ excitation), respectively, the authors determined characteristics of the $A^1\Pi_u^+$ state that turned out to be in acceptable agreement with those of later reports [118,120,131].

Second singlet ungerade state that correlates with the $5^3P_1$ asymptote, $B^11_u$ (see Figure 6), has been investigated in supersonic beams several times by excitation from the $X^1\Sigma_g^+$ state at approx. 221.7 nm (i.e. 45,105 cm$^{-1}$). Strojecki et al. [131] and Koperski et al. [132] studied
the B$^{1}_{1u} \leftarrow X^1O^+_g$ LIF excitation spectrum for rotationally resolved $A_1 + A_2 = 228$ isotopologue in the $(\nu' = 38, \nu'' = 0)$ band. They estimated rotational characteristic $B_{\nu'} = 38$ of the excited state and confirmed presence of a barrier in the B$^{1}_{1u}$-state potential. More thorough investigation of the excitation spectrum has been reported by Ruszczak et al. [103] where the B$^{1}_{1u}$-state potential was determined using IPA methodology with a starting B$^{1}_{1u}$-state potential to be a model potential with a barrier generated by a two-state diagonalisation procedure. In the simulation of the B$^{1}_{1u} \leftarrow X^1O^+_g$ LIF excitation spectrum [119], an influence
of rotational structure of the transition has not been fully taken into account. Effect of the tunnelling through the $B_{11u}$-state potential barrier has not been studied as well.

3.1.2. The $a_{31u}(3\Sigma^+_{u})$ and $b_{30}^+\left(3\Pi^u\right)$ states correlating with the $5^3P_1$ and $c_{31u}(3\Pi^u)$ state correlating with the $5^3P_2$ asymptote

The lowest-lying excited $a_{31u}^3$ triplet $ungerade$ state correlating with the $5^3P_1$ asymptote (see Figure 7) has been studied both theoretically and experimentally only once by Łukomski et al. [128]. They discovered that a lack of success in recording the $a_{31u}^3 \rightarrow X^10^+_g$ LIF excitation
spectrum (in two independent experiments in different laboratories) centred at approx. 350–360 nm (i.e. 27,780–28,570 cm\(^{-1}\)) can be attributed to an extremely small TDM (it is necessary to emphasise here that an oscillator strength \(f\) for the transition is proportional to TDM\(^2\)) – compare with Figure 3 in Łukomski et al. [128].

The other low-lying \(b^30^+_u\) triplet ungerade state correlating with the \(5^3P_1\) asymptote (see Figure 8) has been investigated in supersonic beams by Czajkowski et al. [129], and Czajkowski and Koperski [115] using laser excitation at approx. 325.5 nm (i.e. 30,725 cm\(^{-1}\)) from \(\nu'' = 0\) to several \(\nu'\) vibrational levels (i.e. from 0 to 8). In the simulation of the \(b^30^+_u ← X^10^+_g\) LIF excitation spectrum [115,129] neither an influence of TDM, molecular isotopic composition nor rotational structure of the transition has been taken into account. As a result, the \(b^30^+_u\)-state potential was represented with a Morse function

\[
U_{\text{Morse}}(R) = D_e \left[1 - e^{-\beta (R - R_e)} \right]^2, \tag{5}
\]

where \(R_e\) is an equilibrium bond length, \(\beta = \sqrt{\frac{8\pi^2\hbar^2\omega_x}{m}}\) controls the ‘width’ of the potential well and \(\mu\) is the reduced mass. For the \(b^30^+_u\)-state \(U_{\text{Morse}}\) potential: \(D_e = 260\) cm\(^{-1}\), \(\beta^\prime = 1.0512\) Å\(^{-1}\), \(R_e^\prime = 4.33\) Å has been proposed [115]. Recently, Urbańczyk and Koperski [130] analysed the spectrum using so-called agreement plot [determination of the \((\omega'_e, \omega'_x, \chi'_e)\) pairs that provide a number of satisfactory Morse representations of the \(b^30^+_u\)-state potential, with the \((\omega'_e = 18.40\) cm\(^{-1}\), \(\omega'_x = 0.327\) cm\(^{-1}\)) [130] as most suitable] as well as they modelled shape of rotational profiles of the \((\nu' = 0, \nu'' = 0)\) and \((\nu' = 1, \nu'' = 0)\) bands, and were able to estimate the \(R_e^\prime(b^30^+_u) = 4.05\) Å [130]. The spectrum as a whole was not simulated there.

The \(c^10^+_u\) triplet ungerade state correlating with the \(5^3P_1\) asymptote (see Figure 9) that can be excited at approx. 318.1 nm (i.e. 31,435 cm\(^{-1}\)) from the ground state has been investigated in supersonic beams by Czajkowski et al. [117] and Strojecki et al. [116]. [Note: Asymptotically, i.e. \(5^3P_2 → 5^1S_0\) in Cd, the transition is forbidden, see Figure 1.] In the simulation of the \(c^10^+_u ← X^10^+_g\) LIF excitation spectrum [116,117], an influence of TDM has not been taken into account. As a result of the simulation, the \(c^10^+_u\)-state potential was represented with a Morse function \((D_e' = 723\) cm\(^{-1}\), \(\beta' = 0.9331\) Å\(^{-1}\), \(R_e'^\prime = 3.86\) Å) [116]. It is worthwhile to mention that the \(c^10^+_u\)-state bond length \(R_e'(c^10^+_u)\) that has been determined there is only 0.08 Å shorter than that of the ground state \((R_e'^\prime = 3.78\) Å) [116]), so the \(c^10^+_u ← X^10^+_g\) transition may be considered as a possible way for vibrational cooling of Cd\(_2\) molecules in a MOT, as it was proposed for the Hg\(_2\) by employing the F\(^0^+\)_\(_2\) ← X\(^0^+\)_\(_g\) transition [12,127].

The spectroscopic characteristics that were reported for the low-lying excited singlet and triplet ungerade states of Cd\(_2\) are collected in Table 4.

### 3.1.3. Experiments versus ab initio calculations

Figures 5–9, present results of experiments [115–119] (except Figure 7; Note: Figure 7 is not considered in the comparison as the \(a^31^u\)-state potential has never been determined experimentally) compared with, among others, ab initio calculated potentials of Czuchaj and Krośnicki [155] (blue empty circles/solid line), Koperski et al. [19] (black empty triangles/solid line) and Kulie [156,157] (green empty squares/solid line) for the A\(^10^+\)_\(_u\) (Figure 5), B\(^1^1\)\(_u\) (Figure 6), a\(^3^1\)\(_u\) (Figure 7), b\(^3^0^+_u\) (Figure 8) and c\(^3^1\)\(_u\) (Figure 9), low-lying ungerade excited states of Cd\(_2\). It must be noted that, except the a\(^3^1\)\(_u\) state, due to the overlap of the ground- and excited-state wavefunctions, the low-lying ungerade interatomic potentials
were experimentally characterised in different regions of their potential wells, i.e. for \(A^10_u^+, \nu' = 19–57\) [118], for \(B^11_u^+, \nu' = 33–40\) [119, 132], for \(b^10_u^+, \nu' = 0–9\) [116] and for \(c^31_u^+, \nu' = 0–4\) [115, 116]. Consequently, since the representations of the interatomic potentials presented in Figures 5, 8 and 9 are expanded over the whole range of \(R\), so outside the above mentioned regions they are only extrapolations and should be treated with caution.

The comparisons presented in Figures 5, 6, 8 and 9 show that, especially for the \(B^11_u\) (Figure 6), \(b^10_u^\prime\) (Figure 8) and \(c^31_u\) (Figure 9) states, there are considerably large discrepancies between \textit{ab initio} calculated potentials of Refs. [19, 155] (see blue empty circles/solid line, black empty triangles/solid line) and those determined experimentally (the situation is somewhat better for the \(A^10_u^+\) state – Figure 5). Moreover, for all the \(A^10_u^+, B^11_u^+, b^10_u^\prime\) and \(c^31_u\) \textit{ungerade} excited states, potentials calculated very recently by Kullie [156, 157] (green empty squares/solid line) are always shallower than those of experimental studies reported in Refs. [115–119]. Also, all Kullie’s potentials are well too shallow, and moreover, his potential for the \(B^11_u\) state is located entirely above the \(5^1P_1\) asymptote. Consequently, there is a doubt the Kullie’s potentials can be accepted as a consistent result. There is no doubt, the situation calls for additional studies, especially for the refinement of the \textit{ab initio} calculations of the low-lying \textit{ungerade} \(\text{Cd}_2\) interatomic potentials as well as for supplemental re-analysis of the recorded LIF excitation and dispersed emission spectra.

### 3.1.4. The \(X^10_g^+(\Sigma_g^+)\) ground state

Studies of the \(\bar{X}^10_g^–\) state interatomic potential in \(\text{Cd}_2\) have been performed in a number of supersonic-beam experiments. The investigations concluded with a characterisation of both the potential well and part of the potential’s repulsive branch above the dissociation limit.

As far as the characterisation of the bound part is concerned, the most thorough investigation has been performed by Strojecki et al. [116] via recording of the \(\nu' = 0–4 \rightarrow \nu'' = 0–8\) transitions in LIF dispersed bound \(\rightarrow\) bound (b \(\rightarrow\) b) emission spectra. The study concluded with a determination of the vibrational characteristics (\(\omega'_e = 21.4 \text{ cm}^{-1}, \omega'_e x'_e = 0.35 \text{ cm}^{-1}\)) as well as the dissociation energy \(D'_e = 317.4 \text{ cm}^{-1}\) and well depth \(D''_e = 328 \text{ cm}^{-1}\) of the potential represented up to the energy of \(\nu'' = 8\) by a Morse function. Also, rotational characteristics (\(B''_e\) and \(B_{e,\nu''}\)) were estimated.

More detailed studies of the ground-state rotational energy structure have been performed by Strojecki et al. [131] where rotational structure of six (\(\nu', \nu'' = 0\)) bands, where \(\nu' = 26,27,42,45,46,48\), in (\(^{114}\text{Cd}\)), has been investigated. The study concluded with determination of \(B_{\nu''=0} = 0.0207 \text{ cm}^{-1}, B''_e = 0.0209 \text{ cm}^{-1}\) and \(R''_e = 3.76 \text{ Å}\), the more reliable value for the ground-state bond length. Accordingly, the result obtained by Strojecki et al. [131], the \(R''_e\), distinctly shorter than that obtained with assumption of pure ground-state vdW bonding (\(R''_{e,\text{vdW}} = 4.58 \text{ Å}\) [131]), supported a theoretical prediction of a covalent admixture to the ground-state bonding in \(\text{Cd}_2\).

Another confirmation of an admixed vdW character of the ground state potential came from modelling of its repulsive branch. The repulsive branch has been determined three times, by Łukomski et al. [118], Koperski et al. [132] and Ruszczak et al. [119] from simulations of the \(A^10_u^+ (\nu' = 38\ or\ 39) \rightarrow \bar{X}^10_g^+\) [118] and \(B^11_u^+ (\nu' = 38\ [132]\ or\ 39 \pm 1\ [119]) \rightarrow \bar{X}^10_g^+\) LIF dispersed emission spectra in \(^{226}\text{Cd}_2\). The spectra consisted of \(b \rightarrow b\) (discrete) and bound \(\rightarrow\) free (\(b \rightarrow f\), continuous) transitions which together formed so-called Condon internal diffraction (CID) patterns. As it is well known, a term \textit{reflection spectra} should be rather used here as the regular oscillations in the resulting spectrum are reflections of the...
initial $\nu'$ level wave-function squared, as was originally pointed out by Tellinghuisen [195]. It is necessary to emphasise here, that because the $b \rightarrow b$ parts of the $A^10_u^+ \leftrightarrow X^10_g^+$ [118] and $B^11_u \rightarrow X^10_g^+$ [119,132] spectra have not been fully resolved, one can deduce that the $\nu'$ from which the fluorescence has been emitted, may possess an $\pm 1$ or even $\pm 2$ uncertainty, as it was approved [118,119]. Simulations of the CID patterns resulted in several hybrid-potential representations. Łukomski et al. [118] and Ruszczak et al. [119] proposed a Born-Mayer–Morse-vdW while Koperski et al. [132] a Born-Mayer–Morse, with a short-range $Ae^{-bR}$ (Born-Mayer function) of the Buckingham-type potential. A Lennard-Jones–Morse hybrid representation i.e. L-J($n − m$)–Morse (that would allow to compare it with that determined for Hg$_2$, $n = 6.21$, $m = 6$ [14,196]) was never tried. Only in simulations performed by Łukomski et al. [118], the TDM (its variations with $R$) has been taken into account.

The spectroscopic characteristics that were determined for the ground state of Cd$_2$ are collected in Table 4 while Figure 4(a, b) presents, among others, comparison of the ground-state interatomic potentials determined from ab initio calculations reported in Refs. [19,155–157,162] as well as from experiments of Refs. [115,118,119].

4. Discussion

4.1. The $A^10_u^+ \leftrightarrow X^10_g^+$ spectra – the $A^10_u^+$-state potential

Figures 10(a) and 12(a) (red traces) show LIF excitation and LIF dispersed emission spectra recorded using the $A^10_u^+ \leftrightarrow X^10_g^+$, $\nu'' = 0$ [Figure 10(a)] and the $A^10_u^+, \nu' = 38 \rightarrow X^10_g^+$ [Figure 12(a, a', a'')] transitions, as reported in Ref. [118]; the experimental conditions are given in the figure captions.

4.1.1. The $A^10_u^+ \leftrightarrow X^10_g^+$ LIF excitation spectrum

The excitation spectrum consists of the $\nu' \leftarrow \nu'' = 0$ progression with $\nu'$ spanning the range from $\nu' = 19$ to 54. As can be seen in Figure 5, the location of the excited $\nu'$ is in the lower half of the $A^10_u^+$-state potential well i.e. closer to the bottom of the well than to the dissociation limit.

4.1.1.1. The agreement plot. Re-analysis of LIF excitation spectrum recorded using the $A^10_u^+ \leftrightarrow X^10_g^+$ transition [118] shown in Figure 10(a) (red trace) began with employing of so-called agreement plot method [197] via examination of the $E_v^{\text{expt}}$ energies of vibrational transition recorded in the spectrum for the most abundant $^{114}$Cd$^{112}$Cd isotopologue. The agreement plot illustrates a method of determination of pairs of the $\omega'_e$ and $\omega'_e \chi'_e$ vibrational constants. The method is used under an assumption that in the region of the recorded $E_v^{\text{expt}}$, the $A^10_u^+$-state interatomic potential is represented by a Morse function (a fully justified assumption as shown in Ref. [118]). The main advantage of the method (in comparison to e.g. well known Birge–Sponer (B–S) plot [23]) is accepting the fact that exists a number of pairs of the $\omega'_e$ and $\omega'_e \chi'_e$ values that are highly correlated. In other words, it can be shown that there exist many of the $(\omega'_e, \omega'_e \chi'_e)$ pairs which can be used to perform simulations that are in satisfactory agreement with the experimental spectrum, especially when the rotational structure of the spectrum is not resolved. Using the agreement plot, it can be clearly shown, which of the $(\omega'_e, \omega'_e \chi'_e)$ pairs provide the satisfactory simulation. It is also valuable, that the agreement plot can be employed to determine uncertainties of the obtained $\omega'_e$ and $\omega'_e \chi'_e$ values in a more reliable way than in case of the B–S plot.
For each combination of the \( u_1 \) and \( u_2 \) in the specified ranges of their values (e.g. around their expected values obtained using the B–S plot), the corresponding \( A_{10}^\text{+}u^{-} \)-state Morse representation was determined. Next, for each Morse representation using the LEVEL programme [121], energies of the vibrational transitions \( E_{\text{sim}} \) corresponding to the transitions observed in the experimental spectrum were simulated. Then, the \( E_{\text{sim}} \) were compared with the recorded \( E_{\text{expt}} \). Finally, for each Morse representation, the so-called agreement coefficient was calculated, where

\[
P = 1 / (0.01 + \chi^2)
\]

was calculated, where \( \chi^2 = \sum_{\nu'} (\Delta E_{\nu'}^{\text{expt}} - \Delta E_{\nu'}^{\text{sim}})^2 \) is a sum of squares of the differences between \( \Delta E_{\nu'}^{\text{expt}} \) experimental and \( \Delta E_{\nu'}^{\text{sim}} \) simulated energy separations, and \( \Delta E_{\nu'}^{\text{sim}} = E_{\nu'}^{\text{sim}} - E_{\text{int} \nu'}^{\text{sim}} \) where \( E_{\text{int} \nu'}^{\text{sim}} \) is an energy of the selected e.g. more intense, \( \nu' \leftrightarrow \nu'' = 0 \) transition in the experimental spectrum; the \( \Delta E_{\nu'}^{\text{expt}} \) were calculated similarly to the \( \Delta E_{\nu'}^{\text{sim}} \). The coefficient \( P \) describes the agreement between the simulation and experimental results in a quantitative way.

