IRREGULARITIES IN HIGHLY EXCITED ENERGY STATES OF Cd_2: EXPERIMENT *VS.* *AB INITIO* CALCULATIONS - FIRST STEP TOWARDS AN ENTANGLEMENT OF Cd ATOMS
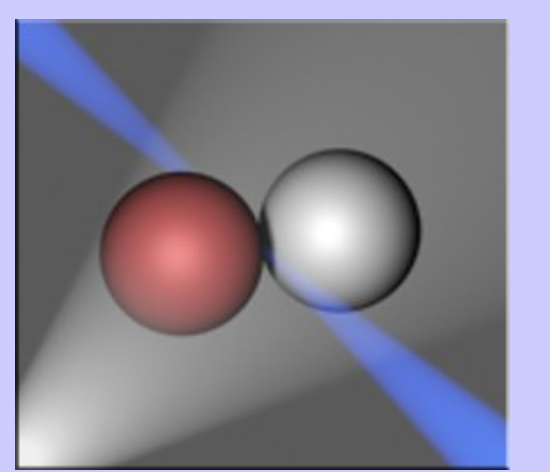
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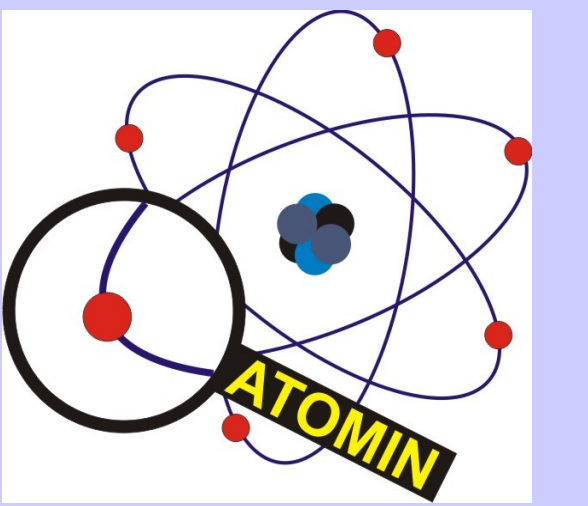[b] *Institute of Theoretical Physics and Astrophysics, University of Gdańsk, Wita Stwosza 57, 80-952 Gdańsk, Poland*
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INTRODUCTION

Vibrational and isotopic structures of highly excited $C^3 1_u$($6^3 S_1$) and $D^1 0_u^+$($6^1 S_0$) electronic energy states of Cd_2 (see Fig. 2) were extensively investigated in cold environment of a free-jet expansion beam. Laser induced fluorescence excitation spectra were recorded in the ultraviolet region (206-218 nm *i.e.*, 48530-45860 cm^{-1}) using the $C^3 1_u \leftarrow X^1 0_g^+$ and $D^1 0_u^+ \leftarrow X^1 0_g^+$ bound←bound transitions.

The measured spectra provided characteristics of the $C^3 1_u$ and $D^1 0_u^+$ -state potentials. At the present stage, it is concluded that the shape of the potential of the experimentally determined $C^3 1_u$ excited state [D_e'($C^3 1_u$) =10085 cm^{-1}, R_e'($C^3 1_u$)=2.68 Å] is close to the result of our *ab initio* calculations. However, for the singlet excited state [D_e'($D^1 0_u^+$)=6569 cm^{-1}, R_e'($D^1 0_u^+$)=3.54 Å] the above statement is not true - the experiment gives result far from the *ab-initio* calculated one (Fig. 4).

