Rotational profiles in the excitation spectrum recorded for the B^31(5^3P_1) ← X^10^+(5^1S_0) transition in CdNe van der Waals complex

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A B S T R A C T
We report rotational profiles in the laser induced fluorescence excitation spectrum recorded for the B^31(5^3P_1) ← X^10^+(5^1S_0) transition in CdNe van der Waals complex. A method of analyzing the rotational structure of overlapping vibrational bands with isotopic spectral contributions is discussed. Rotational characteristics B_v and D_v for the \( \nu' = 0, 1, 2 \) and \( \nu'' = 0 \) are reported.

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1. Introduction

Laser spectroscopy in a supersonic expansion beam is an ideal tool for the investigation of interatomic interactions in MnG (M = a 12-group metal and Ng = a noble gas atoms) van der Waals (vdW) complexes [1–3]. Laser spectroscopy has frequently been used to determine the rotational and vibrational energy structures and the molecular electronic-state potentials of the complexes in order to shed light on the interatomic binding in the simple vDW complexes. The nature of binding is not a trivial problem and is still a subject of experimental and theoretical interest in a number of laboratories. It is indeed a very difficult task to predict the exact balance between the forces of the repulsive overlap and the multitude of attractive forces originating from dispersive, multipole–multipole and charge transfer attractions. The considerable attention focused on such simple questions is connected with the fact that there are strong discrepancies between results of experiments and theoretical predictions (e.g. ab initio calculations) of interatomic potentials [3]. Hence, there is a need for more precise and reliable spectroscopic data.

In general, knowledge on the interatomic interaction in weakly bound MnG vDW complexes (among them in the most weakly bound NhE and MNe) is required in order to describe a variety of phenomena, for instance atomic line broadenings and asymmetries in atomic line shapes of M atom perturbed by Ng atom in the core and near-wing regions [4–9], MnG glow discharges for efficient sources of ultraviolet radiation [10,11] or simulation of M atom spectroscopy in rare gas solids [12]. By studying the M atomic lines perturbed by Ng systems, parameters of interatomic potentials such as equilibrium internuclear separations (i.e., considerably large bond lengths) [13,14], well depth positions [13,15] or long-range vDW coefficients [13,16] can be determined or model potentials for diatomic systems can be deduced [17].

In recent years, CdNg complexes [18–25] (among them one of the lightest CdNe [18–24]) were the subject of numerous experimental studies using method of supersonic expansion beam. The lowest excited A^10^+(5^3P_1), B^11(5^3P_1), C^1(5^3P_1), D^0^+(5^3P_1) as well as the ground X^10^+(5^1S_0) electronic energy states have been investigated using laser induced fluorescence (LIF) excitation and dispersed emission spectra to obtain potential energy curves of the electronic states. In CdNe, the excitation spectra recorded using the A^10^+ ← X^10^+ and C^1 ← X^10^+ transitions were studied with rotational resolution [19,20]. No rotational profiles of the B^31 and D^0^+ states in CdNe have previously been reported.

In this letter we present rotational profiles of LIF excitation spectra recorded for two vibrational components (\( \nu', \nu'' \)) = (0,0) and (1,0) belonging to the B^31 ← X^10^+ electronic transition in the CdNe complex. For the first time, the recorded profiles revealed partially resolved rotational structure. In this letter we also describe simulations of rotationally structured and overlapping vibrational bands with isotopic spectral contributions. The study presented here is an expanded investigation of the energy structures and mechanisms of binding in CdNe that were conducted in our laboratory [24]; it provides new information and extends the knowledge of this simple vDW complex.

