

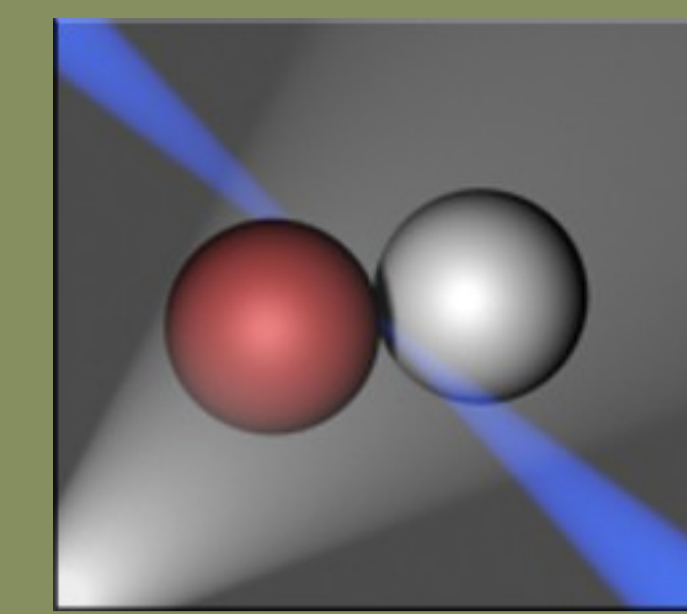
Rotational spectroscopy of cadmium dimer in a free-jet supersonic beam

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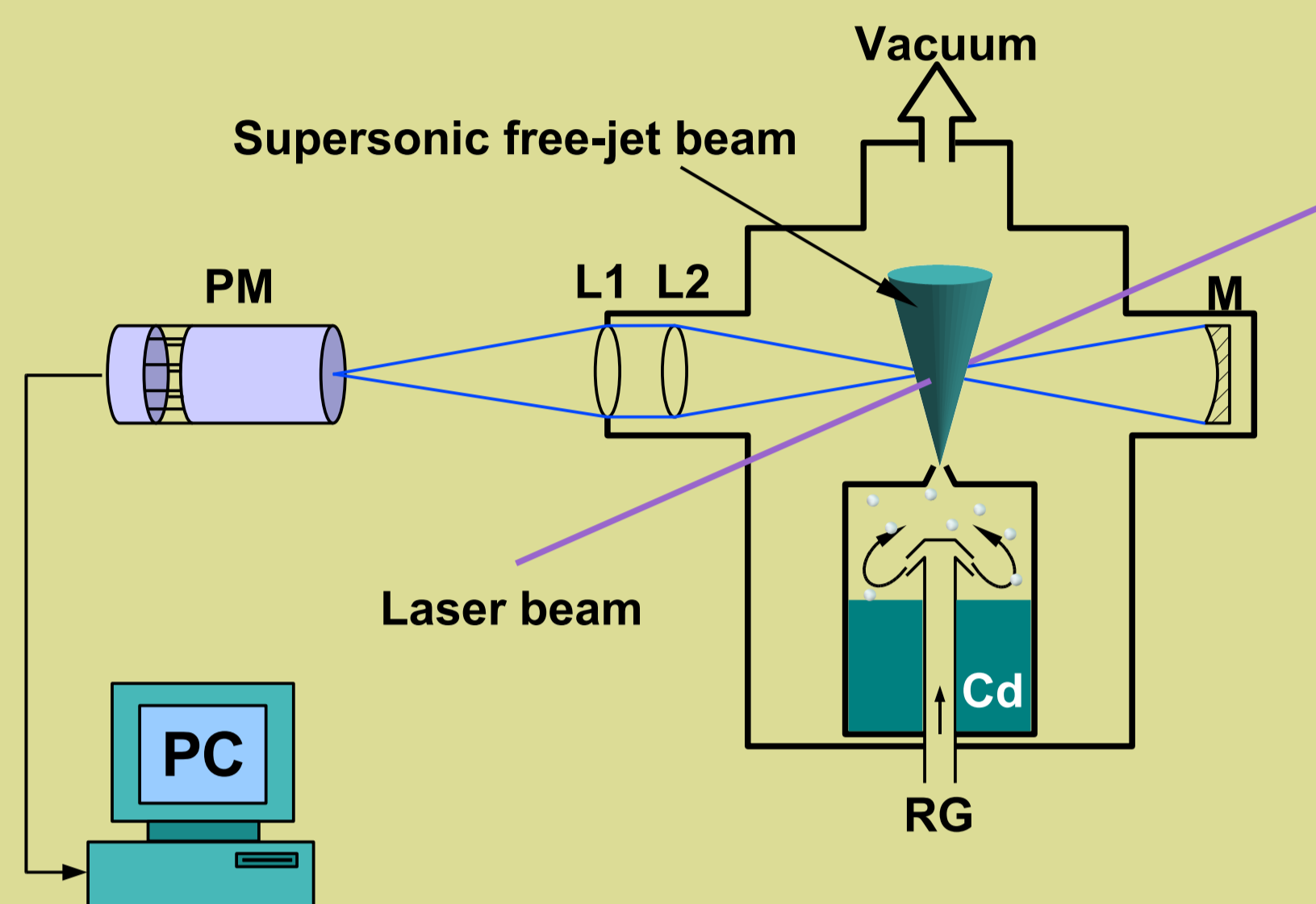
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ABSTRACT