Beside the bound←bound transitions, part of the excitation spectrum *i.e.*, region of 207-208 nm, incorporates features that may indicate a presence of free←bound transitions (see Fig 3). To explain the recorded signal, we assumed proximity of the $E^3 1_u$-state potential that correlates with the $6^3 P_1$ Rydberg atomic asymptote lying above the $6^3 S_1$ and $6^1 S_0$ levels (see Fig. 2), similarly as reported for the case of Hg_2 [1].
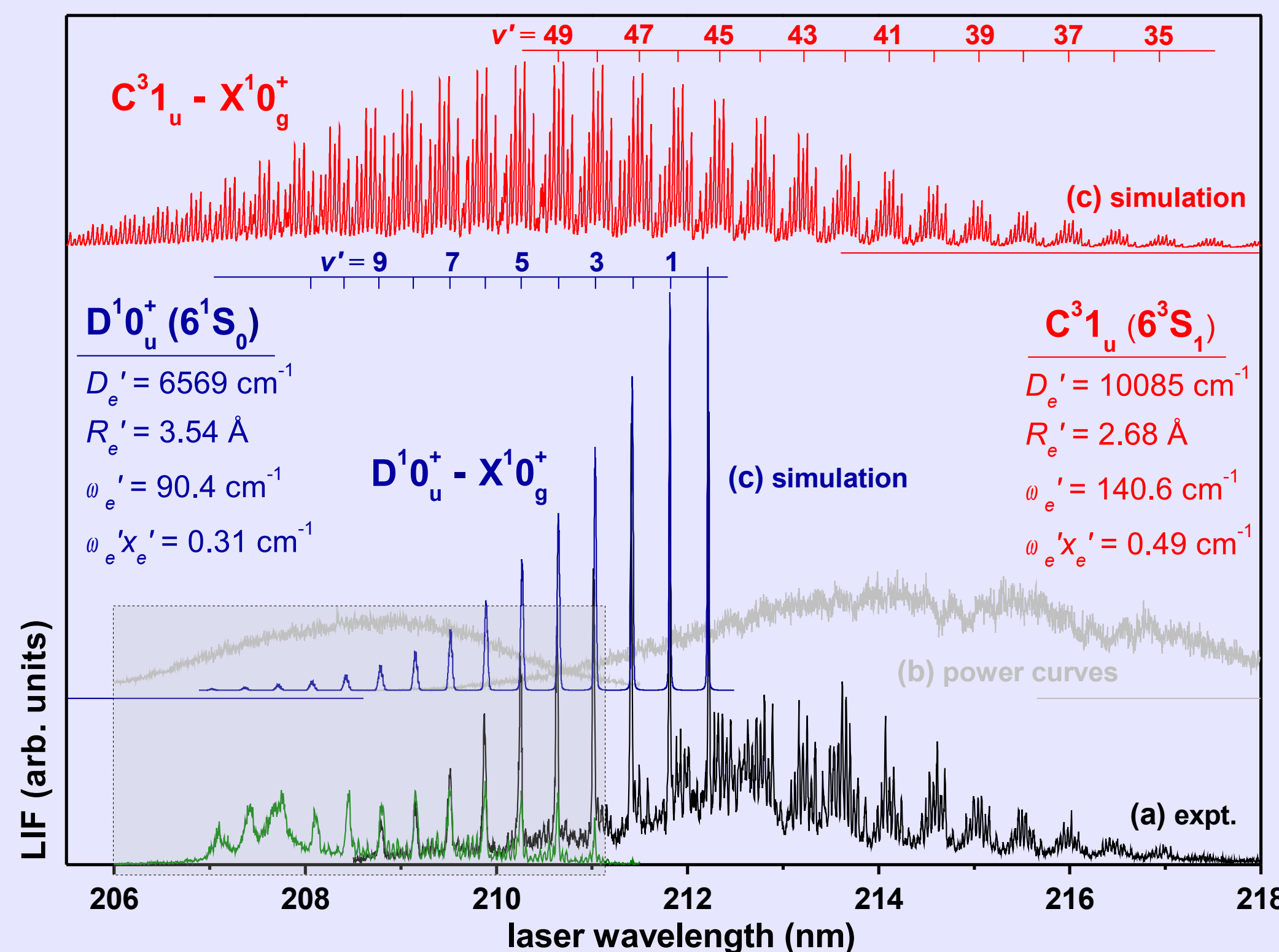
The reported experiment constitutes part of our activity focused on studies of interatomic potentials of ZnRg, CdRg (Rg=rare gas), Zn_2 and Cd_2 van der Waals complexes [2], aiming at a mechanisms of molecular internal vibrational cooling as well as experimental verification of Bell's inequality for a pair of neutral Cd atoms "born" in a controlled dissociation of Cd_2 molecule in an expansion beam [3]. An idea of the proposal – based on that of Fry and co-workers [9] for Hg_2 - is briefly presented below. The experimental apparatus is presently in a preparation stage in our laboratory.

Fig. 1. Scheme of the experimental set-up: **FCU** – **F**requency **C**onversion **U**nit, **L** – **L**enses, **OG** – Argon-filled **O**pto**G**alvanic cell, **PD1**, **PD2** – **P**hoto**D**iodes, **FP** – **F**abry-**P**erot etalon, **PM** – **P**hoto**M**ultiplier tube. Perpendicular direction between direction of the detection and a plane containing laser and molecular beams allows reducing a Doppler broadening.