Figure 10. (Colour online) (a) LIF excitation spectrum (red trace) recorded using the \( A_{10}^\text{+}0_1^+(5\text{P}_1) \leftrightarrow X_{10}^+0_0^+(5\text{S}_0) \) transition in Cd\(_2\) under the following experimental conditions: nozzle diameter \( D = 0.15 \) mm, distance from the nozzle \( x = 6 \) mm, and pressure of the carrier (argon) gas \( p_{\text{ar}} = 12 \) atm as reported in ref. [118]. (b) Simulation [121,125,199] (blue line) performed assuming for the \( A_{10}^\text{+}0_1^\text{+} \)-state representation a shifted (by \(-655.8 \text{ cm}^{-1}\)) Morse potential obtained in this review with the \( D_e = 7882.5 \text{ cm}^{-1}, \beta' = 1.0072 \text{ Å}^{-1}, R_e = 2.75 \text{ Å} \) (see Figure 5). For the \( X_{10}^+0_0^+ \)-state potential-well a Morse representation with the \( D_e = 328 \text{ cm}^{-1}, \beta'' = 1.0826 \text{ Å}^{-1}, R_e'' = 3.76 \text{ Å} \) was used (see Figure 4(b)). The remaining parameters of the simulation are rotational temperature \( T_{\text{rot}} = 4 \text{ K} \), and \( \Delta_{\text{Lorentz}} = 0.25 \text{ cm}^{-1} \) and \( \Delta_{\text{Gauss}} = 0.75 \text{ cm}^{-1} \), representing the values responsible for the bandwidth of the laser beam and a residual Doppler broadening associated with a transversal divergence of the molecular beam, respectively. Vicinity of the \( \nu' = 36–38 \) (depicted by grey bar) is shown in inset. Although both the TDM (that of Czuchaj and Krośnicki [155] and of this review) do show a similar, weak dependence on \( R \) (see Figure 5), the TDM of this review was included in the simulation. Asterisk indicates the \( ^{122}\text{Cd}_2 \) isotopologue component in \( \nu' = 38 \) that is employed in the E–P–R experiment (see Section 5.2.1 and Figure 23).
4.1.1.2. The spectrum. The agreement plot i.e. a contour plot of the agreement coefficient $P$ in function of the $\omega'_e$ and $\omega'_e\chi'_e$ is shown in Figure 11. As one can see, the $(\omega'_e, \omega'_e\chi'_e)$ pair obtained by Łukomski et al. [118] depicted by point B (light blue cross, also representing error bars) is located out of the area where the $P$ gains high values. In the plot, the result obtained here ($\omega'_e = 97.74 \text{ cm}^{-1}$ and $\omega'_e\chi'_e = 0.303 \text{ cm}^{-1}$) is based on simulation of both LIF excitation and dispersed emission spectra. Point B (light blue cross) shows the $\omega'_e$ and $\omega'_e\chi'_e$ and their uncertainties reported by Łukomski et al. [118]. Centre of the plot (black x) is the $\omega'_e - \omega'_e\chi'_e$ pair for which one obtains the best simulation-to-experiment agreement in the analysis only of the LIF excitation spectrum.

![Figure 11](image-url) (Colour online) The $\omega'_e - \omega'_e\chi'_e$ agreement plot drawn using vibrational transition energies $E_{\text{expt}}$ of the most abundant $^{114}\text{Cd}^{112}\text{Cd}$ isotopologue recorded in the $A'^1\Sigma_u^+ (5\text{P}_1) \rightarrow X'^1\Sigma_g^+ (5\text{S}_0)$ LIF excitation spectrum. The simulation-to-experiment agreement [expressed by the value of the parameter $P$, see Equation (6) and details in text] in function of the $\omega'_e$ and $\omega'_e\chi'_e$ is presented using a colour scale. Point A (red cross) corresponds to the $\omega'_e$ and $\omega'_e\chi'_e$ and their uncertainties obtained as a result of analysis performed for this review ($\omega'_e = 97.74 \text{ cm}^{-1}$ and $\omega'_e\chi'_e = 0.303 \text{ cm}^{-1}$) is based on simulation of both LIF excitation and dispersed emission spectra. Point B (light blue cross) shows the $\omega'_e$ and $\omega'_e\chi'_e$ and their uncertainties.

4.1.1.2. The spectrum. The agreement plot i.e. a contour plot of the agreement coefficient $P$ in function of the $\omega'_e$ and $\omega'_e\chi'_e$ is shown in Figure 11. As one can see, the $(\omega'_e, \omega'_e\chi'_e)$ pair obtained by Łukomski et al. [118] depicted by point B (light blue cross, also representing error bars) is located out of the area where the $P$ gains high values. In the plot, the result obtained here ($\omega'_e = 97.74 \pm 0.80 \text{ cm}^{-1}$, $\omega'_e\chi'_e = 0.303 \pm 0.010 \text{ cm}^{-1}$), see also Table 4, is depicted by point A (red cross, also representing error bars). Centre of the plot (black x) that gives the best simulation-to-experiment agreement ($\omega'_e = 96.65 \text{ cm}^{-1}$, $\omega'_e\chi'_e = 0.29 \text{ cm}^{-1}$) does not match the values accepted in this review. It is caused by the result of simulation of LIF dispersed emission spectrum that is discussed below (Section 4.1.2).

First, however, we focused our attention at simulation of the LIF excitation spectrum recorded using the $A'^1\Sigma_u^+ (5\text{P}_1) \rightarrow X'^1\Sigma_g^+ (5\text{S}_0)$ transition shown in Figure 10(a) and reported in Ref. [118]. Due to the high values of $\nu'$, the isotopic structure in each of the vibrational components was easily resolved. As mentioned in Section 3.1.1, in the simulation of the excitation spectrum [118] neither an influence of TDM nor rotational structure of the $\nu' \leftrightarrow \nu'' = 0$ components has been taken into account.

Simulation of the excitation spectrum began with an assumption of a Morse representation of the $A'^1\Sigma_u^+$ state and with the $(\omega'_e, \omega'_e\chi'_e)$ pair as concluded from the agreement plot (black x in Figure 11). However, a simulation of LIF dispersed emission spectrum performed
Figure 12. (Colour online)(a, a', a'', a''') LIF dispersed emission spectrum (red traces) recorded using the A'0^+_u(S^1P_u),\nu' = 38 \rightarrow X^0^+_g(S^3S_g) transition in 226Cd as reported in Ref. [118]. The four experimental traces were detected with increased resolution i.e. for (a) 40 cm\(^{-1}\), (a') 30 cm\(^{-1}\), (a'') 20 cm\(^{-1}\) and (a''') 15 cm\(^{-1}\) monochromator slit widths, under the following experimental conditions: D = 0.15 mm, x = 4 mm, \rho_{Hv} = 14 atm. (b) Simulation [121,122,200] (blue solid lines) performed assuming \nu' = 38 in 226Cd and the A'0^+_u-state representation as shifted (by −655.8 cm\(^{-1}\)) Morse potential obtained in this review with the D'_e = 7882.5 cm\(^{-1}\), \beta' = 1.0072 Å\(^{-1}\) and R'_e = 2.772 Å (see Figure 5); For the X^0^+_g-state, the RPOT-points potential was used (see Figure 4(a)). Spectrum recorded with highest resolution (upper inset) shows also \nu' = 38 \rightarrow \nu'' b \rightarrow b transitions; (c) For every \nu' \rightarrow \nu'' vibrational component, the simulated F–CF (blue vertical bars) was plotted assuming a Gauss convolution function \Delta_{Gauss} = 28 cm\(^{-1}\) (FWHM) (blue solid line). (b') Simulation [121,122,200] (black dot-dashed line) performed assuming the A'0^+_u-state representation as in (b) and for the X^0^+_g-state potential, a L-J(n - m)–Morse hybrid representation with the D''_e = 328 cm\(^{-1}\), \beta'' = 1.0826 Å\(^{-1}\), R''_e = 3.76 Å, n = 4.03, m = 6.0 [see Figure 4(a,b)]. (b'') and (b''') Illustration of an influence of the TDM of Czuchaj and Krośnicki [155] (grey dotted line) and this calculated for the review (grey dashed line) on the simulation, respectively.
Table 5. Isotopic composition of $^{\text{A}_1+\text{A}_2}\text{Cd}_2$. $\text{A}_1$ and $\text{A}_2$ are mass numbers.

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</tbody>
</table>

Simultaneously (see Figure 12 and discussion below) indicated that, despite the simulation-to-experiment agreement was high, the $(\omega'_e, \omega'_x)$ pair chosen from the centre of the agreement plot is not the best choice for the sake of satisfactory success in both simulations. Consequently, other $(\omega'_e, \omega'_x)$ pair was selected (red cross in Figure 11). It is necessary to emphasize that in the $(\omega'_e, \omega'_x)$ pair selection process, a trend towards the result of Łukomski et al. [118] (light blue cross in Figure 11) together with high values of $P$ coefficient was preferred. In the simulation procedure described in details elsewhere [130,198], LEVEL-to-PGOPHER procedure [199], and LEVEL 8.0 [121] and PGOPHER 8.0 [125] programmes were employed, taking into account the full isotopic composition of Cd$_2$ (see Table 5) as well as rotational energy structure of the $^{1}\Sigma_g^+ \leftarrow ^1\Sigma_u^+$, $\Omega' = 0 \leftarrow \Omega'' = 0$ transition. It was concluded that $R'= 2.750 \pm 0.015$ Å. Also, an influence of TDM calculated for this review (red full circles/solid line in upper inset in Figure 5) was included in the simulation. Result is shown in Figure 10(b) (blue trace). It can be verified in inset of Figure 10 that a correct distribution of intensities of Cd$_2$ isotopologues has been reconstructed what was not the case in studies reported in Refs. [118,132] (in Ref. [132] the intensity distribution was partly corrected). Another conclusion that came from the simulation was a lack of pronounced influence of TDM on the simulated spectrum as that of Czuchaj and Krośnicki.
and this calculated for present review have almost constant values for \( R \) for which the transition takes place (see blue area and upper part in Figure 5). In the simulation, a Morse representation \((R''_e = 3.76 \text{ Å} \,[131], \beta'' = 1.0826 \text{ Å}^{-1}, \text{ and } D''_e = 328 \text{ cm}^{-1} \,[116])\) for the ground-state potential in its bound region with parameters from Table 4 was employed. Full discussion of the ground-state representation is given in Sections 4.1.2 and 4.4.

4.1.2. The \( \text{A}^1\text{O}^+_u \rightarrow \text{X}^1\text{O}^+_g \) LIF dispersed emission spectrum

Figure 12(a, a', a'', a''') presents the LIF dispersed emission spectrum (red traces) recorded using the \( \text{A}^1\text{O}^+_u, \nu' = 38 \rightarrow \text{X}^1\text{O}^+_g \) transition, after excitation of the \( ^{226}\text{Cd}_2 \) isotopologue, reported in Ref. [118]. It shows a well-defined CID pattern, consisting of pronounced \( b \rightarrow f \) continuous transitions as well as \( \nu' = 38 \rightarrow \nu'' \) discrete \( b \rightarrow b \) transitions that are located in the high-energy part of the spectrum (see inset in Figure 12). The whole spectrum spans a considerably wide spectral region (6450 \text{ cm}^{-1} \text{ i.e. approx. 52.5 nm}); it has a large number of extrema and it provides an opportunity to perform a simulation that can serve as a reliable verification of the excited- and (mainly) repulsive part of the ground-state potentials.

In order to re-construct the repulsive part of the ground-state potential from the \( \text{A}^1\text{O}^+_u, \nu' = 38 \rightarrow \text{X}^1\text{O}^+_g \) \( b \rightarrow f \) and \( b \rightarrow b \) transitions, the semiclassical RKR-like inversion method (RPOT) of LeRoy [123,124] was adopted. The approach, which is complementary to the ‘exact’ computational and fitting procedures, offers one advantage: It distinguishes between the ‘phase’ and ‘amplitude’ information in the experimental spectrum and shows how the positions of the intensity extrema are determined by the shape of the repulsive potential while the peak heights depend on the TDM(\( R \)). The experimental input data in this case were the energy values of the intensity extrema (maxima and minima) in the recorded LIF dispersed emission spectrum that were determined with accuracy that ranges from 1 to 5 \text{ cm}^{-1} \text{ depending on the high- or low-energy region of the spectrum, respectively. A Gaussian fit was used to represent the positions of the experimental intensity extrema, while the inner and outer turning-point pairs for the \( \text{A}^1\text{O}^+_u \)-state potential were taken from an analysis of the LIF excitation spectrum (see Section 4.1.1 and Figure 10) with small alteration concerning the \( R''_e \). The resulting RPOT points representing the repulsive part of the \( \text{X}^1\text{O}^+_g \) potential are shown in Figure 4(a) (red empty squares). Discussion on the ground-state PEC is presented in Section 4.4.

In the simulation of the CID profile of \( b \rightarrow f \) transitions, BCONT 2.2 [122] and SpectraSim2 [200] programmes were employed, whereas in the simulation of the \( b \rightarrow b \) transitions the LEVEL 8.0 programme [121] was used. Each of the simulated Franck–Condon factors (F–CF) corresponding to the \( \nu' \rightarrow \nu'' \) transition was convoluted with a Gauss function corresponding to the monochromator spectral throughput. [Note: In order to make the simulation procedure more effective, SpectraSim2 [200] programme was employed; This is a graphical overlay whose core is based on LEVEL 8.0 and BCONT 2.2 making possible to using the two programmes simultaneously.] It has to be emphasised that, as for the LIF excitation spectrum, the simulations were carried out assuming the full isotopic composition of \( \text{Cd}_2 \). Also, the procedure used in the simulations assumed a \( \nu^3 \)-dependence on the rate of photon emission (i.e. equivalent to the photomultiplier current) [23]. [Note: Since monochromators normally have a pass band with constant \( \Delta \lambda \), it is appropriate to multiply the F–CF by \( \nu^5 \) rather than \( \nu^3 \). This changes the relative intensities and shapes of the peaks.
in the structured continua, but it does not change the positions of the maxima and minima that constitute the criteria for the 'best fit.'

In the simulation, the original assignment of Ref. [118] i.e. emission from the \( \nu' = 38 \) level was assumed, and, in order to be able to compare the ultimate result directly with the \( \text{Hg}_2 \) ground-state potential [27], above the dissociation [i.e. \( E = 0 \), see Figure 4(a, b)] the repulsive part of the \( \text{X}^10^+_g \) state was approximated by the L-J\((n - m)\) function

\[
U_{L-J(n-m)}(R) = \frac{D_e}{n - m} \left[ m \left( \frac{R_e''}{R} \right)^n - n \left( \frac{R'_e}{R} \right)^m \right],
\]

with \( R'_e = 3.76 \) Å and \( D_e'' = 328 \) cm\(^{-1}\), the parameters confirmed in simulation of the LIF excitation spectrum (see Section 4.1.1 and Figure 10). Similarly, the \( \text{A}^10^+_u \)-state potential was represented with a shifted Morse function, the result from analysis of the excitation spectrum (see Section 4.1.1.2 and Figure 5). During the simulation it became obvious that in order to successfully simulate the experimental emission spectrum it was necessary to exercise a slight change of the \( R'_e \). Taking into consideration a limited accuracy in determination of positions of the extrema in the emission spectrum (1–5 cm\(^{-1}\)), with the modified \( R'_e = 2.772 \) Å (larger by 0.022 Å from that determined in the simulation of excitation spectrum, see Section 4.1.1.2 and Figure 5), it was found that in order to obtain satisfactory simulation-to-experiment agreement, the repulsive part of the \( \text{X}^10^+_u \)-state represented with the RPOT-points potential has to be approximated by the L-J\((n - m)\) function [Equation (7)], with \( n = 4.03 \) and \( m = 6.0 \). The choice of starting \( n \) parameter, \( n_0 = 5.44 \), with assumption of \( m = 6 \) (defining a vdW character of the potential in the long-range region of \( R \)), was performed using formula

\[
n_0 = \frac{2\pi^2 \mu c (\omega''_e)^2 (R''_e)^2}{3h D''_e},
\]

which results from a condition \( d^2U''(R = R''_e)/dR^2 = 2\pi\rho \omega''_e \) within the harmonic oscillator approximation (see e.g. Wallace et al. [201] or Eisel et al. [202]). The resulting repulsive part of the \( \text{X}^10^+_u \)-state potential is shown in Figure 4(a) [RPOT points – red empty squares approximated by a L-J\((n = 4.03 - m = 6)\) function – red solid line]. The result confirms that, in comparison to the \( \text{Hg}_2 \) ground-state L-J\((n = 6.21 - m = 6)\), the repulsive wall of the \( \text{Cd}_2 \) ground-state represented in Equation (7) by \( 1/R^{4.03} \) is much softer (see discussion in Section 4.4.1).