The supersonic beam method [1] combined with techniques of high resolution laser spectroscopy has been used for determination of the excited-state interatomic potentials of the homoatomic Cd₂ van der Waals (vdW) molecules. Low resolution spectra were reported by Lukomski et al. elsewhere [2]. In the experiments, the Cd₂ molecules were produced in a free-jet supersonic beam. The dimers were excited with a spectral narrow dye-laser beam (NarrowScan, Radiant Dyes) in a vacuum chamber and the resulting total fluorescence emitted perpendicularly to the direction of the molecular and laser beams was recorded with a photomultiplier. Bound-bound transitions with rotational structure were first time observed in excitation at $0_u^+(5^1P_1)_{v=26,27,45,46,48} \leftarrow X_0^+(5^1S_0)_{v=0}$ transition (here presented only for $v=26$ and $v=45$) and $1_u(5^1P_1)_{v=38} \leftarrow X_0^+(5^1S_0)_{v=0}$. This spectra were used to evaluate rotational constants $B_{v=0}$ and respective $B_{v'}$. The rotational constants allow to calculate the absolute bond lengths of the ground (R_e) and excited (R_e^*) electronic states for the molecule. In both cases, we analysed the ²²⁸Cd₂ isotopomer because of its relatively high abundance and, what is more important, a nuclear-spin intensity alternation effect. It allowed us to perform both, energy calculations and computer simulations to obtain the best preliminary values of bond lengths. Knowledge about the R_e^* allows to determine how large influence on the dominating vdW bonding has a covalent admixture [3].



Simplified diagram of the apparatus. RG – rare gas (Argon under pressure 7-12 Bar); M – turning mirror; L1, L2 – lenses; PM – photomultiplier. Directions between laser beam, molecular supersonic beam and direction of observation are perpendicular to each other to eliminate a Doppler broadening.