2. Experimental set-up

The scheme of the experimental set-up is similar to that used in studies of CdAr complex that were previously reported from our laboratory [25,26], so we limit the description to the necessary details.
The CdNe complexes were produced using a high temperature, high pressure pulsed source for the supersonic molecular beam [26,27]. The source was filled with cadmium pellets (purity 99.95%, natural abundance, Aldrich) and a carrier gas of high purity neon (99.9999%, Linde Gas) at a pressure \(p_{\text{Ne}}\) of 9 bar was used. Operation of the source was synchronized with a pulsed Nd3+:YAG laser (YG981C, Quantel) using a digital delay generator (DG645, Stanford Research Systems). The second harmonic output of the Nd3+:YAG laser pumped a dye laser (TDL90i, Quantel) which used a dye mixture of LLS (33%) and DCM (67%) in ethanol. The dye laser output was frequency doubled and tuned over the range 30 600 cm\(^{-1}\) to 30 700 cm\(^{-1}\) in 0.03 cm\(^{-1}\) steps. This second harmonic of the dye-laser output was directed into a vacuum chamber (PREVAC) pumped with two rotary pumps (Trivac D258, Oerlikon Leybold Vacuum) and two diffusion pumps (VHS-4, Varian). The vacuum chamber was the laser beam intersected the molecular beam at a distance of 18 mm from the nozzle of the source. During the experiment, the LIF signal from the CdNe complexes in the beam was recorded using a photomultiplier (PM) tube (9893QB/350, Electron Tubes). The PM tube was oriented at an angle of 45° to the laser beam and perpendicular to the molecular beam. For each dye-laser tuning step, the LIF signal corresponding to 64 dye-laser shots was averaged using an oscilloscope (TDS 2024B, Tektronix). Each resulting average waveform was saved in a computer memory along with parameters describing the corresponding tuning step, i.e., the dye-laser frequency and bandwidth; the latter were obtained with a wavemeter (WSU30, HighFinesse). To obtain the resulting experimental spectrum, each of the registered waveforms was integrated within a 2.5-\(\mu\)s integration window. The integration process started 1\(\mu\)s after the dye-laser pulse. Details of the integration procedure can be found in Ref. [28].

3. Results and simulations

Figures 1 and 2 [see traces (a), red lines] present experimental LIF excitation spectra of two vibrational components \(\nu' = 0 \leftrightarrow \nu'' = 0\) and \(\nu' = 1 \leftrightarrow \nu'' = 0\), respectively) of the B^1 → X^10^ transition in CdNe. In both cases, rotational structure is partially resolved. It is necessary to emphasize, that in the B^1-state potential well only three \((\nu' = 0, 1\) and 2\) vibrational levels exist [22,24]. The results presented in Figures 1 and 2 encompass almost all the bound → bound part of the excitation spectrum (compare with Figure 3A of Ref. [24]). Despite numerous attempts, the third vibrational component i.e., \((\nu' = 2 \leftrightarrow \nu'' = 0)\) was not recorded in this study; it has significantly smaller amplitude than the other two and strongly overlap with the \((\nu' = 1 \leftrightarrow \nu'' = 0)\) one (see inset in Figure 2). In order to include the effect of the overlap of the vibrational components, our simulations of the spectrum took into account all three \((\nu' \leftrightarrow \nu'' = 0)\) transitions.

![Figure 1](image1.png)

**Figure 1.** The \(\nu' = 0 \leftrightarrow \nu'' = 0\) vibrational band of the B^1(5^3P_1) → X^10^ (5^3S_0) transition in CdNe recorded in this work. (a) The experimental spectrum (red line) recorded for \(T_{\text{source}} = 873\,\text{K}, T_{\text{interc}} = 921\,\text{K} and p_{\text{Ne}} = 9\,\text{bar}\). (b) Simulation (black line) performed for all \(^{60}\text{Cd}^{20}\text{Ne}\) isotopologues using the PGCHPR program [31]; it is based on the assumption that the potentials of both states are represented by a Morse function (parameters from Table 1), as well as using \(T_{\text{out}} = 4.5\,\text{K}\), \(\Delta_{\text{int}} = \pm 0.15\,\text{cm}^{-1}\) and \(\Delta_{\text{gen}} = \pm 0.15\,\text{cm}^{-1}\). The values of the rotational constants employed in the simulation are from Table 2. Due to the overlap, the neighboring \(\nu' = 1 \leftrightarrow \nu'' = 0\) transition was included in the simulation. Vertical empty, red and black bars below the simulation represent transitions belonging to Q-, P- and R-branches, respectively. Color version on-line.