The resultant simulation of the \( b \to f \) and \( b \to b \) parts of LIF dispersed emission spectrum [with RPOT points/L-J\((4.03 - 6.0)\) and Morse \( \text{X}^10^+_g \)-state representations, respectively] recorded using the \( \text{A}^10^+_u, \nu' = 38 \to \text{X}^10^+_g \) transition is presented in Figure 12(b) (RPOT points, blue solid line), Figure 12(b′) [L-J\((4.03 - 6.0)\), black dot-dashed line] and Figure 12(c) (Morse, blue vertical bars/envelope solid line), respectively. The simulated CID profile that spans almost the entire spectral region covered by the dispersed emission shows a satisfactory simulation-to-experiment agreement; this confirms the correctness of the assumed \( \text{A}^10^+_u \)- and ground-state representations, including a hybrid L-J\((4.03 - 6.0)\)–Morse \( \text{X}^10^+_g \)-state representation.

It is interesting to examine an effect of the calculated TDM (see upper part of Figure 5) on the simulated emission spectrum. Figures 12(b′) (black dot-dashed line), 10(b′) (grey
dotted line) and 10(b"
′″
) (grey dashed line) present the simulated CID profiles assuming no
effect of TDM, and the effect of the TDM of Czuchaj and Krośnicki [155] and this calcu-
lated for the review, respectively. In both cases when the TDM is taken into account, small
changes in the simulation are observed. It is evident that the TDM has no influence on the
simulated spectrum in its middle part. In the low- and high-energy regions, the influence
of the TDM reduces [see Figure 12(b"
′″
), b"
′′″
]] and slightly increases in the b → b part (not
shown in Figure 12) intensities of maxima of the spectrum. This is in accordance with the
conclusion reached in Section 4.1.1.2 where it was determined that the TDM of Ref. [155]
and of this review have no influence on the simulation of the excitation spectrum. It is
necessary to emphasise that, in contrast to the excitation spectrum with relatively narrow
F–C window for the excitation (only from υ″ = 0), in case of the spectrally broad emission
from υ′ to a large part of the ground-state potential it is possible to test a wider part of the
TDM. From the simulation is also evident that in order to approach closer the intensities
of maxima in experimental spectrum (in the low-energy region), the TDM has to reach
larger values while R decreases (R < R′″).

4.1.3. The A10+
-u-state interatomic potential
The A 10+
-u-state PEC obtained here as a result of the re-analysis of the LIF excitation and
dispersed emission spectra reported in Ref. [118] is presented in Figure 5 (red solid line);
It is shifted (by −656.9 cm−1) Morse potential with the following parameters: R′ = 2.750 Å,
β′ = 1.0072 Å −1 and D′ = 7882.1 cm−1. The shift results from the fact that the well depth
calculated using the anharmonic potential approximation [23]

\[ D'_e = \frac{a'_e}{2} / 4o'_e x'_e \]  

is smaller than the well depth resulting from the formulas:

\[ D'_0 = v_{at} - v_{0-0} + D''_0, \]  

\[ D'_e = D'_0 + a'_e / 2 - o'_e x'_e / 4, \]

where v_{at} = 43,692.47 cm−1 [203] is the frequency of the 5P 1−5S 0 atomic transition,
v_{0-0} = 35,519.7 ± 0.1 cm−1 [118] is the frequency of the υ′ = 0−υ″ = 0 vibrational transi-
tion, and D′_{0} = 317.4 cm−1 is the X̃0^\underline{r}\_u-state dissociation energy (see Table 4). Equations
(10) and (11) resulted in D'_0 = 8490.2 ± 22.0 cm−1 and D'_e = 8539.0 ± 22.0 cm−1, respectively.
The ±22.0 cm−1 error margin originated from the fact that the most uncertain value, v_{0-0},
cannot be determined exactly and it is estimated using the ω'_e x'_e, ω'_e and ν_{37-0} from energy
of the υ′ = 37 to energy of the υ′ = 0 down to the bottom of the potential energy well.

The PEC of this review is compared with the result of ab initio calculations of this review
(red full circles). [Note: The A10^+_u-state PEC obtained in this review using the IPA method-
ology [192] overlapped almost entirely with the described above shifted Morse function
that was used as a starting potential in the IPA methodology.] Results of previous experi-
mental investigation [118] (blue dot-dashed line), an earlier ab initio studies by Czuchaj and
Krośnicki [155] (blue empty circles), Koperski et al. [19] (black empty triangles circles) and
a very recent ab initio potential of Kullie [156,157] (green empty squares) are also shown.
It is obvious that, with respect to the A10^+_u-state characterisation of Łukomski et al. [118],
characterisation of this review differs – the largest change (by approx. 10%) concerns the
R'_0 that is shorter than that of Ref. [118] (see Figure 5). Additionally, the ab initio potential
Koperski et al. [19] and of this review are close each other and the latter being somewhat shallower and, at the same time, closest to this determined as a result of this review (as far as the potential well depth is concerned). Ab initio potential of Czuchaj and Krosnicki [155] is approx. 5% deeper than this of the present review. This illustrates a real improvement in ab initio calculations. Ab initio potential of Kullie [156,157] cannot be treated realistically.

The \( \text{A}^1\text{O}^+_\text{u} \) state characteristics are collected in Table 4.

4.2. The \( \text{B}^1\text{I}^+_\text{u} \leftrightarrow \text{X}^1\text{O}^+_\text{g} \) spectra – the \( \text{B}^1\text{I}^+_\text{u} \) state potential

Figures 13A(a) and 14(a) (red traces) show LIF excitation and LIF dispersed emission spectra recorded using the \( \text{B}^1\text{I}^+_\text{u} \leftrightarrow \text{X}^1\text{O}^+_\text{g}, \nu'' = 0 \) [Figure 13A(a)] and the \( \text{B}^1\text{I}^+_\text{u}, \nu' = 39 \pm 1 \rightarrow \text{X}^1\text{O}^+_\text{g} \) [Figure 14(a)] transitions, and reported in Refs. [119,132]; the experimental conditions are given in the figure captions.

4.2.1. The \( \text{B}^1\text{I}^+_\text{u} \leftrightarrow \text{X}^1\text{O}^+_\text{g} \) LIF excitation spectrum

The excitation spectrum consists of the \( \nu' \leftrightarrow \nu'' = 0 \) progression with \( \nu' \) spanning the range from \( \nu' = 33 \) to 40. Similarly as in case of the \( \text{A}^1\text{O}^+_\text{u} \leftrightarrow \text{X}^1\text{O}^+_\text{g} \) (Section 4.1.1), due to the high values of \( \nu' \), the isotopic structure in the recorded vibrational components was resolved. As can be seen in Figure 6, location of the excited \( \nu' \) is above the dissociation limit in the most upper part of the \( \text{B}^1\text{I}^+_\text{u} \) state potential well, and extends up to the top of the potential barrier. Taking into consideration the F–C window for the excitation from the \( \nu'' = 0 \) to the ladder of \( \nu' \) (see blue region in \( R \) depicted in Figure 6), it is justified to expect that in the spectrum both the \( b \leftrightarrow b \) and \( f \leftrightarrow b \) transitions are present. Indeed, as can be seen in Figure 13(a), while moving towards higher energies (higher laser wavenumbers), the last isotopically resolved vibrational component, representing the \( \nu' = 40 \leftrightarrow \nu'' = 0 \) transition, gradually becomes an unstructured feature centred at 45,200 cm\(^{-1}\). The continuum band was assigned as originating from the \( f \leftrightarrow b \) transitions which correspond to those terminating on the repulsive part of the \( \text{B}^1\text{I}^+_\text{u} \) state potential barrier.

Simulation of the LIF excitation spectrum detected using the \( \text{B}^1\text{I}^+_\text{u}, \nu' \leftrightarrow \text{X}^1\text{O}^+_\text{g}, \nu'' = 0 \) transition and reported in Ref. [119] is shown in Figure 13A(b) (black solid line). As mentioned in Section 3.1.1, in analysis of the spectrum performed by of Ruszczak et al. [119], an influence of rotational structure of the \( \nu' \leftrightarrow \nu'' = 0 \) components has not been taken into account. Moreover, an influence of the TDM on the simulated spectrum has been mentioned but without any detailed analysis. For the purposes of this review, simulation of the spectrum began with an assumption of the \( \text{B}^1\text{I}^+_\text{u} \) state potential obtained in Ref. [119] using the IPA methodology (see Figure 6, blue dashed line). In the simulation of the \( b \leftrightarrow b \) transitions, LEVEL-to-PGOPHER procedure [199], and LEVEL 8.0 [121] and PGOPHER 8.0 [125] programmes were employed, taking into account the full isotopic composition of Cd\(_2\) as well as rotational energy structure of the \( ^1\Pi^+_\text{u} \leftrightarrow ^1\Sigma^+_\text{g}, \Omega' \leftrightarrow \Omega'' = 0 \) transition. Results of the \( b \leftrightarrow b \) part of the simulation is shown in Figure 13A(c) (blue solid line). Simulation of second part of the spectrum that contains the \( f \leftrightarrow b \) transitions was performed with the same assumptions. The simulation was carried out using BCONT-and-PGOPHER procedure [204], and BCONT 2.0 [122] and PGOPHER [125] programmes. The BCONT-and-PGOPHER employs a graphical user interface simplifying and speeding up application of BCONT along with PGOPHER that allows to include rotational structure of the \( b \leftrightarrow b \) transitions that appear in the simulation as a result of tunnelling through the potential
In the first step, BCONT-and-PGOPHER procedure prepares an input file independently for each \(^{A}\text{Cd}^{A}\text{Cd}\) isotopologue and conducts simulation using BCONT in order to calculate the \(f \leftarrow b\) transition intensities. In the next step, the procedure combines results

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**Figure 13.** (Colour online) (a) LIF excitation spectrum (red trace) recorded using the \(B^{1}1_u^{(5P)} \leftarrow X^{1}0_g^+\) \((5^1S_g)\) transition in \(\text{Cd}_2\) under the following experimental conditions: \(D = 0.2\) mm, \(x = 7\) mm, \(p_{\text{X}} = 10\) atm as reported in Ref. [118]. (b) Simulation [121,122,125,199,204] (black solid line) performed assuming for the \(B^{1}1_u\)-state representation a shifted (by +5 \pm 2 cm\(^{-1}\)) potential obtained in Ref. [119] using IPA methodology (see Figure 6). For the \(X^{1}0_g^+\)-state potential-well a morse representation with the \(D'' = 328\) cm\(^{-1}\), \(\beta'' = 1.0826\) Å\(^{-1}\), \(R''_{\text{eq}} = 3.76\) Å was used [see Figure 4(a,b)]. The remaining parameters of the simulation are rotational temperature \(T_{\text{rot}} = 4\) K, and \(\Delta_{\text{Lorentz}} = 1.8\) cm\(^{-1}\) and \(\Delta_{\text{Gauss}} = 0.75\) cm\(^{-1}\), representing the values responsible for the bandwidth of the laser beam and a residual Doppler broadening associated with a transversal divergence of the molecular beam, respectively. The simulation shown in (b) consists of two separate simulations of (c) \(b \leftarrow b\) (blue solidline), and (d) \(f \leftarrow b\) (green solid line) transitions to the \(\upsilon'\) within the potential well and on the repulsive wall of the potential barrier, respectively. The TDM of Czuchaj and Krośnicki [155] shifted by +0.16 Å (see Figure 6) was included in the simulation (for a detailed discussion see text). Vicinity of the \(\upsilon' = 40\) with \(f \leftarrow b\) unstructured continuum (depicted by grey bar) is shown in inset. Parts B and C show simulations: the one which includes not shifted TDM of Czuchaj and Krośnicki [155] and the one which does not include TDM at all, respectively.
obtained for different \( A_{1}\)Cd\(^{2+}\)Cd into one simulation of the \( f \rightarrow b \) continuum band taking into account the isotopologue abundances (to speed up the procedure, it is possible to set a lower limit for \( A_{1}\)Cd\(^{2+}\)Cd abundancies, e.g. 1%). In the last step, the procedure joins the resulting simulation of the \( f \rightarrow b \) band with simulation of the \( b \rightarrow b \) transitions conducted using LEVEL-to-PGOPHER procedure [199], and LEVEL 8.0 [121] and PGOPHER 8.0 [125] programmes, and specifying the multiplier of the \( f \rightarrow b \) simulation which provide the best agreement between joined simulations and experimental spectrum. Result of the simulation of the \( f \rightarrow b \) transitions (with these being the result of tunnelling) is presented.

Figure 14. (Colour online) LIF dispersed emission spectrum (red trace) recorded using the \( B^{1}u(5^{1}P_{1}), \nu'=39 \pm 1 \rightarrow X^{1}0_{g}^{+}(5^{1}S_{0}) \) transition in \( ^{228}\)Cd\(_{2}\) under the following experimental conditions: \( D=0.2 \) mm, \( x=5 \) mm, \( p_{av}=10 \) atm and \( 30 \) cm\(^{-1}\) monochromator slit width, as reported in Refs. [119,132]. Arrows indicate places where fragments of the spectrum recorded with different sensitivity of detection system are joined. The asterisk depicts the \( 5^{1}P_{1} \rightarrow 5^{1}S_{0} \) atomic fluorescence occurring after a tunnelling process from the excited \( \nu' \) level through the potential barrier to the region of dissociation. It obscures few nodes in the spectrum, causing the uncertainty in the determined \( \nu' \)-assignment to be \( \pm 1 \) or \( \pm 2 \). (b) Simulation [121,122,200] (blue solid line) performed assuming \( \nu'=39 \), excitation of the \( ^{228}\)Cd\(_{2}\) isotopologue and, as the \( B^{1}u \)-state representation, a shifted (by \( +14 \) cm\(^{-1}\) and \( 0.004 \) Å in \( E \) and \( R \), respectively) potential obtained in Ref. [119] using IPA-methodology (see Figure 6). For the \( X^{1}0_{g}^{+} \)-state, the R POT-points potential was used [see Figure 4(a,b)]. Insets A and B show spectrum in its most high-energy parts; an envelope of the \( \nu'=39 \rightarrow \nu'' \) b → b transitions is shown in inset A: for every \( \nu' \rightarrow \nu'' \) vibrational component, the (c) simulated F–CFS (blue vertical bars) were plotted assuming a Gauss convolution function \( \Delta_{\text{Gauss}}=33 \) cm\(^{-1}\) (FWHM) (blue solid line). (b') Simulations [121,122,200] (black dot-dashed line) performed assuming the \( B^{1}u \)-state representation as in (b) and for the \( X^{1}0_{g}^{+} \)state potential, a L-J\((n-m)\)-Morse hybrid representation with the \( D_{e}'=328 \) cm\(^{-1}\), \( \beta''=1.0826 \) Å\(^{-1}\), \( R_{e}'=3.76 \) Å, \( n=5.16, m=6.0 \) [see Figure 4(a,b)]. (b″) Illustration of an influence of the \( tD_{m} \) of Czuchaj and Krośnicki [155] shifted by \( +0.16 \) Å (grey dotted line) on the simulation. Note: A multiplication factor for simulations of the \( b \rightarrow f \) transitions in inset A was introduced for better visualisation.
in Figure 13A(d) (green solid line). Details of the transition from \( b \leftarrow b \) to \( f \leftarrow b \) are presented in insert of Figure 13. It is evident that going towards lower laser wavenumbers the unstructured \( f \leftarrow b \) continuum becomes a series of the isotopic components belonging to the \( 40 \leftarrow 0 \) vibrational band.

As a result of the simulation, it was concluded that the \( B^1u \) -state IPA-methodology potential can be accepted as determined in Ref. [119], only a small +5 cm\(^{-1}\) shift in energies was necessary. Additional discussion on the \( B^1u \) -state potential will be presented in Section 4.2.3.

As for the \( A^10^+ \leftarrow X^10^+_g \) excitation spectrum, in the simulation a Morse representation of the ground-state potential in its bound region with parameters from Table 4 was employed (see Sections 4.1.2 and 4.4).

### 4.2.1. Significance of the TDM.

Knowledge on the TDM (\( f \sim \text{TDM}^2 \)) and its influence on the simulation of the \( B^1u \leftarrow X^10^+_g \) excitation spectrum requires a broader comment. As seen in insert of Figure 6, both TDM calculated by Czuchaj and Krośnicki [155] (blue empty circles/solid line) as well as this calculated for the review (red full circles/solid line) undergo abrupt changes in the region of F–C window for the excitation from \( \nu'' = 0 \). For the former, the TDM decreases and increases rapidly for \( R < R_e \) and \( R > R_e \), whereas for the latter, a less sudden change occurs for \( R < R_e \).