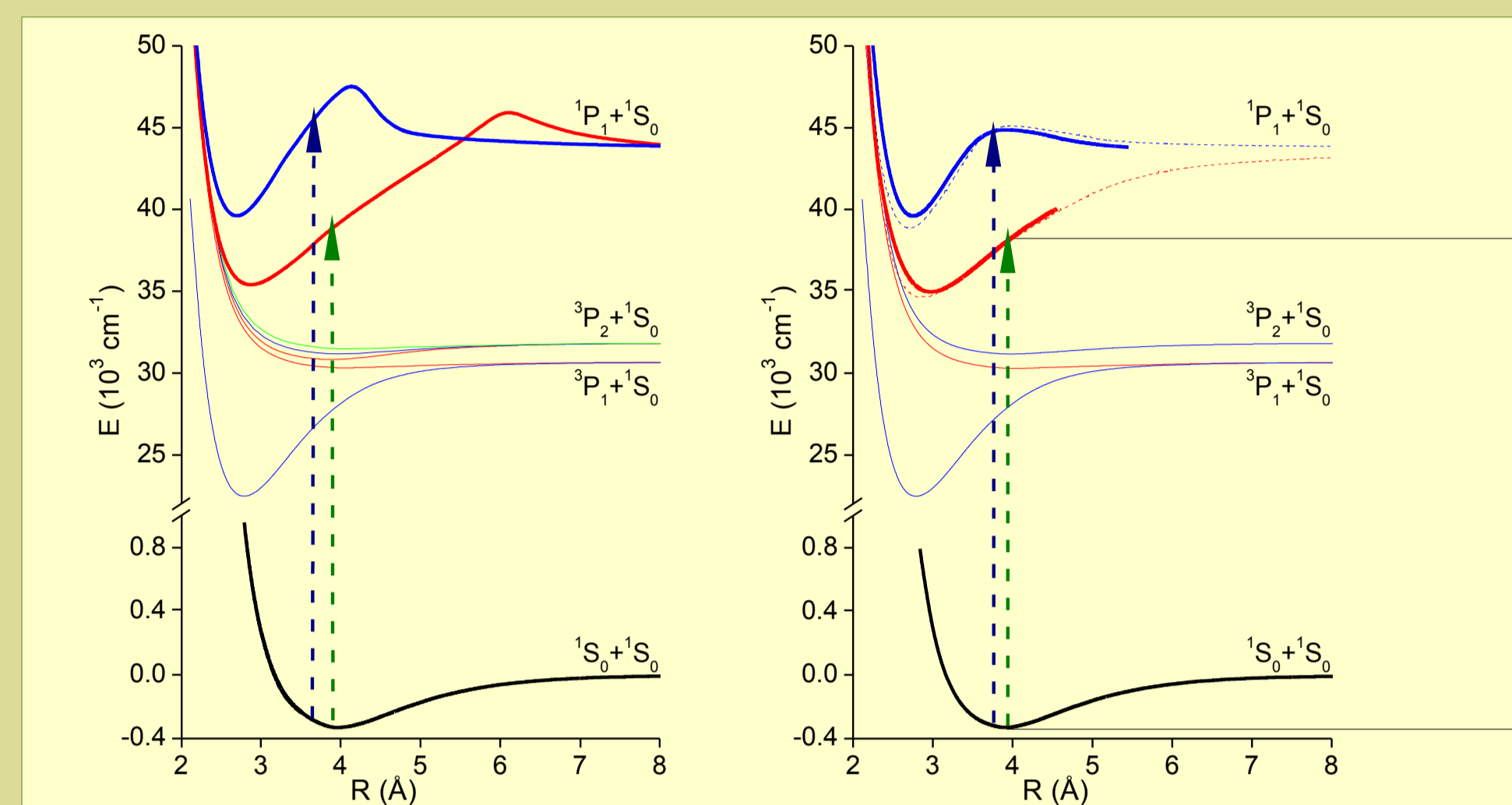


Fig. 1. Result of ab initio calculations for Cd₂ molecule (Czuchaj, private communication, 2005). Black line – X_0^+ ground electronic state; Bold red line – 1_0^+ electronic state; Bold blue line – 1_1 electronic state; Red line – 3_0 electronic states; Blue line – 3_1 electronic states; Green line – 3_2 electronic state; Arrows indicate investigated transitions $1_0^+(5^1P_1+5^1S_0) \leftarrow X_0^+$ and $1_1(5^1P_1+5^1S_0) \leftarrow X_0^+$.