![Figure 2](image2.png)

**Figure 2.** The \(\nu' = 1 \leftrightarrow \nu'' = 0\) vibrational band of the B^1(5^3P_1) → X^10^ (5^3S_0) transition in CdNe recorded in this work. (a) The experimental spectrum (red line) recorded for \(T_{\text{source}} = 873\,\text{K}, T_{\text{interc}} = 921\,\text{K} and p_{\text{Ne}} = 9\,\text{bar}\). (b) Simulation (black line) performed for all \(^{60}\text{Cd}^{20}\text{Ne}\) isotopologues using the PGCHPR program [31]; it is based on the assumption that the potentials of both states are represented by a Morse function (parameters from Table 1), as well as using \(T_{\text{out}} = 3.4\,\text{K}\), and \(\Delta_{\text{int}} = \pm 0.15\,\text{cm}^{-1}\) and \(\Delta_{\text{gen}} = \pm 0.15\,\text{cm}^{-1}\). The values of the rotational constants employed in the simulation are from Table 2. Due to the overlap, the neighboring \(\nu' = 1 \leftrightarrow \nu'' = 0\) transition was included in the simulation. Vertical empty, red and black bars below the simulation represent transitions belonging to Q-, P- and R-branches, respectively. Inset shows simulation of the \(\nu' = 2 \leftrightarrow \nu'' = 0\) vibrational band. Color version on-line.

![Figure 3](image3.png)

**Figure 3.** Interatomic potentials of the B^1(5^3P_1) excited state of CdNe complex. Results of ab initio calculations of Czuľaj et al. [32] (black full circles) and Strojecki et al. [23] (empty circles). Morse representations of Ref. [24] (red dashed line) and of this work (blue solid line). Positions of the \(\nu'\) levels are depicted. Color version on-line.
The first result of the analysis of the experimental data was a determination of the bandhead frequencies for the vibrational transitions \( \nu(0' - 0'' = 0) = 30,672.0 \pm 0.1 \text{ cm}^{-1} \), \( \nu(1' - 1'' = 0) = 30,676.6 \pm 0.1 \text{ cm}^{-1} \); the frequencies were more precisely determined than those in Ref. [24]. In order to obtain the most satisfactory simulation-to-experiment agreement, using these new measurements of \( \nu \), we postulated a modification of the vibrational frequency \( \omega \), and anharmonicity \( \omega \chi ' \) reported in Ref. [24] (see Table 1 for details). We strongly emphasize that, based on the transition energies of only two vibrational levels, a precise and reliable determination of \( \omega \) and \( \omega \chi ' \) is practically impossible. In this study we slightly modified the previously determined values of \( \omega \) = 6.7 cm\(^{-1}\) and \( \omega \chi ' \) = 1.08 cm\(^{-1}\) [24]; these modified values, \( \omega \) = 6.88 cm\(^{-1}\) and \( \omega \chi ' \) = 1.078 cm\(^{-1}\), provided satisfactory agreement between the simulated frequencies of the vibrational transitions and those obtained in the present experiment.

The second and most interesting result of the present study was our simulation of the partially resolved rotational structure in the recorded vibrational bands. To be consistent with method used in previous work from our laboratory, the simulation that took into account the natural isotopic composition of \( ^{111}\text{Cd}^{20}\text{Ne} \) and \( ^{110}\text{Cd}^{20}\text{Ne} \) complexes (\( A_1 \) and \( A_2 \) are stable isotope mass numbers of Cd and Ne, respectively), although, due to small \( \nu \) values and small reduced mass of the complex which consequently lead to a small isotopic shift, there are no significant differences between simulation presented in this letter and simulation conducted for most abundant isotopologue only. For each vibrational component all possible isotopologues of \( ^{111}\text{Cd}^{20}\text{Ne} \) were taken into account [the most abundant i.e., \( \alpha > 1\% \), where \( \alpha \) is the abundance, are: \( ^{114}\text{Cd}^{20}\text{Ne}(26\%), \), \( ^{112}\text{Cd}^{20}\text{Ne}(21.8\%), \), \( ^{111}\text{Cd}^{20}\text{Ne}(11.6\%), \), \( ^{110}\text{Cd}^{20}\text{Ne}(11.3\%), \), \( ^{113}\text{Cd}^{20}\text{Ne}(11.1\%), \), \( ^{116}\text{Cd}^{20}\text{Ne}(6.8\%), \), \( ^{114}\text{Cd}^{22}\text{Ne}(2.7\%), \), \( ^{112}\text{Cd}^{22}\text{Ne}(2.2\%), \), \( ^{111}\text{Cd}^{22}\text{Ne}(1.2\%), \), \( ^{110}\text{Cd}^{22}\text{Ne}(1.1\%), \), \( ^{106}\text{Cd}^{20}\text{Ne}(1.1\%), \)]. In order to calculate vibrational band origins, Franck-Condon factors and rotational constants \( B_0 \) and \( D_0 \), we used the LEVEL program [29] with an assumption of a Morse representation of the \( ^{111}\text{Cd}^{20}\text{Ne} \) and \( ^{110}\text{Cd}^{20}\text{Ne} \) interatomic potentials with vibrational constants from Table 1. The \( B_0 \) and \( D_0 \) are collected in Table 2. In the simulation, we assumed that transition moment function is a constant. Traces (b) in Figures 1 and 2 (black lines) show simulations of two vibrational components \( \nu' = 0 \rightarrow \nu'' = 0 \) and \( \nu' = 1 \rightarrow \nu'' = 0 \), respectively) of the \( B_1 \rightarrow X^0_0 \) transition in CdNe; these were performed with the help of the PGOPHER program using the \( B_0 \) and \( D_0 \) from Table 2.