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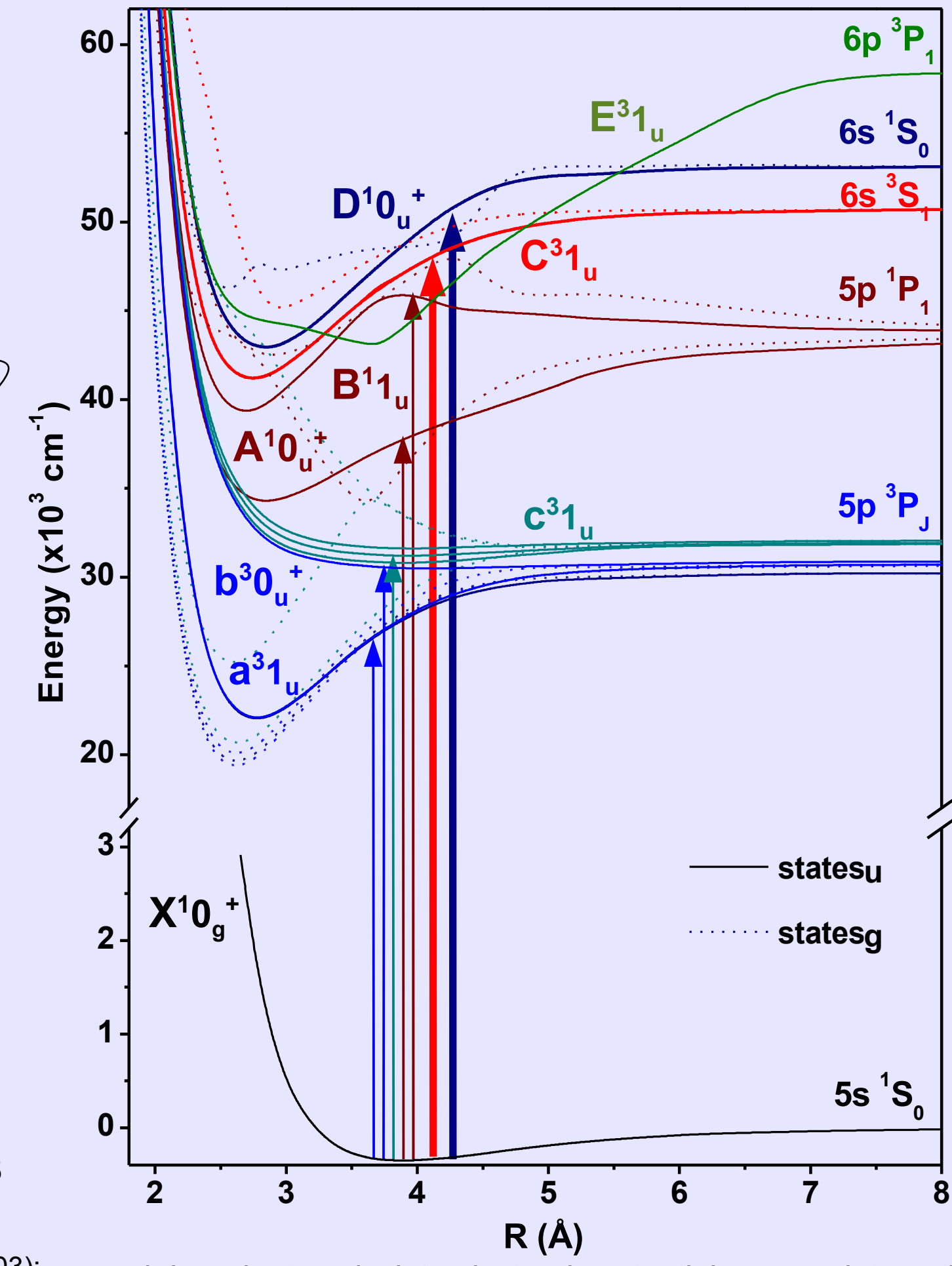
AB INITIO CALCULATIONS

Fig. 2. Interatomic potentials of Cd_2 drawn for the $X^1 0_g^+$ ground as well as the excited *ungerade* (solid lines) and *gerade* states (dotted lines) correlating with the $5^3 P_{J=0,1,2}$, $5^1 P_1$, $6^3 S_1$, $6^1 S_0$ and $6^3 P_1$ atomic asymptotes. The potentials are the result of *ab initio* calculations performed using a CASSCF/CASPT2 method. Vertical thin arrows indicate electronic transitions from the ground to the $a^3 1_u$ [4], $b^3 0_u^+$ [2], $c^3 1_u$ [5], $A^1 0_u^+$ [6,7] and $B^1 1_u$ [8] *ungerade* excited states that were investigated in our laboratory in the past. Vertical thick arrows depict electronic transitions from the ground to the $C^3 1_u$ and $D^1 0_u^+$ *ungerade* excited states reported here. The $E^3 1_u$ Rydberg state is also shown.

Ab initio calculations. 20 electrons of Cd were treated explicitly while the rest *i.e.*, core electrons were replaced by effective core pseudo-potential originated from Stuttgart group. In the calculations an augmented correlation-consistent polarized valence 5-zeta (aug-cc-pV5Z) atomic basis set was used. In order to calculate electronic potentials a complete-active-space multireference second-order perturbation method (CASPT2) was used. The CASPT2 eigenenergies were employed in the subsequent spin-orbit (S-O) calculations as diagonal elements of the S-O matrix but the off-diagonal elements of the S-O operator were calculated using reference wavefunctions taken from the state averaged complete-active-space multiconfiguration self-consisted field CASSCF calculations.