Figure 13C(b,c,d) shows two parts of the simulation [(c) \( b \leftarrow b \), blue solid line and (d) \( f \leftarrow b \), green solid line] as well as the resultant simulation [(b), black line] when no TDM was taken into consideration. It is evident that the resultant simulation does not reconstruct intensities of the vibrational component in the experimental spectrum. Figure 13B(b,c,d) presents the simulation in which the TDM of Czuchaj and Krośnicki [155] is included. The resultant simulation [(b), black line] favours vibrational components with \( \nu' \) lower than these in the experimental spectrum. Thus, it was decided to shift the TDM of Ref. [155] towards larger \( R \) (i.e. by +0.16 Å, see upper part of Figure 6 – navy blue full circles/dashed line) and it was found to be the most suitable one. Figure 13A(b,c,d) shows simulation with the shifted TDM and one may assess that it satisfactorily reconstructs the experimental spectrum. It was also determined that the part of the TDM [155] that includes its decline (for \( R < R_e'' \)) has a critical influence on the simulation. On the other side, it was determined that an influence of the TDM calculated for present review changes simulated spectrum with respect to the experimental one making the TDM a non-realistic even after shifts towards larger (or smaller) \( R \).

### 4.2.2. The \( B^1u \rightarrow X^10^+_g \) LIF dispersed emission spectrum

Figure 14(a) (red trace) presents the LIF dispersed emission spectrum recorded using the \( B^1u, \nu' = 39 \pm 1 \rightarrow X^10^+_g \) transition, after excitation of the \( ^{226}\text{Cd}_2 \) isotopologue in the \( \nu' = 39 \) vibrational component. The spectrum was reported by Koperski et al. [132] and Ruszczak et al. 103], and shows a CID pattern, consisting of pronounced \( b \rightarrow f \) continuous transitions as well as an envelope of the \( \nu' = 39 \pm 1 \rightarrow \nu'' \) discrete \( b \rightarrow b \) transitions that are located in the high-energy part of the spectrum (see inset A). The whole spectrum spans a considerably wide spectral region (10,970 cm\(^{-1}\) i.e. approx. 70 nm), it has a large number of extrema providing an opportunity to determine the \( \nu' \)-assignment. The existing ±1 (or even ±2) uncertainty in the assignment originates from the fact that the \( 5^1P_1 \rightarrow 5^1S_0 \) atomic line that is present in the spectrum (see inset B) obscures at least two of the spectrum nodes.
Similarly as for the $\Lambda^10^+_u \rightarrow X^10^+_g$ LIF emission spectrum, in order to re-construct the repulsive part of the $X^10^+_g$-state potential via simulation of the $B^11^+_u$ $\nu' = 39 \rightarrow X^10^+_g$ b $\rightarrow$ f and b $\rightarrow$ b transitions, LeRoy's RPOT programme [123,124] was used. Again, the experimental input data were energy values of the intensity extrema (maxima and minima) in the recorded spectrum which in this case were determined with somewhat smaller than for the $A^10^+_u \rightarrow X^10^+_g$ spectrum accuracy ranging from 2 to 15 cm$^{-1}$ depending whether it was done in the high- or low-energy region of the spectrum, respectively. The inner and outer turning-point pairs for the $B^11^+_u$-state potential were taken from an analysis of the LIF excitation spectrum (see Section 4.2.1 and Figure 13) with the small alteration concerning its position including the $R'\epsilon$ The resulting RPOT-points representing the repulsive part of the $X^10^+_g$-state potential are shown in Figure 4(a) (green empty squares). They depart from those determined from the analysis of the $A^10^+_u \rightarrow X^10^+_g$ emission spectrum – discussion is presented in Section 4.4.

Simulation of the full CID profile was performed similarly as for the $A^10^+_u \rightarrow X^10^+_g$ emission using a BCONT 2.2 [122], SpectraSim2 [200] and LEVEL 8.0 [121] programmes to simulate of the b $\rightarrow$ f and b $\rightarrow$ b transitions, respectively, with F–CF of each of the $\nu' \rightarrow \nu''$ transition convoluted with a Gaussian function corresponding to the monochromator spectral throughput. The full isotopic composition of Cd$_2$ as well as $\nu^5$-dependence were assumed. In the simulation, the original assignment [119,132] i.e. emission from the $\nu' = 39$ level was assumed and the repulsive part of the $X^10^+_g$-state was approximated by the L-J($5.16 - 6.0$) function [Equation (7)], with $R''_\nu = 3.76$ Å and $D''_\nu = 328$ cm$^{-1}$, the parameters confirmed in simulation of the LIF excitation spectrum (see Figure 13). The $B^11^+_u$-state potential was represented with the IPA-methodology potential slightly shifted in $E$ and also slightly change its $R'\epsilon$. Taking into consideration a limited accuracy in determination of positions of the extrema in the emission spectrum (2–15 cm$^{-1}$), with the IPA potential shifted by +14 cm$^{-1}$ and 0.004 Å in $E$ and $R$, respectively (see Section 4.2.1 and Figure 6), it was found that in order to obtain satisfactory simulation-to-experiment agreement, the repulsive part of the $X^10^+_u$-state represented with the RPOT-points potential has to be approximated by the L-J($n - 6.0$) function, with $n = 5.16$. The resulting repulsive part of the $X^10^+_g$-state potential is shown in Figure 4(a) (RPOT points – green empty squares and L-J(5.16 – 6.0) function green solid line). The result, although somewhat different from that obtained in Section 4.1.2 confirms also that the repulsive wall of the Cd$_2$ ground-state represented in Equation (7) by $1/R^{3.16}$ is softer than that of Hg$_2$ (see discussion in Section 4.4.1).

The resultant simulation of the b $\rightarrow$ f and b $\rightarrow$ b parts of dispersed emission spectrum [with RPOT points/L-J(5.16 – 6.0) and Morse $X^10^+_g$-state representations, respectively] recorded using the $B^11^+_u$, $\nu' = 39 \rightarrow X^10^+_g$ transition is presented in Figure 14(b) (blue solid line)/Figure 14(b') (black dot-dashed line) and (c) (blue vertical bars/envelope solid line), respectively. As far as the simulation using RPOT-points-Morse representing the $X^10^+_g$-state repulsive wall and potential well is concerned, the simulated CID profile shows a satisfactory simulation-to-experiment agreement. This confirms the correctness of the assumed $B^11^+_u$-state modified (shifted) IPA-methodology point-wise and $X^10^+_g$-state RPOT-points-Morse ground-state hybrid representations. However, as concerns the L-J(5.16 – 6.0) potential, because it only approximates positions of RPOT points [see Figure 4(a)], the simulation
shown in Figure 14(b’) ‘de-phases’ with the experimental spectrum in two regions, around 38,000 and 44,000 cm⁻¹.

It is interesting to examine an effect of the calculated TDM (see upper part of Figure 6) on the simulated emission spectrum. Figures 14(b’) (black dot-dashed line) and 13(b’’) (grey dotted line) present the simulated CID profiles assuming no effect of TDM and the effect of the TDM of Czuchaj and Krośnicki [155] shifted by +0.16 Å (a conclusion from simulation of the B'1_u ← X'1_0^+ excitation spectrum), respectively. When the TDM of Czuchaj and Krośnicki [155] shifted by +0.16 Å is taken into account, no real improvement of the simulation from trace (b’’) is observed except small increase and decrease of intensities of the simulated maxima in the low and high-energy regions of the spectrum. The TDM calculated for this review completely changes the intensity distribution in the simulated CID profile (not shown in Figure 14): It causes a large intensity increase of the simulated spectrum in the low-energy region. See also discussion in Section 4.2.1.1.

4.2.3. The B'1_u-state interatomic potential

The B'1_u-state PEC obtained here as a result of re-analysis of the LIF excitation and dispersed emission spectra reported in Refs. 102,103] is presented in Figure 6 (red solid line). The potential obtained using IPA methodology is shifted (by +5 cm⁻¹ in energies and +0.004 Å in R) with respect to that of Ref. [119]. Note: The modified B'1_u-state potential of this review overlaps almost entirely with that of Ref. [119] (blue dashed line – not visible, overlapped by red solid line) and that which was used there as a starting potential in the IPA methodology (black dashed line – visible in the region of the potential barrier).

The modified B'1_u-state PEC of this review is compared with the result of ab initio calculations of this review (red full circles/solid line). Results of earlier ab initio studies by Czuchaj and Krośnicki [155] (blue empty circles/solid line), Koperski et al. [19] (black empty triangles/solid line) and a very recent ab initio potential of Kullie [156,157] (green empty squares/solid line) are also shown. During the analysis of the LIF excitation and emission spectra it became clear that the potential has to be slightly modified by shift in energies and R, respectively. As can be seen in Figure 6, the three ab initio potentials i.e. of Refs. [155], Ref. [19] and of this review, differ in both, depth of the potential well and height and width of the potential barrier. In the region of the potential well, ab initio potential Koperski et al. [19] and modified IPA potential of this review are very close each other, however, in the region of the potential barrier the closest to the modified IPA potential of this review is ab initio potential of Czuchaj and Krośnicki [155]. This illustrates a lack of improvement as far as ab initio calculations are concerned. The situation calls for additional investigations. It is obvious that ab initio potential of Kullie [156,157] as entirely situated above the 5¹P₁ atomic asymptote cannot be treated as realistic one. The B'1_u-state characteristics are collected in Table 4.

4.3. The a³1_u ← X'1_0^+ , b³0_0^+ ↔ X'1_0^+ and c³1_u ← X'1_0^+ spectra – the a³1_u-, b³0_0^+ and c³1_u-state potentials

4.3.1. The a³1_u ← X'1_0^+ LIF excitation spectrum from calculated potentials

Result of newest ab initio calculations for the a³1_u-state interatomic potential is presented in Figure 7 (red full circles/solid line). It is very close to the results of Koperski et al. [19] (black empty triangles/solid line), and Czuchaj and Krośnicki [155] (blue empty circles/solid line).
The result of Kullie [156,157] (green empty squares/solid line), shown for comparison, is somewhat off the other presented results. It is justified to expect that the real, but not experimentally determined so far, potential of the $a^31_u$ state would not depart substantially from the calculated ones [19,155]. Because there is no experimental evidence of a LIF excitation spectrum recorded using the $a^31_u ← X^10_g^+$ transition (as attributed to an unusually small TDM [128]), it was decided to examine the spectrum that results from the simulation only using results of \textit{ab initio} calculations. Similarly, as for the excitation spectra recorded using the $A^10_u^+ ← X^10_g^+$ and $B^11_u ← X^10_g^+$ transitions (see Sections 4.1.1.2 and 4.2.1), simulations were performed employing LEVEL-to-PGOPHER procedure [199], and LEVEL 8.0 [121] and PGOPHER 8.0 [125] programmes, taking into account the full isotopic composition of Cd$_2$ as well as rotational energy structure of the transition. In the simulation, both calculated TDM were taken into account (i.e. that of Czuchaj and Krośnicki [155] and this of the present study – see upper part of Figure 7). The $a^31_u$-state potential was represented either, with the \textit{ab initio} calculated potential of this review or with that of Ref. [155], whereas the bound part of the ground-state potential with a Morse representation of this review (see Table 4). The resultant spectra are shown in Figure 15. They consist of long $\nu'$-progressions (from approx. $\nu' = 25$ to $\nu' = 59$) with vibrational components possessing well resolved isotopic structure as the $\nu'$ reach considerably large values. Spectra (a) (red line) and (a') (blue line)
present pronounced vibrational progressions obtained using representations of this review and of Czuchaj and Krośnicki [155], respectively. Spectra (b) (red line) and (b′) (blue line) show progressions (a) and (a′) modified by taking into account the TDM of this review and of Ref. [155], respectively. Different dependencies of TDM vs. R cause different shifts of the spectra and, consequently, change in the maximum of the vibrational component intensities distribution. It is apparent that future search for the spectrum, if any, should be focused at the 345–392 nm (i.e. 25,500–29,000 cm\(^{-1}\)) spectral range.

### 4.3.2. The \(b^30^+_u \leftarrow X^10^+_g\) LIF excitation spectrum

Figure 16(A) and (B) presents LIF excitation spectra (red traces) – supplementary recorded here using the \(b^30^+_u \leftarrow X^10^+_g\) transition [(a), ‘cold’ spectrum] and reported in Ref. [115] [(b), ‘hot’ spectrum], respectively. The experiments were performed under conditions specified in the figure captions. The excitation spectrum consists of the \(\nu' \leftarrow \nu'' = 0\) (Figure 16(A)) and \(\nu' \leftarrow \nu'' = 0, 1, 2\) (Figure 16(B)) progressions with \(\nu'\) spanning the range from \(\nu' = 0\) to 7. As can be seen in Figure 8, the location of the excited \(\nu'\) are in the lower half of the \(b^30^+_u\) state potential well.

#### 4.3.2.1. The agreement plot.

Additional analysis of LIF excitation spectrum recorded here using the \(b^30^+_u \leftarrow X^10^+_g\) transition [Figure 16A(a)] began with using of a \(\omega'_e - \omega'_e'\) agreement plot method [197] via examination of the \(E^\text{exp}_{\nu'}\) energies of vibrational transition recorded in the spectrum. The agreement plot is shown in Figure 17 and the method was described in Section 4.1.1.1. In Figure 17 the simulation-to-experiment agreement is presented in function of the \(\omega'_e\) and \(\omega'_e'\) for eight vibrational components \(\nu' \leftarrow \nu'' = 0\) using a colour scale (see legends in inset). The agreement is expressed by the value of parameters \(P_1\) [see Equation (6)] and \(P_2\) [see Equation (12)]. Parameter \(P_1\) denotes the agreement coefficient described in 4.2.1.1 i.e. for \(\Delta E^\text{exp}_{\nu'}\) determined with respect to different than the 0 \(\leftarrow 0\) transition (e.g. one of the most intense \(\nu' \leftarrow 0\) transitions in the spectrum), while parameter \(P_2\) denotes the coefficient describing an agreement between experimental \(E^\text{exp}_{\nu'}\) and simulated \(E^\text{sim}_{\nu'}\) absolute values of the energy transitions with respect to a selected vibrational transition (e.g. 0 \(\leftarrow 0\)):

\[
P_2 = 1/(0.01 + |E^\text{exp}_{\nu'} - E^\text{sim}_{\nu'}|)
\]

Point A (red cross) shows recommended values of this review, \(\omega'_e = 18.40 \pm 0.10\) cm\(^{-1}\) and \(\omega'_e' = 0.327 \pm 0.010\) cm\(^{-1}\), and their uncertainties as reported by Urbańczyk and Koperski [130]. [Note: point A is an intersection of the two plots.] Points B (light blue cross), C (orange cross) and D (white cross) correspond to the \(\omega'_e\) and \(\omega'_e'\) values and their uncertainties reported in Refs. [115,116], and obtained as a result of analysis of B–S plot performed in this review (\(\omega'_e = 18.32 \pm 0.07\) cm\(^{-1}\) and \(\omega'_e' = 0.318 \pm 0.008\) cm\(^{-1}\)), respectively (see also Table 4).

#### 4.3.2.2. The spectrum.

As mentioned in Section 3.1.2, in the simulation of LIF excitation spectrum recorded using the \(b^30^+_u \leftarrow X^10^+_g\) transition [115,129] neither an influence of TDM, isotopic composition nor rotational structure of the transition has been taken into account. Here, using the recommended (\(\omega'_e, \omega'_e'\)) pair obtained in the analysis offered by the agreement plot (Figure 17, point A, red cross), we simulated the ‘cold’ and ‘hot’ LIF
Figure 16. (Colour online) A and B. ‘Cold’ and ‘hot’ LIF excitation spectra, respectively, recorded (red traces) (a) additionally for this review and (b) in Ref. [115] using the $b^3\Sigma_u^+(5^3\Pi_1) \rightarrow X^1\Sigma_g^+(5^1\Sigma_g^+)$ transition in Cd under the following experimental conditions: (a) $D = 0.3$ mm, $x = 23$ mm, $p_{ar} = 2$ atm, and (b) $D = 0.15$ mm, $x = 2.5$ mm, $p_{ar} = 0.8$ atm. Simulations [121,125,199] (blue solid lines) performed for (c) ‘cold’ and (d) ‘hot’ spectra, respectively, assuming a Morse representation of the $b^3\Sigma_u^+$-state potential with $D_e / \text{uni} = 258.8$ cm$^{-1}$, $\beta' = 1.0464$ Å$^{-1}$ (see Table 4 and Figure 8), as well as for (c) $R' = 4.06$ Å, $T_{vib} = 10$ K, $T_{rot} = 5$ K, $\Delta_{\text{Gauss}} = 0.12$ cm$^{-1}$, $\Delta_{\text{Lorentz}} = 0.08$ cm$^{-1}$, and (d) $R' = 4.04$ Å, $T_{vib} = 15$ K, $T_{rot} = 17$ K, $\Delta_{\text{Gauss}} = 0.1$ cm$^{-1}$, $\Delta_{\text{Lorentz}} = 0.25$ cm$^{-1}$. For the $X^1\Sigma_g^+$-state potential-well, a Morse representation with the $D_e / \text{uni} = 328$ cm$^{-1}$, $\beta'' = 1.0826$ Å$^{-1}$, $R_{e}'' = 3.76$ Å was used [see Figure 4(a,b)]. In the simulations, the TDM of Czuchaj and Krośnicki [155] was taken into account.
excitation spectra from Figures 16A(a) and 15B(b), respectively. In the simulation, a Morse representation of the $b^3\Sigma^+_{\alpha} \rightarrow X^1\Sigma^+_{\alpha}(5^3P_1)$ transition is assumed with the following parameters: $R/\text{uni} = 4.05$ Å, $\beta = 1.0464$ Å$^{-1}$ and $D/\text{uni} = 258.8$ cm$^{-1}$ (see Table 4). As in analyses of the LIF excitation spectra discussed above, in the simulation LEVEL-to-PGOPHER procedure [199], and LEVEL 8.0 [121] and PGOPHER 8.0 [125] programmes were employed, taking into account the full isotopic composition of Cd$_2$ as well as rotational energy structure of the $3\Sigma^+_\alpha \rightarrow 1\Sigma^+_\alpha$ transition. An influence of TDM calculated by Czuchaj and Krośnicki [155] (blue empty circles/solid line in upper inset in Figure 8) was also taken into account.