The simulations were performed using a rotational temperature \( T_{\text{rot}} \) in the beam that was in the range from 3 K to 4.5 K; the simulations also employed convolutions corresponding to the Doppler residual broadening (\( \Delta_{\text{lorentz}} \)) and spectral bandwidth of the laser beam (\( \Delta_{\text{gau}} \)), both equal 0.15 cm\(^{-1}\). Due to the overlapping of neighboring bands, all vibrational components \( \nu' = 0,1,2 \rightarrow \nu'' = 0 \) were included in the simulation. Figures 1 and 2 also show components of the \( P_-, Q- \) and \( R- \) branches present in the rotational structure. An important conclusion can be derived: In the case of the \( \nu' = 1 \rightarrow \nu'' = 0 \) transition, a distinct overlap of the rotational components of different branches explains the better resolution of the rotational structure in the recorded spectrum. A similar conclusion was reached in Refs. [25] and [30] where the rotational structures of CdAr and Cd\(_2\) were investigated.

4. Conclusions

The most important result of this work is the first detection of two vibrational components \( \nu' = 0, 1 \rightarrow \nu'' = 0 \) with partially resolved rotational structure in the LIF excitation spectrum of the \( B_1 \rightarrow X^0_0 \) transition in CdNe. Based on the recorded spectra, we propose modified (with respect to those of Ref. [24]) vibrational constants \( \omega \) and \( \omega \chi ' \) as well as values of rotational constants \( B_0 \) and \( D_0 \) for the vibrational levels \( \nu' = 0,1 \) and \( \nu'' = 0 \). Analysis of the components of the P, Q and R rotational branches in the simulation of the recorded vibrational bands revealed the origin of a better resolution for the rotational structure than that which was achieved in the detection of the \( (\nu',\nu'') = (1,0) \) band.

The results presented here add a new characterization that describes rotational energy structure in the \( B_1 \) electronic energy state (see Table 2). The results also extend and modify the vibrational characterization of the \( B_1 \) state presented in Ref. [24] (see Table 1). Furthermore, due to the simulation of the rotational transitions between the ground and \( B_1 \) states, the rotational characterization of the former for the \( \nu'' = 0 \) has been presented. The vibrational spectroscopic description as well as the Morse representation of the \( X^0_0 \) state were adopted from Ref. [24].

Figure 3 shows the representations of the \( B_1 \)-state interatomic potential for the CdNe complex. The Morse representations are the results of the experimental studies reported in both Ref. [24] and this work (red dashed and blue solid lines, respectively). They are compared with results of \( ab \) \textit{initio} calculations by both Czuchaj et al. [31] (black full circles) and Strojec et al. [23] (empty circles). One has to notice that all representations (\( ab \) \textit{initio} and experimental) are very consistent considering the well depth (\( D_0 \)) and the bond length (\( R_0 \)). This creates a very reliable characterization of the \( B_1 \)-state interatomic potential, one of the shallower vdW potentials of the MNx class of complexes.

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References