RESULTS

Fig. 3. (a) Laser induced fluorescence (LIF) excitation spectrum recorded using the $C^3 1_u \leftarrow X^1 0_g^+$ and $D^1 0_u^+ \leftarrow X^1 0_g^+$ transitions in Cd_2. The envelopes of the vibrational progressions depend on **(b)** excitation-laser power curves, therefore do not represent a real Franck-Condon factor intensity distribution. The spectrum is compared with **(c)** the computer simulated ones obtained with an assumption that the excited and ground state interatomic potentials are represented with Morse functions using parameters shown in the figure. The experimentally determined $C^3 1_u$ and $D^1 0_u^+$-state potentials were compared with those of *ab-initio* calculated in Fig. 4.
The most short-wavelength part of the spectrum departs from a regular vibrational progression indicating *e.g.*, a presence of free←bound transitions juxtaposed on the distinct bound←bound
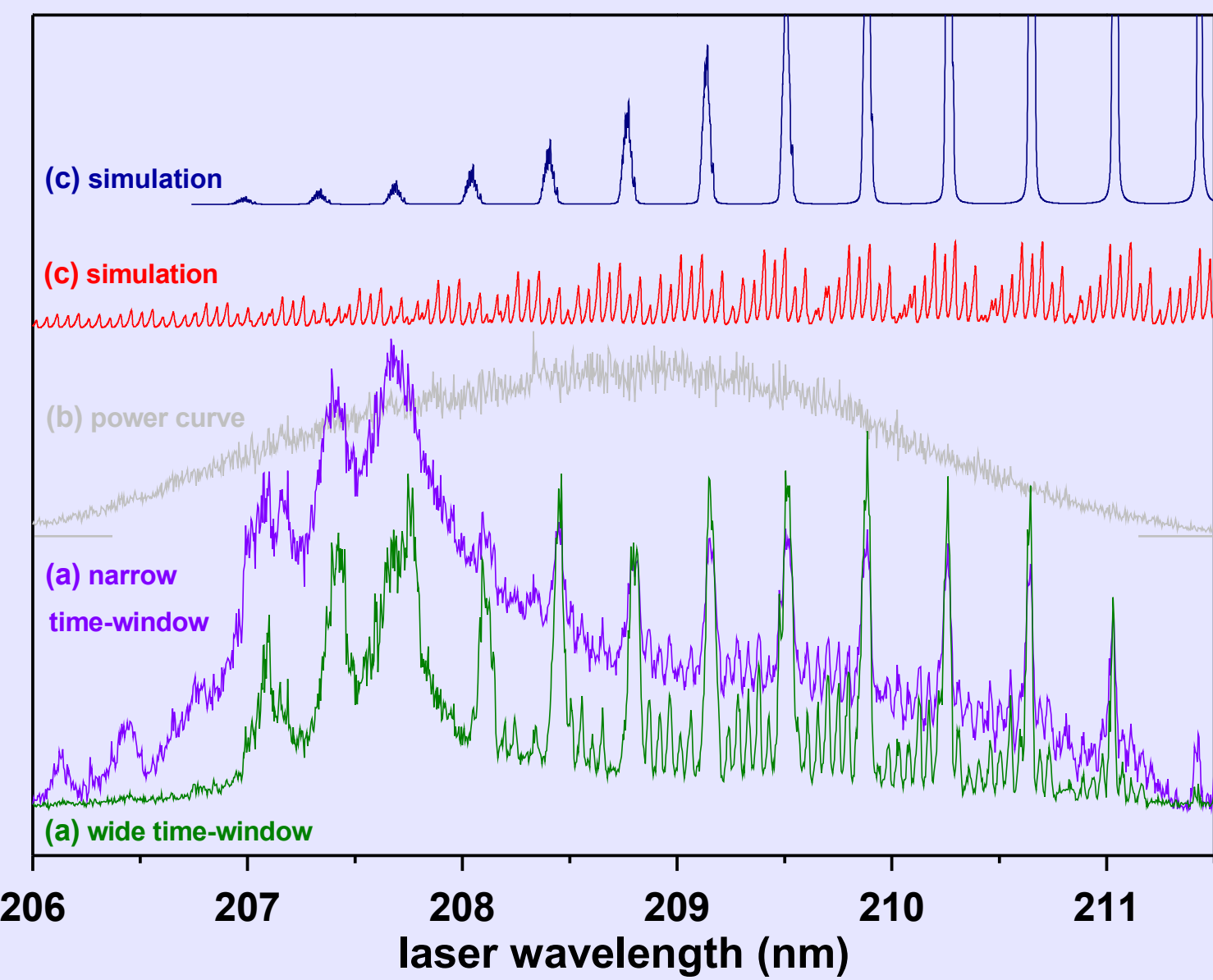
transitions. A possible explanation includes a proximity of the $E^3 1_u$-state potential that correlates with the $6^3 P_1$ Rydberg atomic asymptote lying above the $6^3 S_1$ and $6^1 S_0$ levels (see Figs. 2 and 4). However, an excitation energy transfer via $B^1 1_u$-state potential barrier through the intermediate $C^3 1_u$ state is also possible. The question remains open. Future experiments are planned to provide a plausible explanation of the observed features.

$C^3 1_u - X^1 0_g^+$
$v' = 49\ 47\ 45\ 43\ 41\ 39\ 37\ 35$
(c) simulation

$v' = 9\ 7\ 5\ 3\ 1$

$D^1 0_u^+$ ($6^1 S_0$)
$D_e' = 6569\ cm^{-1}$
$R_e' = 3.54$ Å
$\omega_e' = 90.4\ cm^{-1}$
$\omega_e' x_e' = 0.31\ cm^{-1}$

$C^3 1_u$ ($6^3 S_1$)
$D_e' = 10085\ cm^{-1}$
$R_e' = 2.68$ Å
$\omega_e' = 140.6\ cm^{-1}$
$\omega_e' x_e' = 0.49\ cm^{-1}$

$D^1 0_u^+ - X^1 0_g^+$
(c) simulation
(b) power curves
(a) expt.