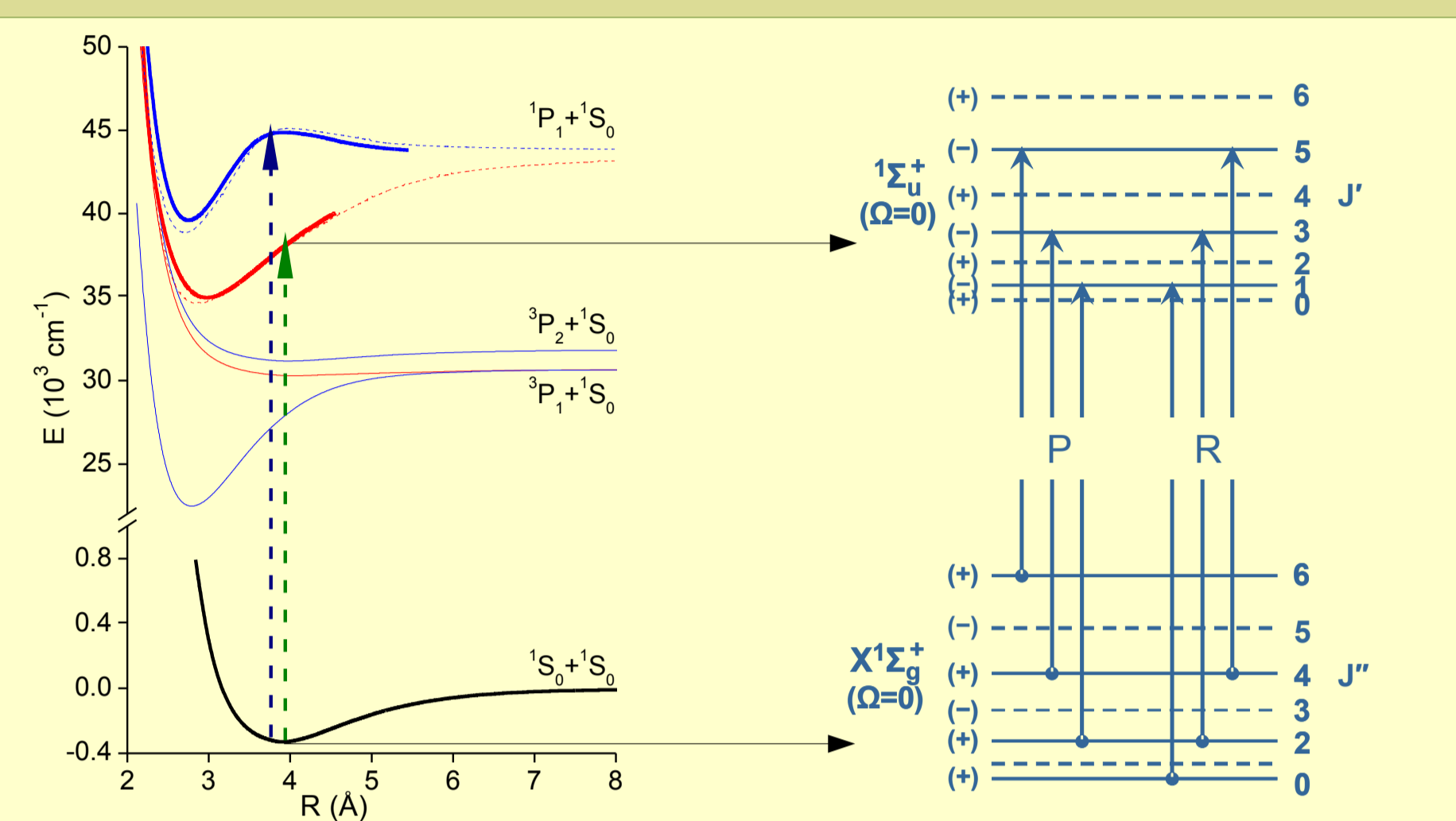


Fig. 2. Potential energy curves for the Cd₂ molecule. Experimental results: Bold black line – X_0^+ ground electronic state; Bold red line – 1_0^+ electronic state; Bold blue line – 1_1 electronic state; Red line – 3_0 electronic states; Blue line – 3_1 electronic states; Dashed red line – 1_0^+ electronic state; Dashed blue line – 1_1 electronic state; Red line – 3_0 electronic states; Blue line – 3_1 electronic states; Arrows indicate investigated transitions $1_0^+(5^1P_1+5^1S_0) \leftarrow X_0^+$ and $1_1(5^1P_1+5^1S_0) \leftarrow X_0^+$.

Fig. 3. Schematic explanation of nuclear spin alternation and rotational-levels symmetry properties in $1_0^+(5^1P_1) \leftarrow X_0^+$ transition. For homonuclear dimers with zero nuclear spin (e.g. ¹¹²Cd¹¹²Cd) transitions between dashed levels are forbidden while for homonuclear dimers with non zero nuclear spin instead of missing every second transition there is an intensity alternation of neighbouring transitions caused by statistical weight of these levels.