Note: It was concluded that in the F–C window for the excitation, the TDM of Ref. [155] and this calculated for the review (red full circles/solid line) have similar dependency on $R$ – see blue area, upper part in Figure 8 – and minor influence on the simulation.

Result of the simulation is shown in Figure 16A(c) and B(d) (blue lines) for the ‘cold’ and ‘hot’ spectra, respectively. In the simulation, a Morse representation of the $b^3\Sigma^+_{\alpha}$ state was assumed with the following parameters: $R'\text{uni} = 4.05$ Å, $\beta' = 1.0464$ Å$^{-1}$ and $D'\text{uni} = 258.8$ cm$^{-1}$ (see Table 4). As in analyses of the LIF excitation spectra discussed above, in the simulation LEVEL-to-PGOPHER procedure [199], and LEVEL 8.0 [121] and PGOPHER 8.0 [125] programmes were employed, taking into account the full isotopic composition of Cd$_2$ as well as rotational energy structure of the $3\Sigma^+_\alpha \rightarrow 1\Sigma^+_\alpha$, $\Omega' = 0 \leftrightarrow \Omega'' = 0$ transition. An influence of TDM calculated by Czuchaj and Krośnicki [155] (blue empty circles/solid line in upper inset in Figure 8) was also taken into account. Note: It was concluded that in the F–C window for the excitation, the TDM of Ref. [155] and this calculated for the review (red full circles/solid line) have similar dependency on $R$ – see blue area, upper part in Figure 8 – and minor influence on the simulation.

Result of the simulation is shown in Figure 16A(c) and B(d) (blue lines) for the ‘cold’ and ‘hot’ spectra, respectively. It is important to emphasise, that in order to achieve the best simulation-to-experiment agreement, the simulation for the ‘cold’ and ‘hot’ LIF excitation spectrum was performed for the $R'\text{uni} = 4.06$ Å and $R'\text{uni} = 4.04$ Å, respectively. It was due to the fact that a correct reconstruction of the relative intensities of the $v' = 0 \leftrightarrow v'' = 0$ and $1 \leftrightarrow 0$ components in the spectrum required slightly different $R'\text{uni}$. What is more, the properly adjusted $R'\text{uni}$ had to be associated with an appropriately chosen $\Delta_{\text{Gauss}}$ (or $\Delta_{\text{Lorentz}}$) convolution for each rotational transition in each isotopologue of the corresponding $0 \leftrightarrow 0$ and $1 \leftrightarrow 0$
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vibrational component. Additionally, a special attention was required for a correct adjust-
ment of the $\Delta_{\text{Gauss}}$ convolution [see Figure 18(a–d)]. Note: A change of the $\Delta_{\text{Gauss}}$ from (c)
0.1 cm$^{-1}$ to (d) 0.2 cm$^{-1}$ results from a wrong to a correct relative intensities of the 0
←0 and 1 ←0 components.

In the simulation, a Morse representation of the ground-state potential in its bound
region with parameters from Table 4 was employed [see also Figure 4(a, b)].

4.3.3. The $b^3\Pi_u \rightarrow X^1\Sigma_g^+$ LIF dispersed emission spectrum
In the LIF dispersed emission b → b spectra presented in Figures 19(A)–(E) [(a), red traces],
$\nu''$ spans the range from $\nu'' = 0$ up to approx. $\nu'' = 8$, so almost up to the middle of the
ground-state potential well [see Figure 4(b)]. This provides a good opportunity to confirm

![Figure 18](https://example.com/figure18.png)

**Figure 18.** (Colour online) Simulation (blue solid lines) of the $\nu' = 0 \leftarrow \nu'' = 0$ and $1 \leftarrow 0$ components of
’cold’ $b^3\Pi_u(5\text{P}_1) \leftarrow X^1\Sigma_g^+(5\text{S}_0)$ LIF excitation spectrum from Figure 16A(a) performed for $\Delta_{\text{Gauss}}$ and $\Delta_{\text{Lorentz}}$
equal to (a) 0.01 cm$^{-1}$, (b) 0.05 cm$^{-1}$, (c) 0.1 cm$^{-1}$ and (d) 0.2 cm$^{-1}$. The remaining simulation parameters
as in Figure 16A(c). Black bars correspond to F–CF calculated without rotational structure included.
the applicability of the Morse representation of the \( X^10^+_g \)-state concluded in Section 4.1.2, for the \( \nu'' \) levels (i.e. below the dissociation limit). The simulation was performed using the LEVEL 8.0 programme [121] with each of the simulated F–CF corresponding to the \( \nu' \rightarrow \nu'' \) transition convoluted with a Gauss function \( \Delta_{\text{Gauss}} \) that represents the monochromator
spectral throughput. Moreover, as in the simulation of the LIF excitation spectrum, the full isotopic Cd₄ composition was taken into account.

The simulations shown in Figure 19(A)–(E) [(b), blue solid lines] were performed with Morse representations of the b₃0⁺ and X₁0⁺ state potentials, with the same parameters as in the case of the LIF excitation spectra shown in Figure 16, however, with one exception: During the simulation it was found that a small change of the ΔRₑ = Rₑ' − Rₑ'' (i.e. by −0.06 Å) with respect to that obtained in simulation of the excitation spectrum had a significant impact on the simulation-to-experiment agreement. Therefore, here the Rₑ'' = 4.05 Å from the simulation of the excitation spectrum was slightly altered within the error margin down to Rₑ'' = 3.99 Å (see Figure 8). In the simulations shown in Figure 19(A)–(E), the influence of TDM calculated by Czuchaj and Krośnicki [155] [(c), black dashed line] and this performed for this review [(d), grey dotted lines] were exercised and compared with these performed without influence of TDM [(b), blue solid lines]. The comparison concluded with a suggestion that the b → b LIF emission spectra are well reconstructed with no TDM taken into consideration but the TDM of Ref. [155] or this review taken into account give somewhat better simulations, especially for the υ' = 2,3,4 → υ'' transitions. With respect to the simulations presented by Strojecki et al. [116], these presented here, which test the novel representation of the Cd₄ ground-state potential, are in full agreement with simulations of the LIF excitation spectra recorded at the same b₃0⁺ ← X₁0⁺ transition as well as give an opportunity to exercise an influence of the TDM calculated by Czuchaj and Krośnicki [155] and for the purpose of this review.

4.3.4. The b₃0⁺-state interatomic potential

Figure 8 presents the b₃0⁺-state PEC (red solid line) obtained as a result of additional analysis of the LIF excitation spectrum reported in Ref. [115], the spectrum supplementary recorded here and re-analysis of the LIF dispersed emission spectra reported in Ref. [116]. It is a Morse potential with the following parameters: Rₑ'' = 4.05 Å, β' = 1.0464 Å⁻¹ and Dₑ'' = 258.8 cm⁻¹, drawn only in the energy region up to υ' = 7 for which the excitation spectrum was recorded.

In Figure 8, the b₃0⁺-state PEC of this review is compared with the result of ab initio calculations performed for this review (red full circles/solid line). Results of experimental investigation of Ref. [116] (blue dot-dashed line), ab initio studies performed by Czuchaj and Krośnicki [155] (blue empty circles/solid line), Koperski et al. [19] (black empty triangles/solid line) and very recently by Kullie [156,157] (green empty squares/solid line) are also shown. It is obvious that, with respect to the b₃0⁺-state characterisation of Strojecki et al. [116], characterisation of this review almost does not differ – the largest change (by approx. 0.7%) concerns the Rₑ'' that is slightly longer than that of the experimental study of Ref. [116] (Rₑ'' = 4.02 Å). From the three ab initio potentials (i.e. Czuchaj and Krośnicki [155], Koperski et al. [19] and of this review) the potential calculated here is closest to the experimental one however, being too deep by approx. 25%. The remaining ones are even deeper. This illustrates a real improvement in ab initio calculations that are presented in this review. Ab initio potential of Kullie [156,157] cannot be treated realistically, indeed. The supplementary analyses of the LIF excitation and dispersed emission spectra resulted in changes of spectral characterisation of the b₃0⁺-state potential (see Table 4).
4.3.5. The c\textsuperscript{3}1\textsubscript{u} ← X\textsuperscript{1}0\textsuperscript{+} \textit{LIF excitation spectrum}

As already explained in Section 3.1.2, characterisation of the c\textsuperscript{3}1\textsubscript{u} state was performed without taking the TDM into account in simulation of the spectrum. Moreover, the characterisation was performed without analysis of the rotational energy structure in vibrational bands [116]. As also concluded: The c\textsuperscript{3}1\textsubscript{u} state was characterised sufficiently well (see a Morse representation in Figure 9) and the spectrum was satisfactorily reconstructed.

4.3.5.1. The spectrum. In this review, the characterisation is supplemented: An influence of the TDM and rotational structure of the vibrational bands is included in the analysis. As a result, subtle corrections to the characterisation of the c\textsuperscript{3}1\textsubscript{u}-state potential are introduced. The corrections are related to the $D_0'$ (by 0.2%), $\alpha'_e x'_e$ (by 1.5%) and $D'_e$ (by 0.15%) (see Table 4), and result directly from Equations (10) and (11) and modified values for the $D_0''$ and $D''_e$ obtained in this study. Consequently, better simulation-to-experiment agreement is obtained as far as the c\textsuperscript{3}1\textsubscript{u} ← X\textsuperscript{1}0\textsuperscript{+} \textit{LIF excitation spectrum} is concerned.

The LIF excitation spectrum recorded using the c\textsuperscript{3}1\textsubscript{u} ← X\textsuperscript{1}0\textsuperscript{+} transition (as that reported in Refs. [116]) is shown in Figure 20A [(a), red trace]. It consists of the $\nu' = 0, 1, 2 ← \nu'' = 0$ progression and $\Delta \nu = 0, 1, 2$ sequences. (Note: in Ref. [117], the 3 ← 0 and 4 ← 0 were recorded as well, however, their intensities were small.) Location of the recorded $\nu'$ is in the lower half of the c\textsuperscript{3}1\textsubscript{u}-state potential well close to the bottom of the well (see Figure 9), so, it enables to characterise the potential in the vicinity of its bottom rather than in the middle of its well or close to its dissociation limit.

Simulation of the spectrum is shown in Figure 20A [(b), blue solid line]. In the simulation, a Morse representation of the c\textsuperscript{3}1\textsubscript{u} state was assumed with the following parameters: $R_e = 3.86$ Å, $\beta' = 0.9259$ Å\textsuperscript{-1} and $D'_e = 721.4$ cm\textsuperscript{-1} (see Table 4). As in other analyses of the LIF excitation spectra discussed above, in the simulation LEVEL-to-PGOPHER procedure [199], and LEVEL 8.0 [121] and PGOPHER 8.0 [125] programmes were employed, taking into account the full isotopic composition of Cd\textsubscript{2} as well as rotational energy structure of the $^1\Pi_u ← ^1\Sigma_g^+$, $\Omega' = 1 ← \Omega'' = 0$ transition. An influence of the TDM (see blue empty circles/solid line and red solid circles/solid line in upper part of Figure 9) on the simulated spectrum deserves a comment. It appears that the TDM of this review presents almost no influence on the simulation as it has a relatively weak dependency on $R$, only with small maximum in the F–C window. This is in contrast to the result of Ref. [155] according to which the TDM has a distinctive minimum and its strong $R$-dependency has a dramatic influence on the simulated spectrum. However, taking into account of the TDM of Ref. [155] resulted in unrealistic simulation, even when the TDM was gradually shifted in $R$ towards both, larger or smaller $R$ values. Consequently, simulation presented in Figure 20A(b) is presented without taking the TDM into account, for $\Delta_{\text{Gauss}} = 0.2$ cm\textsuperscript{-1} and $\Delta_{\text{Lorentz}} = 0.3$ cm\textsuperscript{-1} convolutions (FWHM) for each rotational transition in each vibrational components, as well as for $T_{\text{vib}} = 17$ K, $T_{\text{rot}} = 10$ K.

In the simulation, a Morse representation of the ground-state potential in its bound region with parameters from Table 4 was employed [see also Figure 4(a, b)].

4.3.5.2. Rotational structure of the $\nu' = 0 ← \nu'' = 0$ band. Inset in Figure 20A shows details of the $\Delta \nu = 0$ sequence band in which P (grayscale), Q (green scale) and R (blue scale) rotational branches were depicted to compare their structure with analogous $\Delta \nu = 0$ sequence recorded for the $Γ^3\textsuperscript{0+}_u(6^3P_1) ← X\textsuperscript{1}0\textsuperscript{+}_g$ transition in LIF excitation spectrum of Hg\textsubscript{2}.
The reason, the \( c^1 u \leftarrow X^1 0^+_g \) transition in \( \text{Cd}_2 \) can be considered as the one for which the internal vibrational cooling is also possible, is a very small \( \Delta R_e = R_e^\prime - R_e^\prime \) (here, for the \( c^1 u \) state, it is \(-0.10 \pm 0.02 \) Å) as it is for the \( F^3 0^+_u \) and \( X^1 0^+_g \) states in \( \text{Hg}_2 \) (0.04 \pm 0.01 Å [27]). Figure 20B shows simulation [121,125,199] [(b), blue solid line] performed with an assumption of \( T_{rot} = 10 \) K, \( \Delta_{Gauss} = 0.2 \) cm\(^{-1}\), \( \Delta_{Lorentz} = 0.3 \) cm\(^{-1}\) i.e. as for \( \text{Cd}_2 \) in Figure 20A [(b), blue solid line]. It is compared with the simulation in Figure 20B [(b'), blue solid line] performed for \( \Delta_{Gauss} = 0.3 \) cm\(^{-1}\), \( \Delta_{Lorentz} = 0.7 \) cm\(^{-1}\) i.e. as reported in Ref. [27]. The main difference between \( \text{Cd}_2 \) and \( \text{Hg}_2 \) spectra, is presence of branch Q in the former and...
larger separation of corresponding \( \nu' \leftarrow \nu'' \) bands belonging to different \( \nu' \). The problem of possible internal cooling in Cd\textsubscript{2} will be discussed in Section 5.2.2.

### 4.3.6. The \( \text{c}^{3}1_{u} \)-state interatomic potential

The \( \text{c}^{3}1_{u} \)-state PEC obtained as a result of additional analysis of the LIF excitation spectra reported in Refs. [116,117] is presented in Figure 9 (red solid line). It is a Morse potential with the following parameters: \( R'_{\text{e}} = 3.86 \text{ Å}, \beta' = 0.9259 \text{ Å}^{-1} \) and \( D'_{\text{e}} = 721.4 \text{ cm}^{-1} \), that does not depart from that reported in Ref. [116]. The PEC is drawn only in the energy region close to the bottom of the potential well, close to the \( \nu' \) for which the LIF excitation spectrum was recorded.