(c) simulation
(c) simulation
(b) power curve
(a) narrow time-window
(a) wide time-window

laser wavelength (nm)
LIF (arb. units)

COMPARISONS

Fig. 4. Theory *vs.* experiment: a comparison between the Cd_2 interatomic potentials *ab-initio* calculated using a CASSCF/CASPT2 method (dashed lines) with those obtained experimentally in our laboratory in the past [2,4-8] as well as reported here (solid lines). As can be seen, for the $A^1 0_u^+$, $B^1 1_u$ and $C^3 1_u$ states the theory-to-experiment agreement is satisfactory. Case of the $D^1 0_u^+$ state is somewhat different: the experiment gives strong evidence that the $D^1 0_u^+$-state potential well is much shallower than that obtained as a result of the calculations. An explanation of this disagreement remains an open question. Some possibility offers the $E^3 1_u$ Rydberg state which - having considerably deep potential well reaching the $C^3 1_u$ and $D^1 0_u^+$-state energy regions - may influence the excitation from the ground state. The energy regions investigated in the experiment are depicted with thick bars on the vertical axis.

PROJECT OF THE EXPERIMENT - ENTANGLED ^{111}Cd ATOMS FROM Cd_2 MOLECULES

The knowledge on the Cd_2 interatomic potentials (Fig.4) is essential with respect to the planned experiment aiming at a verification of Bell's inequality for a pair of neutral ^{111}Cd atoms "born" in a controlled dissociation of $^{111}Cd_2$ molecules in a free-jet expansion beam [3].
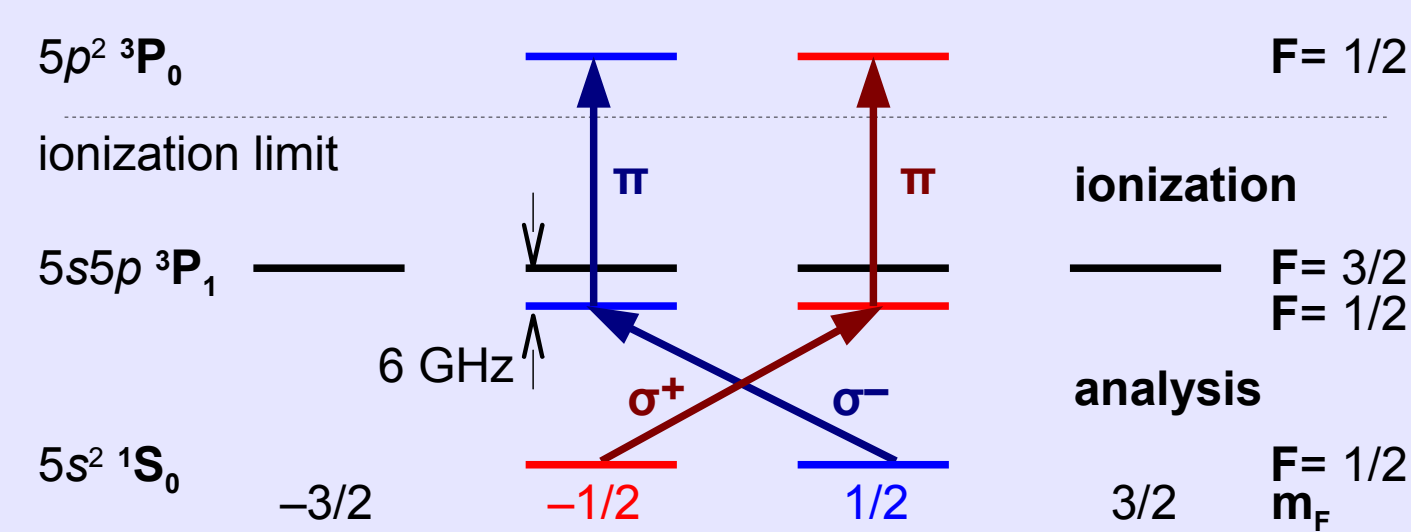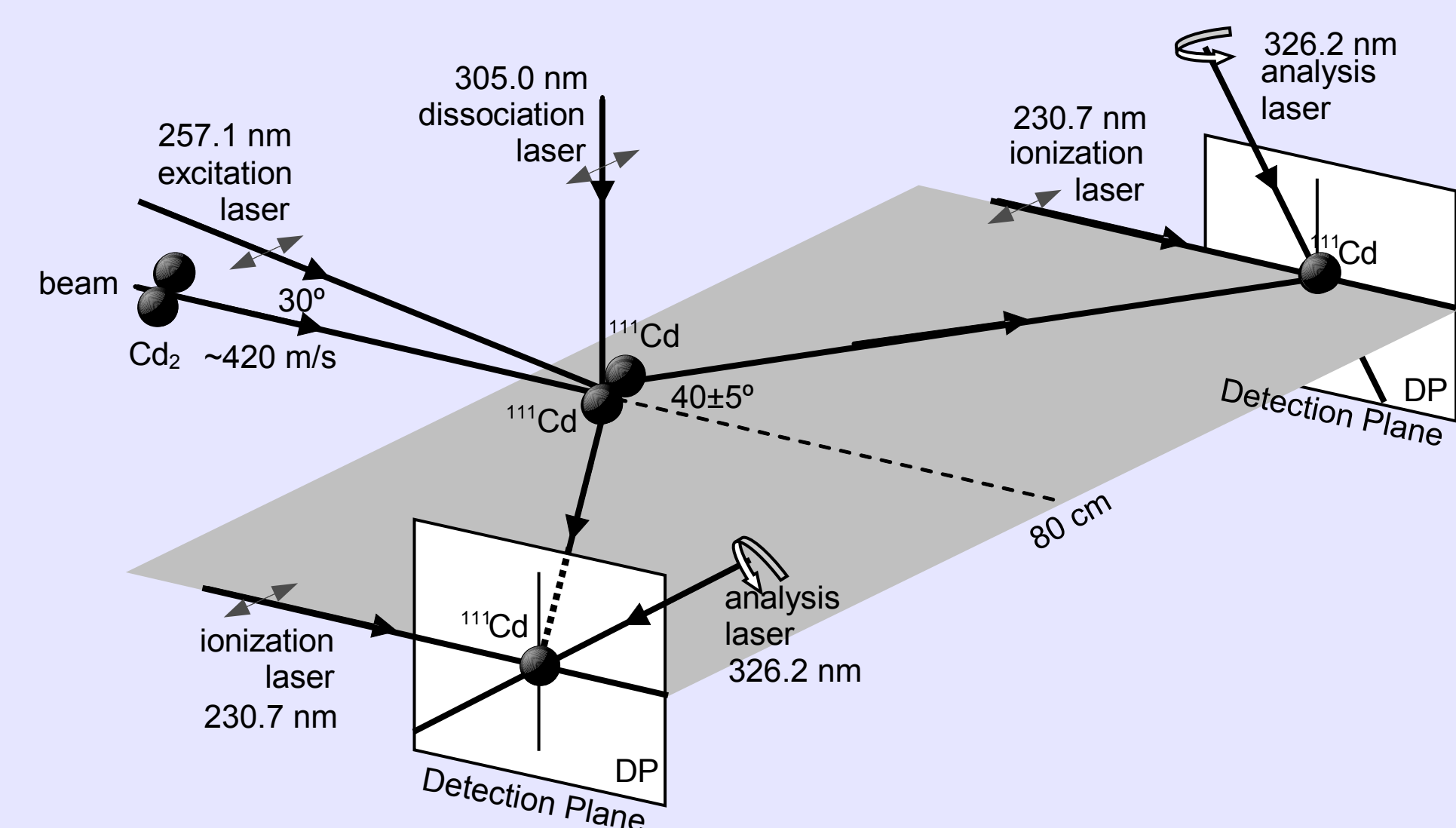