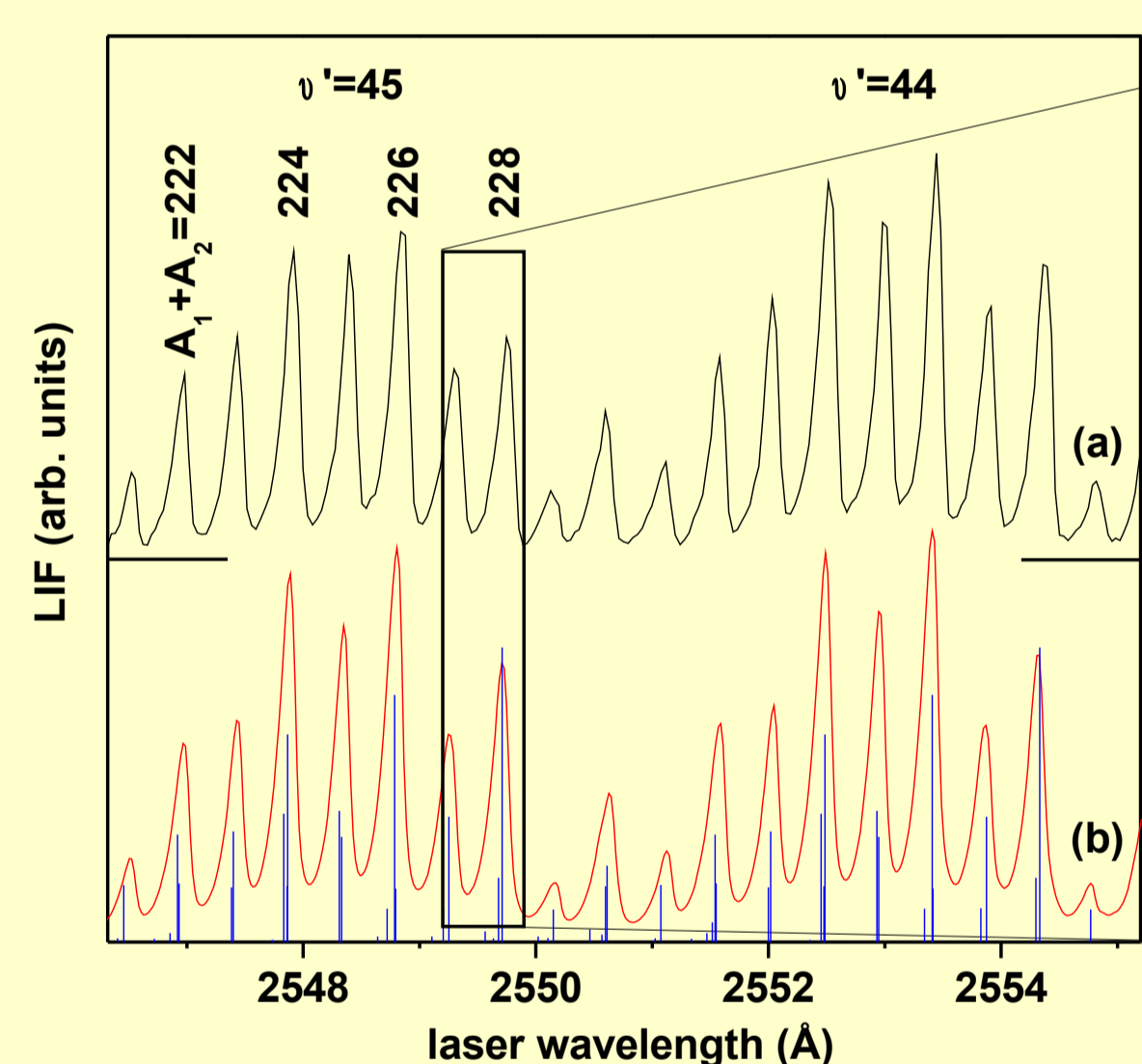


Fig. 4. a) Two vibrational low resolution components recorded at the $0_u^+(5^1P_1) \leftarrow X_0^+(5^1S_0)$ transition. Isotopic peaks marked A_1+A_2 values consist of different isotopomer mass combinations m_1+m_2 (see Fig. 5) b) Computer simulated (red line) profile resulted in convoluting every isotopic component (blue bars) with a Lorentzian (FWHM=0.13Å).