In Figure 9, the \( \text{c}^{3}1_{u} \)-state PEC of this review is compared with the result of \textit{ab initio} calculations performed for this review (red full circles/solid line). Results of experimental investigation of Ref. [116] (blue dot-dashed line), \textit{ab initio} studies performed by Czuchaj and Krośnicki [155] (blue empty circles/solid line), Koperski \textit{et al.} [19] (black empty triangles/solid line) and a very recently by Kullie [156,157] (green empty squares/solid line) are also shown. It is obvious that, with respect to the \( \text{c}^{3}1_{u} \)-state characterisation of Strojecki \textit{et al.} [116], characterisation of this review practically does not differ – the largest change (by approx. 1.5%) concerns the \( R'_{\text{e}} \) that is slightly smaller than that of the experimental study of Ref. [116] \( (\omega' x'_{\text{e}} = 0.26 \text{ cm}^{-1}, \text{see Table 4}) \). However, the most significant result of this review concerns the \textit{ab initio} calculated potentials. From the three (i.e. Czuchaj and Krośnicki [155], Koperski \textit{et al.} [19] and this review) the \textit{ab initio} potential obtained here is closest to the experimental one being too deep only by approx. 3.5%; As can be seen in Figure 9, the remaining ones are deeper (Ref. [19]) and shallower (Ref. [155]). This illustrates a real improvement in \textit{ab initio} calculations that are presented in this review. \textit{Ab initio} potential of Kullie [156,157] is not credible, indeed. Additional analysis of the LIF excitation spectrum resulted in changes of spectral characterisation of the \( \text{c}^{3}1_{u} \)-state potential. Its characteristics are collected in Table 4.

### 4.4. Interatomic potential of the \( X^{1}0^{+}_{g} \) ground state

Figure 4 shows a comparison of the \( X^{1}0^{+}_{g} \)-state interatomic potential obtained here \( \text{via} \) additional simulations of the \( b^{3}0_{u}^{+} \leftarrow X^{1}0^{+}_{g}(\nu' \leftarrow \nu'' = 0–2), \text{c}^{3}1_{u} \leftarrow X^{1}0^{+}_{g}(\nu' \leftarrow \nu'' = 0–2), A^{1}0_{u}^{+} \leftarrow X^{1}0^{+}_{g}(\nu' = 0) \) and \( B^{1}1_{u} \leftarrow X^{1}0^{+}_{g}(\nu' = 0) \) LIF excitation as well as the \( b^{3}0_{g}^{+} \rightarrow X^{1}0^{+}_{g}(\nu' = 0–4 \rightarrow \nu''), A^{1}0_{u}^{+}(\nu' = 38) \rightarrow X^{1}0^{+}_{g} \) and \( B^{1}1_{u}(\nu' = 39) \rightarrow X^{1}0^{+}_{g} \) LIF dispersed emission spectra. As already has been emphasised, in the region of the potential well, the Cd\textsubscript{2} ground-state potential of this study is represented by a Morse (red dashed line) function with the following parameters: \( R'_{\text{e}} = 3.76 \text{ Å} \) [131], \( \beta' = 1.0826 \text{ Å}^{-1} \) and \( D'_{\text{e}} = 328 \text{ cm}^{-1} \). On the other hand, the repulsive branch of the ground-state potential should be represented by the RPOT-points (red empty squares) approximated by a L-J(\( n = 4.03 - m = 6.0 \)) function (red solid line). But, it is possible to allow for increase of \( n \) in the L-J function up to 5.13, the conclusion from simulation of the \( B^{1}1_{u} \rightarrow X^{1}0^{+}_{g} \) emission spectrum, however, performed with smaller accuracy. Consequently, it is proposed here that Born–Mayer–Morse hybrid representations of Łukomski \textit{et al.} [118] and Ruszczak \textit{et al.} [119] are replaced by L-J–Morse hybrid representation that can be straightforwardly compared with that obtained for Hg\textsubscript{2} [i.e. L-J(6.21 – 6.0), see Figure 21]. The L-J(4.03 – 6) and L-J(5.16 – 6) functions are adequate representations of the repulsive branch down to approximately 3.07–3.14 Å.
In case of the \( X^10^+_{g} \) state potential-well region [see Figure 4(b)], the \textit{ab initio} potentials calculated by Pahl \textit{et al.} [162,163] (green empty circles/solid line) and for this review (see Section 2.3.1, red empty circles/solid line) provide a satisfactory agreement between experiment (this review) and theory. Specifically, the \( D_e'' \) and \( R_e'' \) are only 9 cm\(^{-1}\) shallower and 0.13 Å longer for the Pahl \textit{et al.} results, and are only 8 cm\(^{-1}\) deeper and 0.10 Å longer for the results of this review. The other four \textit{ab initio} calculated results of Czuchaj and Krośnicki [155] (blue empty circles/solid line), Koperski \textit{et al.} [19] (black empty triangles/solid line) as well as Kullie [156,157] (green full squares/solid line) and of this review (see Section 2.3.1, red full circles/solid line) have wells that are too shallow (Refs. [19,155]) or too deep (Refs. [156,157] and this review); it just proves the difficulty associated with the relatively heavy Cd\(_2\) system in the ground state. Note: The \( X^10^+_{g} \) state calculated for this review (see Section 2.3.1, red full circles/solid line) does not compare well with the experimental result.
However, we have calculated the ground state within the CASSCF/CASPT2 methodology mainly because the ground-state wave function was needed in order to perform the TDMs calculations within the RASSI method (see Section 2.5), and the active space and the basis set were not specially optimised for the ground state.

In order to acknowledge the state-of-the-art ground-state calculations, the reader is referred to the works of Pahl et al. [162] and to Section 2.3.1 of this review. It has to be emphasised that Morse representation of the ground-state potential well was verified in simulation of the b → b transitions present in the LIF dispersed emission spectra analysed here. The transitions occurred for all \( v'' \) up to the dissociation limit (the \( A^{1}0_u^+ \rightarrow X^{1}0_g^+ \) and \( B^{1}1_u \rightarrow X^{1}0_g^+ \) spectra) and their envelopes were simulated satisfactorily only using a Morse representation. The simulations failed for the L-J\((n - 6.0)\) representation.

The repulsive branch of the ground-state potential deserves a comment. For the purpose of this review, the repulsive part of the ground-state potential was characterised analysing simultaneously the \( A^{1}0_u^+ \rightarrow X^{1}0_g^+ \) and \( B^{1}1_u \rightarrow X^{1}0_g^+ \) dispersed emission spectra recorded by one of the authors (JK) in different laboratories (i.e. under different experimental conditions) and reported separately [118,119]. As compared with the \( A^{1}0_u^+ \rightarrow X^{1}0_g^+ \) spectrum, one has to take into account a somewhat lower ‘quality’ of the \( B^{1}1_u \rightarrow X^{1}0_g^+ \) spectrum [higher level of noise and an obscuring character of the \( 5^1P_1 \rightarrow 5^1S_0 \) atomic line present in its CID pattern; it lowers an accuracy of determination of the emitting \( v' \) (i.e. \( v' \pm 1 \) or even \( v' \pm 2 \)) and diminishes an accuracy of determination of the extrema positions in the spectrum]. To the above, the ground-state repulsive wall determined from simulation of the \( B^{1}1_u \rightarrow X^{1}0_g^+ \) dispersed emission has to be considered as less accurate with comparison to that determined from the \( A^{1}0_u^+ \rightarrow X^{1}0_g^+ \) spectrum. Also, vicinity of the \( E = 0 \) requires a comment. There is a slight discrepancy at \( E = 0 \), where two representations, Morse for \( E < 0 \) and RPOT-points/L-J\((n - 6.0)\) for \( E > 0 \), joins together. The RPOT-points/L-J\(((0.03 - 6.0)\) and RPOT-points/L-J\((5.16 - 6.0)\) are shifted with respect to the Morse potential-well representation by \(-0.05\) and \(+0.02\) Å, respectively. It was determined that it does not interfere noticeably with simulations at the junction of the b → b and b → f transitions. The \( X^{1}0_g^+ \) -state potential characteristics are collected in Table 4.

### 4.4.1. Covalent contribution to the bond in the ground-state of the group 12 dimers

The unusually soft repulsion between two Cd atoms in the region of the potential wall \([n\) between 4.03 and 5.16 in L-J\(_{Cd2}\)(\(n - 6\))] is attributed to strong induction effects (and a covalent admixture to the pure vdW interactions) as pointed out by Yu and Dolg [135] and Flad et al. [159] in their relativistic quantum chemical \(ab initio\) calculations, Schautz et al. [158] in pure diffusion quantum Monte-Carlo study, and Lukeš et al. [160] in their supermolecular CC calculations (see Table 3). The induction effects provide an important contribution to the stabilisation of Cd2 in the electronic ground-state; for a pure vdW interaction we would rather have \( n = 12\) [see Equation (7)].

In general, the induction effects that were taken into account in a correct manner in \(ab initio\) calculations and Monte-Carlo study have a large influence, among others, on an accurate description of the ground-state bonding as far as the M–M interaction is concerned (M = group 12 metal atom: Zn, Cd, Hg). Figure 21 presents a comparison of between group 12 Zn2 (green solid line), Cd2 (blue solid/dot-dashed line) and Hg2 (red solid line) ground-state repulsive branches and potential wells determined in this review from re-analysis of available data [116–120,130–132]. The potentials are represented by Morse\(Zn2\).
L-J_{Cd2}(4.03–6.0)/L-J_{Cd2}(5.16–6.0) and L-J_{Hg2}(6.12–6.0) functions with parameters adopted from Ref. [26] for Zn2, taken from Table 4 for Cd2, and adopted from Refs. [27] for Hg2. In order to visualise the degree of repulsion in region of E > 0, the main part of Figure 21 was drawn for L-J_{Cd2}(Zn2) = [R''_{Cd2}(Cd2) = 3.76 Å] = L-J_{Cd2}(Hg2). The L-J_{Cd2}(n = 12 – m = 6) potential (see Equation (7)) is shown for comparison (black dashed line). As one can see, the degree of repulsion in the ground-states of Zn2, Cd2 and Hg2 is evidently smaller (Zn2 < Cd2 < Hg2) than that of L-J_{Cd2}(12–6). Comparison of the experimental result of this review [i.e. slope of the repulsive branch of the L-J_{Cd2}(4.03–6.0)/L-J_{Cd2}(5.16–6.0) functions in Figure 4(a)] with results of ab initio calculations of Czuchaj and Krośnicki [155], Koperski et al. [19] and of this review illustrates a satisfactory agreement [better with the L-J_{Cd2}(5.16–6.0), though]. Conversely, results of Pahl et al. [162,163] (not shown in the main part of Figure 4) does not agree – is too steep.

Additional information can be derived from comparison of ground-state bond lengths R''_{e}. At this stage of the discussion, the acknowledged result for the value of Cd2 X^{10 -g} state bond length, R''_{e,calc} = 3.76 Å, that was obtained as a result of rotational spectroscopy [120,131], and it was adopted (and fully confirmed) in this review, should be compared with the R''_{e,calc} – result of ab initio studies of this review: 3.87 Å, Pahl et al.: 3.873 Å [162], Czuchaj and Krośnicki: 3.97 Å [155], Koperski et al.: 3.98 Å [19], Figgen et al.: 3.97 Å [134] as well as that of Peterson and Puzzarini: 3.894 Å [174] and Bučinský et al. [161]. On the other hand, the R''_{e,exp} has to be compared with the R''_{e,calc} – results of calculations that were explicitly devoted to investigate a covalent contribution to the ground-state bond length i.e. Schautz et al.: 4.05 Å [158], Flad et al.: 4.23 Å [159], Yu and Dolg [135] and Lukeš et al. [160] who obtained the R''_{e,calc} at different levels of theory. The overall comparison of the Cd2 ground-state bond lengths R''_{e} is presented in Figure 22(b). It is accompanied by comparison of the Cd2 ground-state bond depths D''_{e}. One can draw a general conclusion: The experimentally determined R''_{e,exp} (black full circles) are always smaller than the R''_{e,calc} (black empty circles), calculated using a variety of ab initio methods (for description of the methods of calculation see Table 3). As expected, as far as the D''_{e,exp} and D''_{e,calc} are concerned (red full circles and empty squares), the trend is opposite. For comparison, Figure 22(a) and (c) presents R''_{e} and D''_{e} plotted for Zn2 and Hg2, respectively. However, the trend is not so distinct as it is for Cd2. One may say, that also for Hg2, the R''_{e,exp} are smaller than R''_{e,calc}, but it is not true for Zn2 – the trend is opposite.

At this point it would be interesting to compare the bond lengths R''_{e,exp} and R''_{e,calc} in Figure 22 with these calculated assuming a pure vdW interaction, R''_{e,vdW} (see Equation (4) and blue full triangles). It is expected that the covalent admixture to the ground-state bonding reflects itself in a deviation from the R''_{e,vdW} obtained using a formula for pure vdW interaction proposed by London [206,207] and Drude [208–210] (see Section 2.3). For Cd2, the R''_{e,exp} obtained elsewhere [115,116,119,120,131] and used in this review are considerably smaller than the R''_{e,vdW} = 4.56 Å obtained from Equation (4) by substituting I_{Cd} = 72,517.3 cm\(^{-1}\) [203], a_{Cd} = 7.36 Å\(^{3}\) [211] and D''_{exp} = 328 cm\(^{-1}\). The R''_{e,vdW} is also larger than all the R''_{e,calc} – see Figure 22(b) – that may support the covalent admixture hypothesis. Note: According to Yu and Dolg [135], the group 12 bond in M2 is a mixture of \(\frac{3}{4}\) vdW and \(\frac{1}{4}\) covalent interactions. This, together with the soft repulsion in the region of the potential wall validates a non-pure vdW character of the Cd2 molecule in its ground state.

Next, it is essential to compare the R''_{e,exp} and R''_{e,calc} bond lengths with the R''_{e,vdW} calculated according to the London formula for pure vdW interaction [Equation (4)] for whole group
12 homoatomic dimers. The comparison is shown in Figure 22. It is apparent that for Zn$_2$ [Figure 22(a)] and Hg$_2$ [Figure 22(c)], as it is for Cd$_2$, the $R''_{e,\text{vDW}}$ are larger than the $R''_{e,\text{expt}}$ (but not so much as for Cd$_2$). Also, the $R''_{e,\text{calc}}$ are all smaller than the $R''_{e,\text{vDW}}$ but, the tendency is less distinct as it is in case of Cd$_2$ (especially, as it is evident for Hg$_2$). Thus, one can safely conclude [having in mind lower than in the L-J(12-6) repulsion in the short range region]
that in group 12 dimers the covalent admixture to the vdw bonding is larger for Cd₂ than it is for Hg₂, but nothing definitive can be deduced for Zn₂, most of all because the $R_{expt}^{\text{expt}}(Zn)$ has not been determined from rotational spectroscopy as it was done for Cd₂ [120,131] and Hg₂ [212,213]. Also because a steepness of the repulsive wall for the ground-state Zn₂ was approximated from a Morse potential only. Measurements of rotational profiles and LIF dispersed spectra in Zn₂ are planned in our laboratory.

5. Conclusion and summary

Knowledge on experimentally determined interatomic potentials is assessed here against the results of ab initio calculations. In the perspective of group 12, group 2 and lanthanide Yb₂ dimers, this article critically reviews experimental studies and ab initio calculations of the low-lying ungerade excited and ground state interatomic potentials of Cd₂ – one of the group 12 weakly bound vdw dimers. Consistency as well as discrepancies between experimental results and ab initio calculations were probed here to illustrate available approaches, methods, tests and programmes for the comparison paving the way for similar reviews devoted to other group 12, group 2 and lanthanide dimers.

5.1. Experimental and ab initio calculated potentials of Cd₂ – conclusions from the comparison

In order to make review more complete, the AE ab initio calculations were performed here for the $A^{1}0_u^+(5^1P_1)$, $B^11_u(5^1P_1)$, $a^31_u(5^3P_1)$, $b^30_u^+(5^3P_1)$ and $c^31_u(5^3P_2)$ ungerade excited states of Cd₂; furthermore, the state-of-the-art $X^10_g^+$ ground state potential of Cd₂ was obtained here within (ECP) ab initio calculations. The results are presented in Figures 4–9 (red full circles/solid line, also red empty circles/solid line in case of the $X^10_g^+$ state) where they are compared with ab initio results of other investigators [19,155–157,162] as well as with results of experimental studies reported in Refs. [116,118,119] (except the $a^31_u$ state – it has not been studied experimentally).