Fig. 5. Selective detection of the ^{111}Cd atoms performed in detection planes after dissociation of $^{111}Cd_2$ isotopologue. The detection is sensitive for the m_F=1/2 or m_F=-1/2 component of the total angular momentum **F=I+J**, where I(^{111}Cd)=1/2 and **J=L+S=0** for the $5^1 S_0$ ground state.
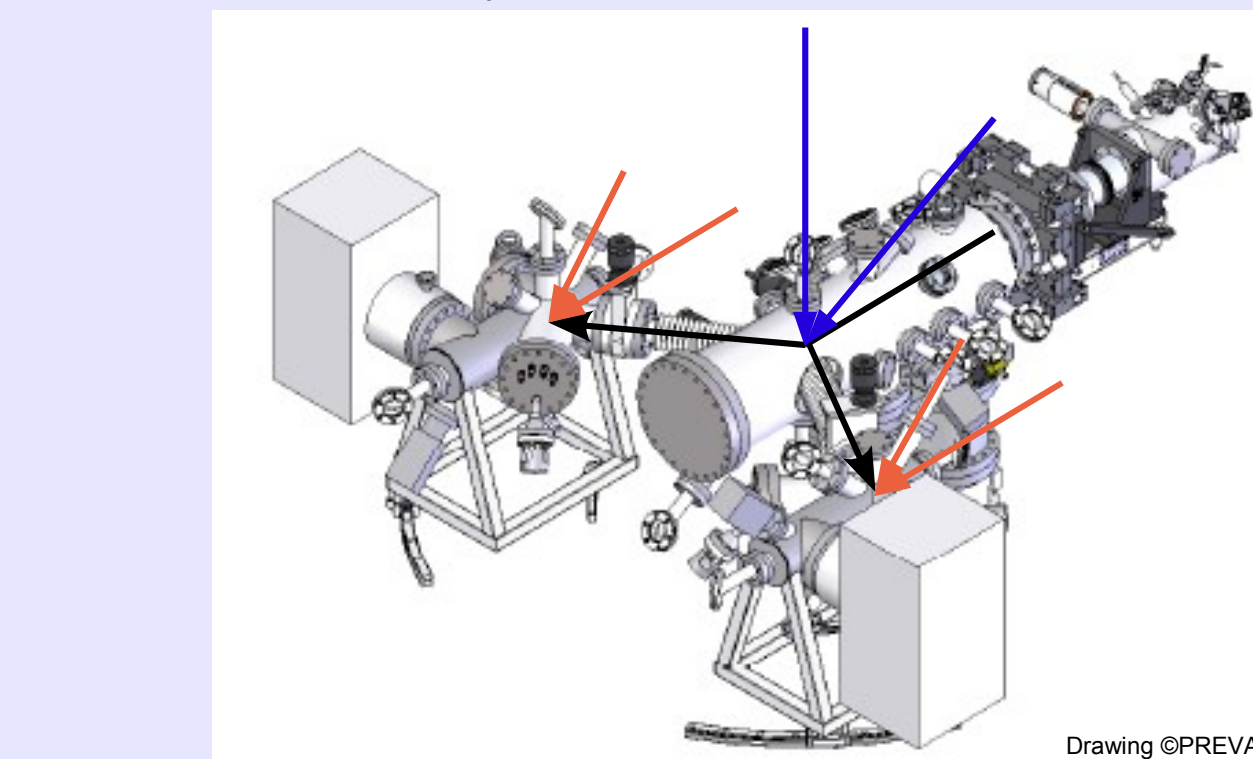