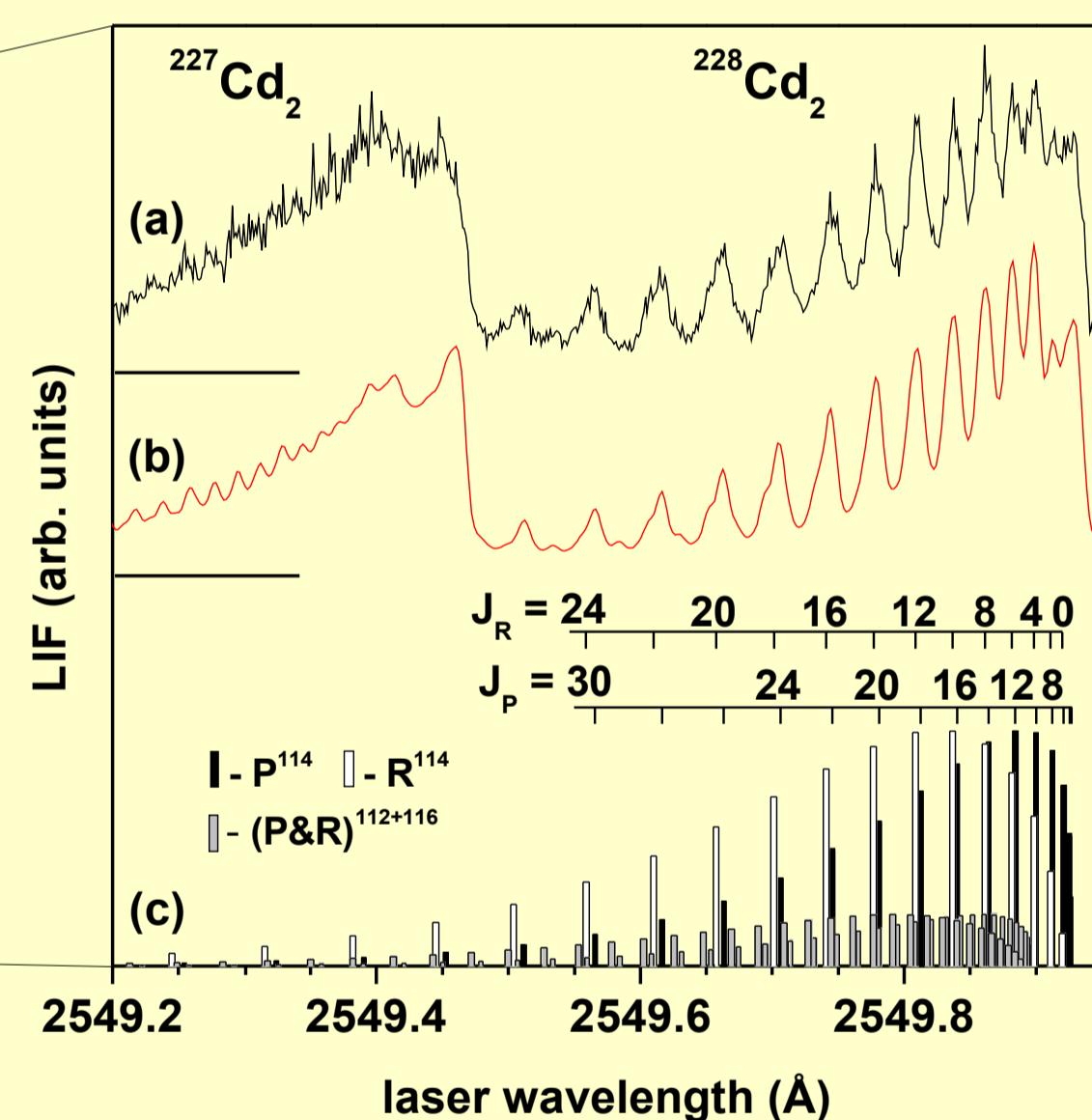


Fig. 5. a) Rotationally resolved spectrum of $A_1+A_2=228$ isotopic component recorded for $v'=45$ consisted on two different isotopomer combinations (¹¹⁴Cd¹¹⁴Cd and ¹¹²Cd¹¹⁶Cd). b) Simulated profile obtained as a result of convolution of every rotational component (bars in Fig. 5c) with a Voigt function. c) White and black bars represent R and P-branch of ¹¹⁴Cd¹¹⁴Cd component respectively (Q-branch does not occur in this transition) while both R and P branches of ¹¹²Cd¹¹⁶Cd component are represented by grey bars.