For the deepest $A^{1}0_u^+(5^1P_1)$ (Figure 5) and also for the $c^31_u$ (Figure 9) excited ungerade states as well as for the $X^10_g^+$ ground state [Figure 4(b)], the theory-to-experiment agreement is very good especially for the ground state. For the $c^31_u$ and $X^10_g^+$ states, the ab initio potentials calculated for the purpose of this study provide potential well depths $D_e$ and equilibrium bond lengths $R_e$ that are in satisfactory agreement with the experimental values obtained via additional analysis of the experimental findings (see Table 4). Especially, for the $c^31_u$ state one acknowledges an improvement as far as the agreement between the experiment and ab initio result of this review is concerned – the other results of Czuchaj and Krośnicki [155] and Koperski et al. [19] provide shallower and deeper potential wells, respectively. For the remaining $B^11_u$ ungerade state with the potential barrier (Figure 6) and the shallowest $b^00_u^+$ state (Figure 8), the theory-to-experiment agreement is not as good as for the $A^{1}0_u^+$, $c^31_u$ or $X^10_g^+$ states. However, for the $b^00_u^+$ state, the agreement between ab initio results of this review and experiment is much better than for the ab initio potentials of Refs. [19,155] – the potential calculated here is much closer to the experimental one than are the deeper potentials of Czuchaj and Krośnicki [155], and Koperski et al. [19]. In case of the $B^11_u$ state, it is necessary to make separate comparisons in the region of potential well and in the region of barrier. The theory-to-experiment agreement for the well is better for the result of
Ref. [19]. As far as the barrier is concerned, Ref. [155] provides most satisfactory \textit{ab initio} calculated potential. For the $X^1_0^+$ state (see Figure 4(a,b)) the best theory-to-experiment agreement is achieved for newly calculated \textit{ab initio} potentials of this review and that of Pahl et al. [162]. By coincidence, they are 2.7% deeper and 2.7% shallower, respectively, as compared to the experimental PEC of this review.

Relativistic time-dependent density-functional calculations of Kullie [156,157] (see green full squares/solid line in Figures 4 and green empty squares/solid line in Figures 5–9) can be considered as acceptable only for the $a^1_u$ state, however, the criterion for this conclusion constitute only \textit{ab initio} results analysed here [19,155–157,162] – no comparison with the experimental findings could be made. For the remaining \textit{ungerade} excited states, Kullie calculations lead to the potentials that are much too shallow – this is true for the $B^1u$ and $A^10^+$ singlet states, and the $b^0_0$ and $c^1_0$ triplet states. An unrealistic behaviour is present in the calculated potentials i.e. well depth too small, strange ‘wavy’ features present in the potentials for the $b^0_0$ and $c^1_0$ states or lack of the barrier in the $B^11_u$ state potential along with the fact that the entire $B^11_u$-state PEC is localised above the respective atomic asymptote. Unfortunately, Refs. [156,157] does not provide explanation for such results, but as communicated by the author: ‘Generally the performance of the density functional theory (DFT) has difficulty to deal with dispersion interaction or weakly (shallow) bound states as its central quantity is electronic density – it works well for strongly (or covalent) bound states as the electronic density is predominantly localised in the bond region. However, DFT has a good performance regarding the effort of the computation; It is less expensive in computation than other methods, especially for large molecules or relativistic cases’ [214].

In this review, additional thorough analysis of an influence of the calculated TDM on the simulated spectra has been performed. As expected, the influence is dramatic when the TDM undergoes an abrupt change in the F–C window for excitation as it is e.g. for the $B^11_u ← X^10^+$ or $c^31_u ← X^10^+$ transition (see Figures 6 and 9, respectively). An adequate illustration is the simulation of LIF excitation spectra recorded using both the $B^11_u ← X^10^+$ and $c^31_u ← X^10^+$ transitions (see Figure 13 and discussion in Section 4.3.5.1, respectively). It has to be stressed, however, that influence of the TDM adds additional degree of freedom to the simulations of the recorded spectra making the process more complex and difficult. On the other hand, having fixed (or determined) e.g. the $\Delta R_e$, the simulation may be a source of more accurate (modified) TDM($R$) dependency. Figures 12 and 14 illustrate also and influence of the TDM on simulation of the LIF emission spectra; in it concluded that the TDM-effect can cause a significant change in the simulated spectrum.

5.1.1. Revisit of simulations – remarks

To conclude the review, several additional observations associated with revisit of LIF spectra should be pointed out.

In order to help rationalise and draw together the literature reviewed here, LIF excitation and LIF dispersed emission experimental spectra reported in Refs. [19,115–120] were revisited and their analyses were refined, employing the LeRoy’s LEVEL [121], BCONT [122] and RPOT [123,124], Western’s PGOPHER [125] programmes, and LEVEL-to-PGOPHER [199], BCONT-and-PGOPHER [204] and SpectraSim2 [200] procedures that were omitted in original reports due to their unavailability. Also, the full isotopic composition of Cd as well as the rotational energy structure of its transitions were taken into account. The
characterisation of the excited- and ground-state interatomic potentials depends on (i) experimental data that are recorded using LIF excitation and/or LIF dispersed emission spectra for specified molecular transitions; (ii) specified procedures that are employed to determine the PEC.

- Simulation of the \( A^10^+ \leftarrow X^0^+ \) LIF excitation spectrum that spans large spectral region was refined including its full isotopic composition, rotational energy structure and employing so-called agreement plot which was postulated as a superior over traditional B–S plot analysis.
- In additional simulation of the \( B^11^u \leftarrow X^0^+ \) LIF excitation spectrum, an influence of rotational structure of the transition was taken into account; also, influence of the TDM was re-analysed thoroughly; the tunnelling effect through the potential barrier was accounted for.
- LIF excitation spectrum of the \( a^31^u \leftarrow X^0^+ \), that has not been possible to record due to too small TDM \( \sim f \), was re-examined in this regard by taking into account full isotopic composition and rotational energy structure of the transition.
- LIF excitation spectrum of the \( b^30^+ \leftarrow X^0^+ \) transition was re-measured for cool conditions in the beam and its analysis was refined by taking into account an influence of TDM, isotopic composition and rotational energy structure of the transition; an agreement plot was used to improve determination of the \( \omega' \) and \( x' \).
- Influence of rotational branches were included in re-analysis of the \( c^31^u \leftarrow X^0^+ \) transition recorded in LIF excitation spectrum allowing to estimate a possibility of internal vibrational cooling.
- The \( A^10^+ \rightarrow X^0^+ \) and \( B^11^u \rightarrow X^0^+ \) LIF dispersed emission spectra were re-analysed and simulated simultaneously; the result is an extension of the characterisation of the repulsive branch for the ground-state potential up to 10,000 cm\(^{-1}\) above the dissociation limit; an influence of the TDM was included in the re-analysis.

5.1.2. **Ground and excited state potentials – observations**

In the short-range region of \( R \), two Cd atoms in Cd\(_2\) (as well as Hg atoms in Hg\(_2\) [27] and Zn atoms in Zn\(_2\) [14]) experience a lower degree of repulsion than that which is characterised by the L-J(12-6) function representative for vdW interaction; also, the determined \( R''_{\text{expt}} \) that is smaller than the \( R''_{\text{vdW}} \) characteristic for pure vdW bonding, suggests that in the ground-state bonding Cd\(_2\) (as well as Hg\(_2\) and Zn\(_2\)) should be characterised including a covalent admixture – the fact confirmed in \textit{ab initio} studies of interatomic charge fluctuations as well [135,158–160].

In order to improve the theory-to-experiment agreement, AE \textit{ab initio} calculations of the interatomic potentials for the \( A^10^+, B^11^u, a^31^u, b^30^+\) and \( c^31^u \) lowest ungerade, and the \( X^0^+ \) states of Cd\(_2\) were performed. Indeed, a significant improvement and increased agreement with the experimental interatomic potentials was presented for the \( A^10^+, b^30^+, c^31^u \) and \( X^0^+ \) as compared to the earlier calculations of Czuchaj [154], Czuchaj and Krośnicki [155], Koperski \textit{et al.} [19], and, especially, for all the analysed electronic states calculated recently by Kullie [156,157].

Implementation of analytical and/or point-wise representations for the Cd\(_2\) lowest \textit{ungerade}- and ground-state potentials was introduced. Refined analytical representations of the Cd\(_2\) lowest excited \textit{ungerade}-state potentials (Morse and shifted Morse) or ground-state
potentials [point-wise and L-J\((n-6)\) for \(n\) in the 4.03–5.16 range] were obtained; for the \(B_1^1\) electronic state an IPA-methodology representation was modified.

For the LIF excitation spectra, the relative position of the excited- and ground-state PECs defines an overlap of the upper- and lower-level wavefunctions. This, in turn, specifies the range of the \(v'\) and \(v''\) vibrational levels in the excited- and ground-states for which the spectra are recorded. Consequently, the analytical functions for PECs are determined reliably between these \(v'\) and \(v''\) (see Figures 4–6, 8, 9). In this review, Morse and L-J\((n-6)\) functions were used. For other energy regions corresponding to the remaining \(v'\) and \(v''\), a shape of the PECs is only an extrapolation. It is well known [14] that a Morse extrapolation works better when approaching the \(R_e\) equilibrium bond length (i.e. at the bottom of the potential well) rather than in the long-range \((R >> R_e)\). Recently, a Morse/long-range (Morse/LR) modification of a Morse potential has been proposed [215–218] – compare with formula (5),

\[
U_{\text{Morse/LR}}(R) = D_e \left[ 1 - \frac{u_{LR}(R)}{u_{LR}(R_e)} e^{-\alpha(R)y_p(R)} \right]^2 ,
\]

where \(u_{LR}(R)\) is a function which defines the long-range (attractive) behaviour of the \(U(R)\) potential to be \(U_{LR}(R) = D_e - u_{LR}(R)\), factor \(u_{LR}(R_e)\) is the value of \(u_{LR}\) at the \(R_e\), \(y_p(R) = (R^p - R^p_e)/(R^p + R^p_e)\) is a dimensionless radial variable in which an integer \(p > 1\) is defined by the nature of the model chosen for the long-range potential \(u_{LR}(R)\) and \(\alpha(R)\) is a slowly varying function approximating specified value \(\alpha_\infty\) as \(R \rightarrow \infty\) [217]. Morse/LR potential worked well for ground-state representations of \(N_2\) [215], \(Ca_2\) [216] and \(Li_2\) [217], as well as for excited states of \(Li_2\) [217] and \(KLi\) [218].

What is very important and deserves a great deal of attention is an investigation of the long-range interaction potentials [see Equation (13)] of the ground (and excited) states of \(Cd_2\) (or other neutral–neutral closed-shell vdW dimers) using just PA spectroscopy. For two neutral closed-shell atoms (i.e. without permanent electric dipole moment), the vdW-type interaction is of dispersion type \((E_{\text{disp}})\) only and it will dominate the long-range tail of the diatomic molecular potential. If the two atoms are sufficiently far apart that their electron clouds overlap is negligible, the inter-atomic potential in the long-range region can be written as

\[
E_{\text{disp}}(R) = D - \sum_{k=3}^{\infty} \frac{C_{2k}}{R^{2k}} = D - \frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} + \ldots ,
\]

where \(D\) is the dissociation energy limit relative either to the well minimum \((D = D_e)\) or to the energy of the lowest vibrational energy level \(v = 0\) \((D = D_0)\), and \(C_6, C_8\) and \(C_{10}\) are constants already mentioned in Section 2.3.2. For large \(R\), one power of \(R\) usually dominates and the potential can be approximated as \(E(R) = D - C_m/R^m\), where \(m\) is in general not an integer, and for a pure vdW interaction \(m = 6\) [see also Equation (7) for L-J\((n-m)\) potential]. The \(-1/R^6\) represents instantaneous dipole–dipole interaction while additional terms represent contributions arising from the interactions of higher-order instantaneous multipoles, such as dipole–quadrupoles \((-1/R^8)\), quadrupole–quadrupole and dipole–octupole \((-1/R^{10})\), etc., interactions.

In order to determine a shape of PEC using the same set of experimental data, the situation is better if one employs an IPA-methodology approach. This method provides an
entire PEC; however, to successfully use the IPA, a sufficiently large set of data is needed i.e. at least a few tens of transition energies must be measured. The method worked well for the $D_{1u}(5^3P_{1})$ and $G_{0u}^1(5^3P_{1})$ states of $Hg_2$ [27], and also for the $A_{0u}^1$ and $B_{11u}$ states of $Cd_2$ [118,119] where importance of a correctly postulated so-called starting potential was demonstrated. Here the $B_{11u}$-state IPA-representation was modified in order to better simulate the $B_{11u} \rightarrow X_{10u}^g$ LIF excitation spectrum.

For the LIF dispersed emission spectra, it is obvious that the more extended the spectrum the better (see examples of the $A_{0u}^1 \rightarrow X_{10u}^g$ and $B_{11u} \rightarrow X_{10u}^g$ in Figures 12 and 14, respectively). Specifically, using the available experimental evidence, characterisation of the repulsive part of the ground-state potential is obtained for the largest achievable energy region. What is unique, the repulsive part of the potential was determined using two sets of spectra originating from different $\nu'$ located in different electronic energy states. Moreover, the procedure that was used (semiclassical RKR-like inversion method – RPOT) allowed for determination of a point-wise 'exact' shape of the repulsive branch as far as the quality of input data is concerned.

5.2. Application of the results

5.2.1. Recommendations for the cadmium-atom-pairs E–P–R experiment

As mentioned in the Introduction, one of the applications of a supersonic expansion beam of diatomic molecules and precise knowledge on their interatomic potentials is associated with fundamental tests of quantum mechanics, i.e. tests of Bell’s inequalities [219], using particles (atoms) which possess a large rest mass. It involves creation of a quantum entanglement between the atoms produced via dissociation of a diatomic molecule. In 1995 Fry et al. [11] proposed a loophole-free experimental realisation of Bohm’s spin-1/2 particle version of the E–P–R experiment. For a more detailed discussion, the reader is referred to Refs. [11,220]. Note: In 1981, Lo and Shimony [126] had proposed an E–P–R experiment with Na$_2$ molecules in the beam for spin-1/2 entangled Na atoms; presently, similar experiment with H$_2$ in the beam dissociated into spin-1/2 entangled H atoms using electrons is realised in Orsay [221–223].

Two of the authors (TU, JK) approached realisation of the experiment which is a cadmium-version of a mercury-proposal of Fry et al. presented for $^{199}$Hg [11] (Bohm’s 1/2-spin version [224]). Here, an entanglement of orientations of $^{111}$Cd-atom nuclear spins is created via dissociation of ($^{111}$Cd)$_2$ isotopologue employing a STIRAP process (see Figure 23). Next, the $^{111}$Cd–$^{111}$Cd entanglement is detected in a spin state selective two photon excitation–ionisation (TPEI) process [11]. During the STIRAP process in the beam, the ($^{111}$Cd)$_2$ that are produced among other $A_{0u}^1Cd^A_{0u}Cd$ isotopologues, are excited to a selected $(\nu', J')$ ro-vibrational level in the $A_{0u}^1$ state [here $(\nu'=38, J'=3)$] and subsequently stimulated to undergo the $A_{0u}^1 \rightarrow X_{10g}^1$ transition to the ground-state dissociation continuum. [Note: In the cadmium-version of the E–P–R experiment is impossible to use the triplet $a_{31u}^3(5^3P_{1})$ electronic state (the analogue to the $D_{1u}^1$ state in Hg$_2$) as the $a_{31u}^3 \rightarrow X_{10g}^1$ transition has a very small TDM and the transition was not experimentally recorded.] In the process, pairs of the ground state $^{111}$Cd atoms are produced. Thanks to the momentum conservation principle and proper selection of both ground and excited states of the molecular transition [11], the nuclear spins of resulting $^{111}$Cd atoms in a pair are oriented antiparallelly (the initial molecular singlet state). In the TPEI process, the entanglement created between the two


$^{111}\text{Cd}$ atoms is studied using the $5s5p \ ^3P_1 \leftarrow 5s^2 \ ^1S_0$ (326.2 nm i.e. 30,656.0 cm$^{-1}$) and $5p^2 \ ^3P_0 \leftarrow 5s5p \ ^3P_1$ (230.7 nm i.e. 43,340.2 cm$^{-1}$) transitions in $^{111}\text{Cd}$ and $^{111}\text{Cd}^+$, respectively [18].