Fig. 6. Experimental apparatus – the main and side vacuum chambers. The latter accommodate detection planes. The apparatus is planned to be used in realization of the scheme shown on the left.
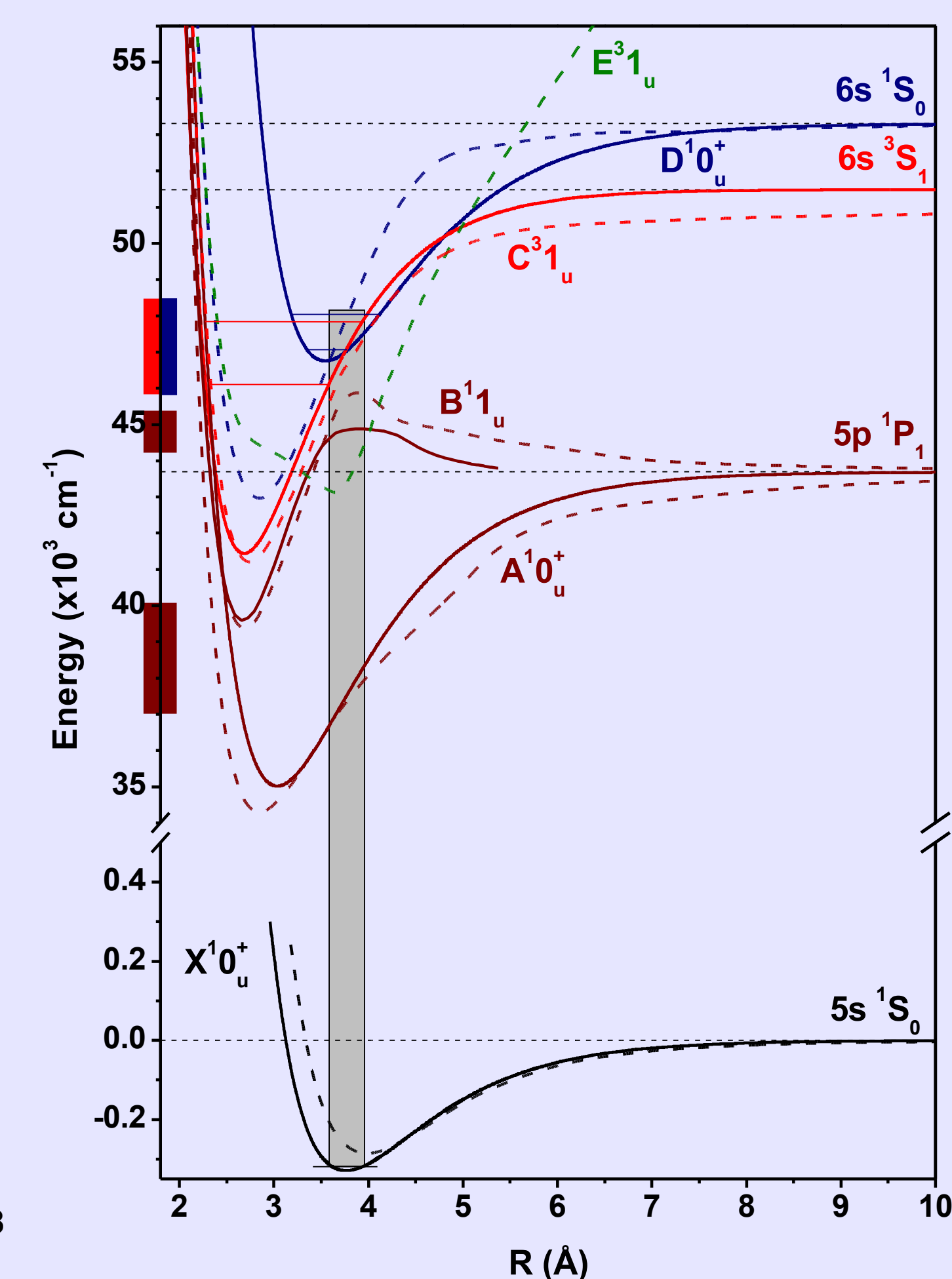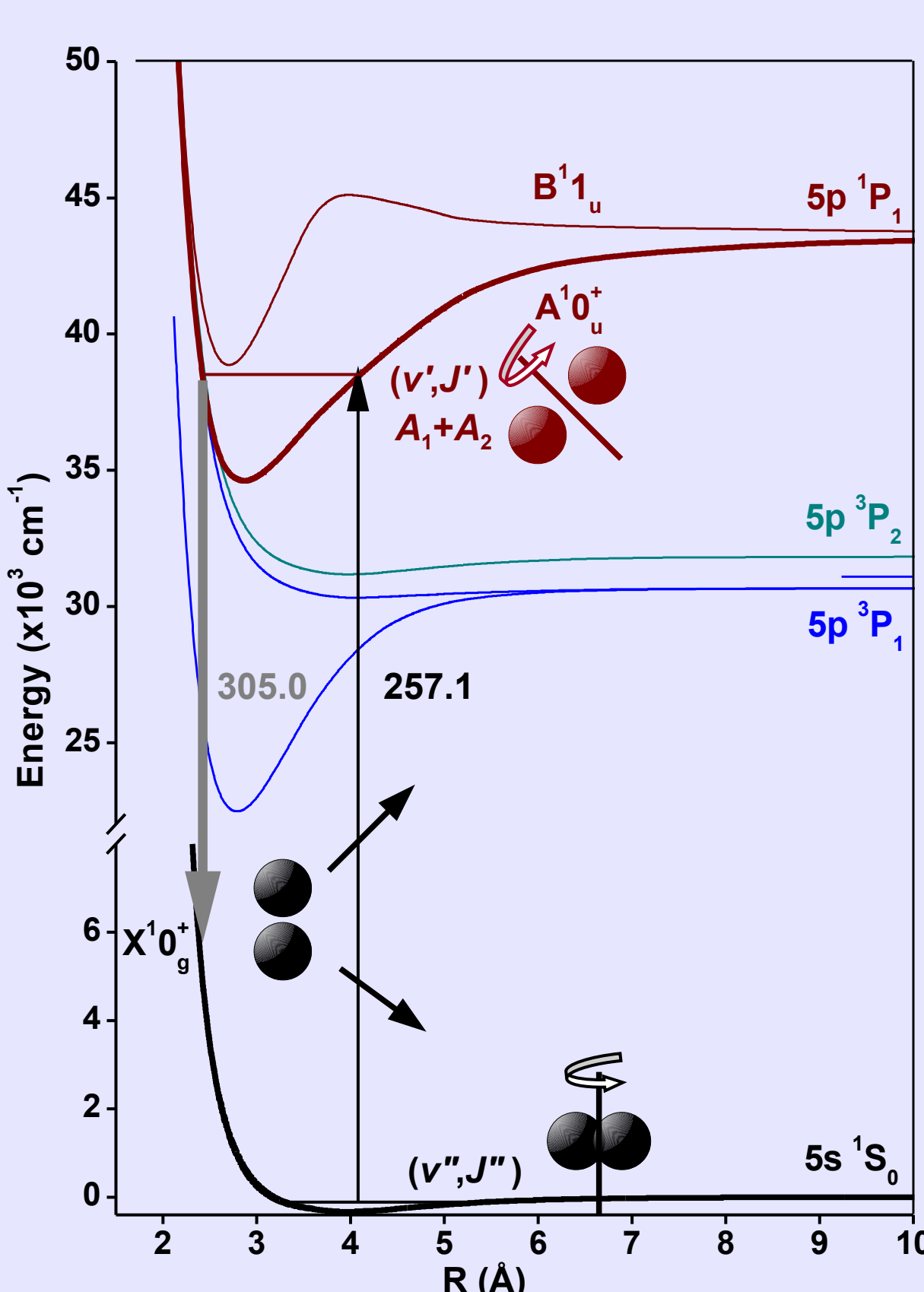

Fig. 7. Creation of a pair of entangled ^{111}Cd atoms. Diagram of the interatomic potentials of Cd_2 and the relevant stimulated Raman passage STIRAP leading to an excitation (at 257.1 nm) of the (v',J') ro-vibrational level in the $A^1 0_u^+$-state potential well and a subsequent laser dissociation (at 305.0 nm) of the $^{111}Cd_2$ (A_1+A_2=111) molecule to the repulsive part of the $X^1 0_g^+$ state leading to *creation of a pair of entangled ^{111}Cd atoms "born" from one $^{111}Cd_2$ molecule*. The proposal considers excitation of the rotating (v''=0, J''=6) ground-state molecule in a free-jet beam to the ro-vibrating (v'=40, J'=5) level, and a subsequent dissociation resulting in 80±10° separation angle and 0.78 eV center-of-mass kinetic energy.