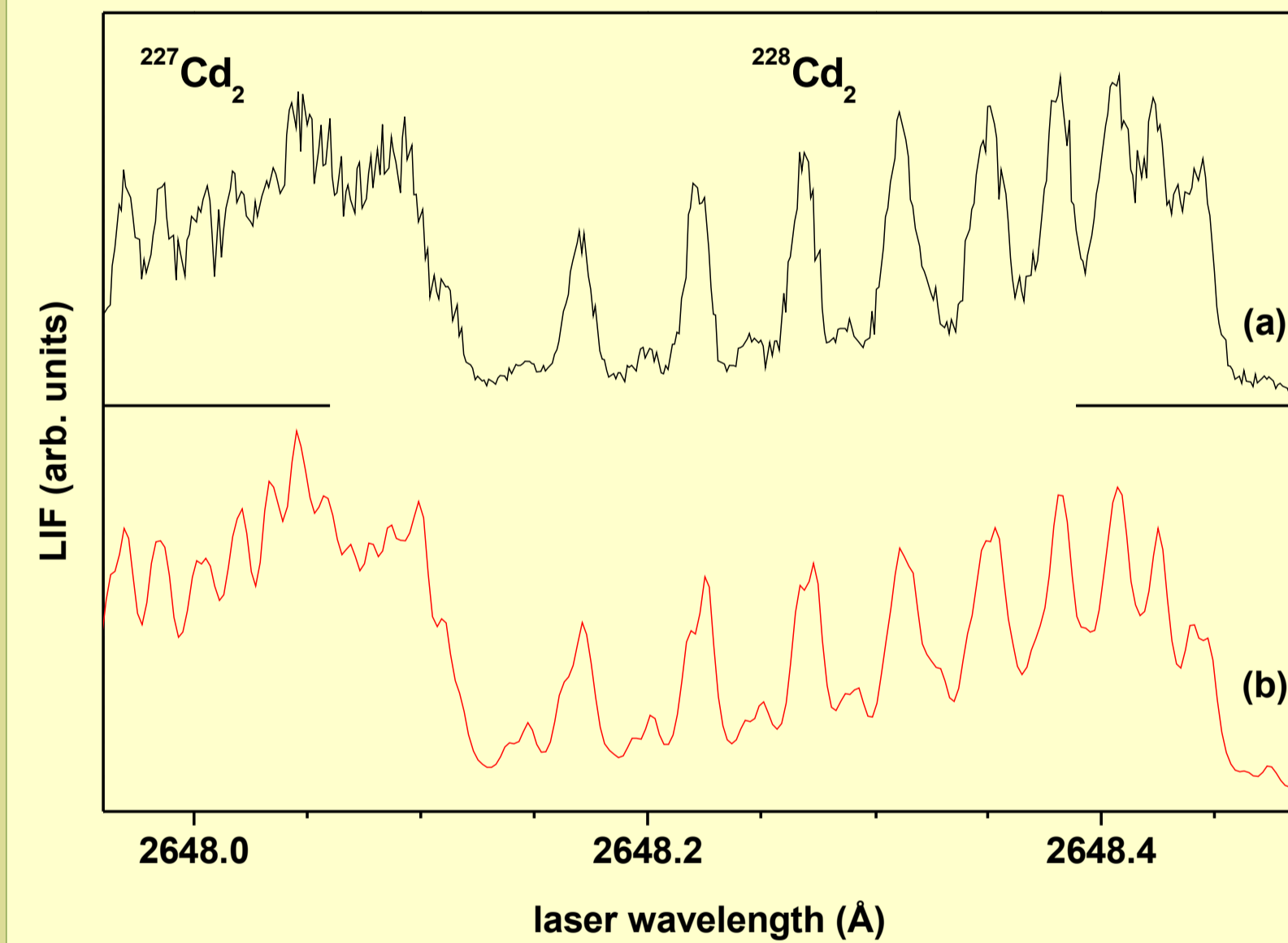


Fig. 6. a) Rotationally resolved spectrum of one isotopic component $A_1+A_2=227$ recorded for $v'=26$. b) Simulated profile obtained analogically as in Fig. 5.