To realise the two-step STIRAP process in the above configuration, it is crucial to selectively excite only one $J'$ rotational level in a single $J' \leftarrow J''$ transition. To fulfil this requirement, a narrowband laser beam with $\Delta_L = 30$ MHz (FWHM) should be employed. Besides of using a narrowband excitation laser to serve the first step in STIRAP process, there is crucial to find a $J' \leftarrow J''$ rotational transition which is spectrally sufficiently well separated, also from those taking place in different $^A_1\text{Cd}^A_2$ isotopologues. Using results of this review...
(see Section 4.1 and Table 4), a simulation [121,125,199] of vicinity of a band-head of the 
\((u', v'') = (38, 0)\) vibrational band in the A\(^1\)0\(_u^+\) \(\leftrightarrow\) X\(^1\)O\(_g^+\) electronic transition (see asterisk in inset in Figure 10) was performed. The result of simulation is presented in inset (a) of Figure 23. The analysis of parity considerations [11] indicates that in order to selectively excite spectroscopically isolated \(J' \leftrightarrow J''\) transition and fulfil requirements for creation the \(^{111}\)Cd--\(^{111}\)Cd entanglement, it is necessary to select even \(J''\) in the chosen (e.g. \(P\)) rotational branch. Simulation in Figure 23 shows the \(J' = 3 \leftrightarrow J'' = 4\) rotational transition that satisfies the symmetry requirements. To selectively excite the \((^{111}\)Cd\)_2\, it is necessary to employ a narrowband laser beam which, in our version of experiment, is provided by a third harmonic of laser-diode injected pulsed alexandrite ring laser with 30-MHz spectral bandwidth [21]. In the second step of STIRAP process, the dissociating transition can be stimulated by a second harmonic of tunable Nd:YAG-laser-pumped dye laser with 2-GHz spectral bandwidth. The choice of the second laser-pulse energy that can be used is illustrated in inset (b) of Figure 23 where the A\(^1\)0\(_u^+\) \(\rightarrow\) X\(^1\)O\(_g^+\) dispersed emission spectrum is shown. It was calculated that for the chosen second laser energy range, the separation angle between the \(^{111}\)Cd atoms after dissociation should be included in 86.5–94.7° range with initial velocity 800 ± 50 m/s of the \((^{111}\)Cd\)_2 in the beam and energies 0.728–0.756 eV of both atoms with respect to the \((^{111}\)Cd\)_2 dissociation energy after the STIRAP process [11,18].

5.2.2. On the perspective of internal vibrational cooling mechanism in Hg\(_2\)

5.2.2.1. The Walther’s scheme for Hg\(_2\). Detailed information on the mutual positions of interatomic potentials and ro-vibrational energy structure can be used in realisation of internal cooling of molecular degrees of freedom as it was proposed by Walther for Hg\(_2\) [12,127] by employing the F\(^3\)0\(_u^+\) \(\leftrightarrow\) X\(^1\)O\(_g^+\) transition. The crucial for the proposal are, a very small \(\Delta R_e\) (i.e. \(\Delta R_e = R_e' - R_e'' = 0.04\) Å as recently concluded [27]) and small differences \(\Delta \omega_e = \omega_e' - \omega_e''\) and \(\Delta \omega_x = \omega_x' - \omega_x''\) (1.08 and –0.057 cm\(^{-1}\), respectively [27]). Figure 24 shows ro-vibrational structure of the F\(^3\)0\(_u^+\) \(\leftrightarrow\) X\(^1\)O\(_g^+\) transition that is the basis of the Walther scheme. In the proposal, the molecule-forming process starts upon a collision of two trapped (in MOT or BEC) ground-state \(^{202}\)Hg atoms (for the sake of clarity, description is limited for one isotopologue only). Due to the 253.7 nm laser (i.e. 39,412.3 cm\(^{-1}\), the 6\(^3\)P\(_1^0\) \(\leftrightarrow\) 6\(^1\)S\(_0^0\) transition) the \(^{202}\)Hg atoms undergo a free-bound PA transition to a vibrationally-excited level \(v'\) of the F\(^3\)0\(_u^+\)(6\(^3\)P\(_1^0\)) or D\(^3\)1\(_u^0\)(6\(^3\)P\(_1^0\)) state [27], from where they can decay back down to \(v''\) bound or free-continuum levels of the X\(^1\)O\(_g^+\) state (those decaying to the continuum are lost). It is generally known that a single-step PA process leaves a translationally cold molecule in rather high \(T_{\text{vib}}\), i.e. in a relatively high \(v''\) level [225]. Specifically, in PA process molecules are generally rotationally cold as the process starts with cold atom collisions and generally only low-\(J\) partial waves are important. The population of the \(v''\) levels, however, is determined by the F–CF when the molecules make the transition from the excited state into the ground state. Thus, the \(T_{\text{vib}}\) can be high.

As determined by Koperski et al. [205], due to a very small \(\Delta R_s\), the F\(^3\)0\(_u^+\) \(\leftrightarrow\) X\(^1\)O\(_g^+\) bound-bound transitions in \((^{202}\)Hg\)_2, especially those with \(\Delta v = v' - v'' = 0\), are strongly allowed (for values of the F–CF see Figure 24(a)). The proposed mechanism for the vibrational cooling is shown in Figure 24(a), and the excitation laser with wavelengths close to 254.1 nm (i.e. 39,354.6 cm\(^{-1}\), \(v' = 0 \leftrightarrow v'' = 0\) transition) is used for the process. The cooling relies on decreasing the \(v''\) by continuous blue detuning of the laser, and successive acts of laser-induced excitation (at \(\Delta v = -1\) transitions) and fluorescence decays (at \(\Delta v = 0\) transitions that
are favoured over those at \( \Delta \nu = -1 \) since the former are characterised by much larger F–CFs). Diagram in Figure 24(a) shows the cooling process for the \( \nu' = 4 \leftrightarrow \nu'' = 5 \) transition as the starting one, with the excitation laser continuously detuned up to 1.13 cm\(^{-1} \) from the starting wavenumber 39,335.16 cm\(^{-1} \). In addition, rotational heating does not occur during the process. This can be understood by noticing that when tuning the excitation laser from the red to the blue, the P-branch – at least for rotational levels with a low \( J \) – is always in resonance first [see Figure 24(b)]. For instance, let us consider a molecule in the \((\nu'' = 2, J'' = 2)\) ro-vibrational level of the ground state. The laser is tuned from the red to the blue until it is resonant with the \( \nu' = 1 \leftrightarrow \nu'' = 2 \) transition. The P-branch comes into resonance first (1) i.e. the molecule is pumped into the \((\nu' = 1, J' = 1)\) level from where it spontaneously decays to the ground-state \( \nu'' = 1 \) level. In this transition, the rotational quantum number is either reduced by one \( (\Delta J'' = -1, \text{rotational cooling}) \), or goes back to \( J'' = 2 \) \( (\Delta J'' = 0, \text{no rotational cooling or heating}) \). If one tunes the laser slow enough, all molecules initially in the \((\nu'' = 2, J'' = 2)\) will have been pumped into the \( \nu'' = 1 \) level by this procedure before the laser comes into resonance with the R-branch transition \((2) \leftrightarrow (1)\), which of course would cause rotational heating (see inset with diagram of P- and R-branches simulated for \( T_{rot} = 3 \) K and \( T_{vib} = 50 \) K). But as no population is left, this does not happen and, ultimately, there should be no significant rotational heating. Finally, transitions at e.g. 37,000–38,000 cm\(^{-1} \) \((D^1 \nu_g, \nu'' \leftrightarrow X^1 \Omega^+_g, \nu'' = 0)\) or 48,800–49,800 cm\(^{-1} \) \((G^1 \nu_o, \nu' \leftrightarrow X^1 \Omega^+_g, \nu'' = 0)\) can be used for detection of the \((^{202}\text{Hg})_2\) in \( \nu'' = 0 \) [27]. As stated in Ref. [127], motivations for the internal cooling study in \( \text{Hg}_2\) (or in \( \text{Cd}_2\), see below in Section 5.2.2.2) are, among others, an investigation of the possibility of observing BEC in \( \text{Hg} \) (or \( \text{Cd} \)) by determining its \( s \)-wave scattering length, and the exploration of possibilities for observing BEC in \( \text{Hg} \) (or \( \text{Cd} \)) by purely optical means (cooling via the \( n^3P_2 \leftrightarrow n^1S_0 \) transition, \( n = 6 \) or 5 for \( \text{Hg} \) or \( \text{Cd} \), respectively).

5.2.2.2. The \( ^31u \leftrightarrow X^1 \Omega^+_g \) transition in \( \text{Cd}_2 \). Conditions for vibrational internal molecular cooling is somewhat more difficult for the \( ^31u \leftrightarrow X^1 \Omega^+_g \) states in \( \text{Cd}_2 \) than it is for \( \text{Hg}_2\) as described in Refs. [12,127] and referred here as a Walther scheme [127]. For the sake of simplicity, the proposal is described for one \( ^{114}\text{Cd} \) isotope only. The similarity with conditions for \( \text{Hg}_2\) concerns considerably small (negative) \( \Delta \omega_e = -0.10 \) Å and small \( \Delta \omega x_e = -0.094 \) cm\(^{-1} \) as determined in this review. The differences are a considerably bigger (and positive) \( \Delta \omega_e = 5.8 \) cm\(^{-1} \) and presence of an additional rotational Q-branch. Even though, a similar vibrational internal cooling process, as presented for \( (^{202}\text{Hg})_2 \) in Figure 24, can be suggested (see Figure 25). With considerably small \( \Delta R_e \) and the \( ^31u \leftrightarrow X^1 \Omega^+_g \) transitions with \( \Delta \nu = 0 \) that are preferred due to the F–CF values in the range from 0.38 to 0.83, the mechanism is similar as that presented for \( (^{202}\text{Hg})_2 \) in Figure 24(a), with the blue-detuned excitation laser emitting close to 321.3 nm (i.e. 31,119 cm\(^{-1} \), \( \nu' = 0 \leftrightarrow \nu'' = 0 \) transition). For the cooling process that begins at the \( \nu' = 4 \leftrightarrow \nu'' = 5 \) transition [as in Figure 24(a)], the excitation laser has to be continuously detuned up to 23.5 cm\(^{-1} \) from the starting wavenumber 31,443.33 cm\(^{-1} \). Even with Q-branch taken into account, rotational heating does not occur during the process. Figure 25(b) shows P-, Q- and R-branches simulated for the \( \Delta \nu = \nu' - \nu'' = -1 \) sequence of the \( ^31u \leftrightarrow X^1 \Omega^+_g \) transition in \( ^{114}\text{Cd} \), assuming \( T_{rot} = 10 \) K and \( T_{vib} = 50 \) K. If one detunes to the blue the excitation laser slow enough from (1) to (2) through (3), all molecules initially e.g. in the \((\nu'' = 2, J'' = 2)\) are pumped into the \( \nu'' = 1 \) level before the laser comes into resonance with the Q-branch transition to \((\nu' = 1, J' = 1)\).
$J' = 2$ and $R$-branch transition to $(\nu' = 1, J' = 3)$, which would cause also rotational heating. But this would not happen as no population in the $(\nu'' = 2, J'' = 2)$ is left, and there should be no significant rotational heating. Finally, transitions at e.g. 38,000–39,500 cm$^{-1}$ $(A^{1}O_{+}^{0}, \nu' \leftarrow X^{1}O_{+}^{0}, \nu'' = 0)$ can be used for detection of the $(^{114}Cd)^{2}$ in $\nu'' = 0$ (see Figure 10).

As stated in Section 1 of this review and in Ref. 27, Cd$_{2}$ and Hg$_{2}$ are important for testing new approaches to ab initio calculations due to the presence of relativistic effects and correlations. The measurements for vibrationally (and rotationally) cold Cd$_{2}$ and Hg$_{2}$ (and also Yb$_{2}$) may result in important input data for these models. However, to the best of the authors knowledge, there is no more favourable configuration of the excited- and ground state interatomic potentials among the group 2 alkaline earth metal atoms and group 12 transition metal atoms (including lanthanides) to be predestined to propose the internal molecular cooling mechanism.
5.3. Future directions

One of the conclusions that comes from the review and discussion presented above indicates that the future work should be focused on both theoretical and experimental aspects, mainly associated with high-lying (Rydberg) Cd$_2$ interatomic potentials. The high-lying potentials offer great challenge for both theorists and experimentalists.

Figure 25. (Colour online) Absence of rotational heating that accompanies a vibrational internal cooling process in (114Cd)$_2$ isotopologues as described in Section 5.2.2.2. Right part shows diagrams with P-branches (red scale), R-branches (blue scale) and Q-branches (green scale) simulated for the $^3$I$_1(5^3P_2)$ $\rightarrow$ $^1X^0_u$ transition in (114Cd)$_2$ assuming $T_{vib} = 50$ K and $T_{rot} = 10$ K. Scale from darker to lighter colours indicate the successive $\nu' = 0 \rightarrow \nu'' = 1$, $1 \rightarrow 2, 2 \rightarrow 3, \ldots$ transitions. No resulting heating in the rotational structure is illustrated while tuning the excitation laser towards blue: (1) Excitation in P-branch ($\Delta J = J'' - J' = -1$) of the $\nu' = 1 \rightarrow \nu'' = 2$ transition (red thick arrow) results in $\Delta J'' = -1$ (cooling, blue thick arrow) and $\Delta J'' = 0$ (no cooling, no heating, grey thick arrow) in the $\nu' = 1 \rightarrow \nu'' = 1$ fluorescence decay. Note: (2) Excitation in R-branch ($\Delta J = 1$) of the $\nu' = 1 \rightarrow \nu'' = 2$ transition (blue thin arrow) results in $\Delta J'' = 1$ (rotational heating, red thin arrow) and $\Delta J'' = 0$ (no cooling, no heating) in the $\nu' = 1 \rightarrow \nu'' = 1$ decay, (3) excitation in Q-branch ($\Delta J = 0$) of the $\nu' = 1 \rightarrow \nu'' = 2$ transition (green thin arrow) results in $\Delta J'' = -1$ (rotational cooling) and $\Delta J'' = 1$ (rotational heating) in the $\nu' = 1 \rightarrow \nu'' = 1$ decay. For additional explanation, see text.
As the theoretical aspect is concerned, calculations of Cd$_2$ interatomic potentials for high-excited states is a difficult endeavour. For large atomic separations, above the 5s6s $^1S_0$ atomic asymptote (i.e. in the 58,390–63,087 cm$^{-1}$ spectral range), there is a manifold of close lying electronic levels originating from an excitation of single electron into 6$p$, 5$d$ or 7$s$ atomic orbital. What is more, the energy of a simultaneous single excitation of both Cd atoms falls into this spectral range (i.e. above 60,200 cm$^{-1}$). It results in a large number of close-lying molecular electronic energy states. Due to the interaction with ionic states, some of the Δ and Π PECs originating from single excitation to 6$p$ orbitals have deep minima and can be observed using LIF excitation at around 45,500–50,000 cm$^{-1}$ i.e. approx. 200–220 nm (using single-laser-frequency excitation e.g. see [19]). Thus, their presence must be taken into account during interpretation of the experimentally recorded spectra.

In order to properly describe chemical nature of electronic states originating from a single-frequency excitation of an electron on molecular counterpart of 6$p$ orbital, one has to employ a large atomic basis set which contains small exponents in order to properly describe the radial behaviour of the electron. On the restricted active space self-consisted field (RASSCF) level of theory, the starting basis set must contain Rydberg orbitals. Presence of Rydberg orbitals is crucial for proper description of molecular counterparts of 6$p$ and 7$s$ orbitals for relatively small interatomic distances. Major computation difficulty of state averaged RASSCF/multi state restricted active space second-order perturbation theory (sa-RASSCF/MS-RASPT2) calculations, which are performed for interatomic distances varying from near dissociation up to almost united atoms limit, is keeping a track of chemical character of all the averaged electronic states. This is the main challenge and should be undertaken in the nearest future. Simultaneously, calculations of high-excited electronic energy states of CdNg complexes (Ng = noble gas atom) are planned. The calculations are necessary to be able to distinguish between LIF excitation spectra originating from Cd$_2$ or CdNg that are produced together in a supersonic beam and are recorded in one experiment as their spectra overlap (see e.g. [130]).

The experimental approach should be pushed towards using a step-by-step excitation of Cd$_2$ via one of the A$^10_u$ and B$^11_u$ or b$^10_u$ and c$^11_u$ intermediate states. It should allow to investigate high-lying electronic energy states, those correlating with the 6$s$ $^3S_1$, 6$s$ $^1S_0$, 6$p$ $^3P_1$ or 6$p$ $^3P_2$ atomic asymptote. With such an approach, the studies can be performed in larger region of $R$ i.e. using the A$^10_u$ and B$^11_u$ or b$^10_u$ and c$^11_u$ to investigate potentials of high excited in regions of shorter or longer internuclear distances $R$, respectively (see Figure 2).

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**Supplementary material**

All the *ab-initio* calculated: 1) basis set \((27s24p19d8f4g2h)/[18s16p16d8f4g2h]\), 2) excited-state interatomic potentials of \(\text{Cd}_2\) and 3) electronic transition dipole moments (TDM) obtained for this review are available in one of the authors (MK) web page: [http://iftia9.univ.gda.pl/~kroch/potentials.html](http://iftia9.univ.gda.pl/~kroch/potentials.html). The *ab-initio* calculated ground-state interatomic potential of \(\text{Cd}_2\) obtained for this review are available on request from one of the authors (PSŻ).

**References**


[154] E. Czuchaj, University of Gdansk (private communication, 2004).

[155] E. Czuchaj and M. Krośnicki, University of Gdansk (private communication, 2005).


[157] O. Kullie, University of Kassel (private communication, 2015).


[214] O. Kullie, University of Kassel (private communication, 2016).