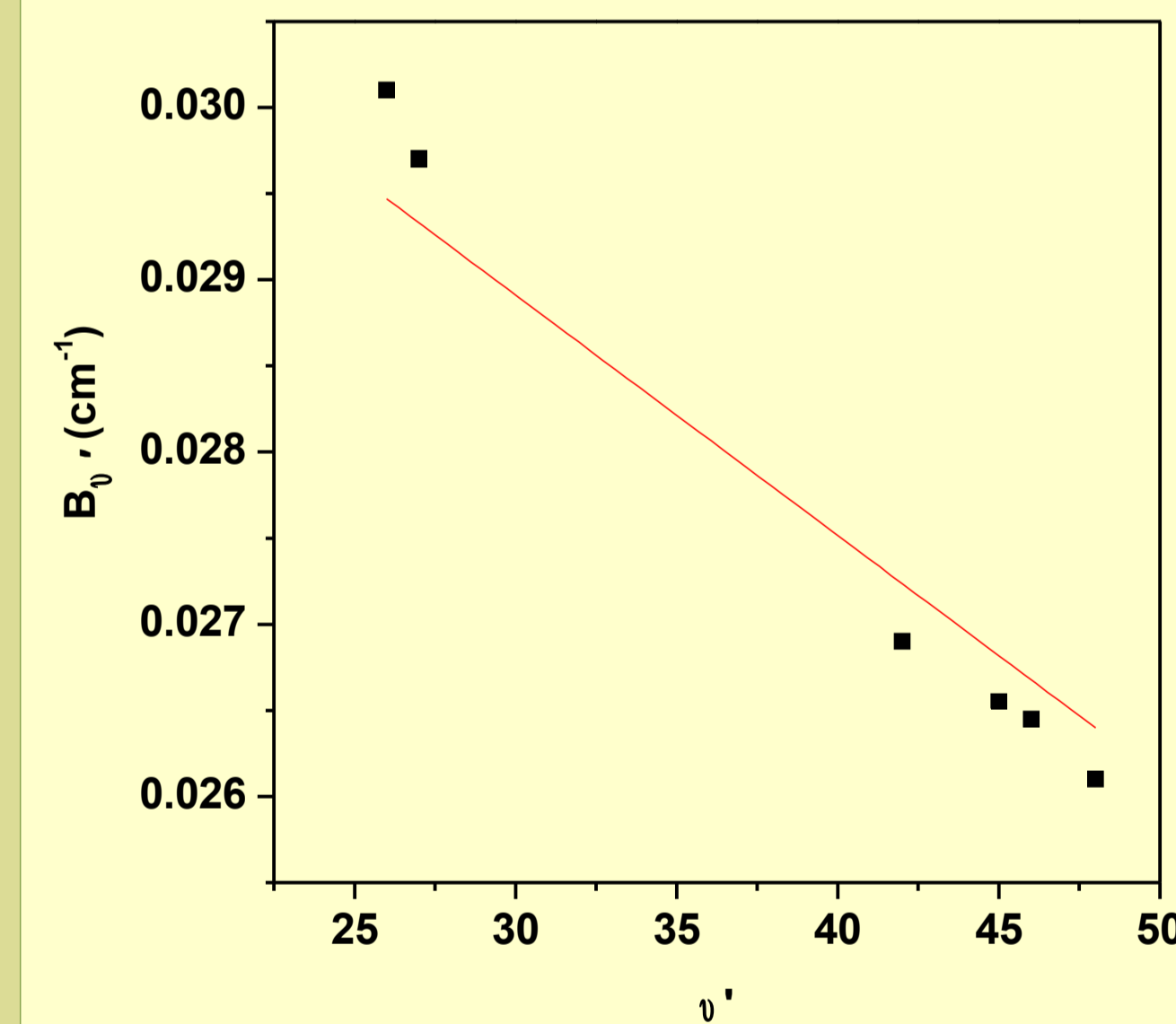


Fig. 7. Squares represents measured $B_{v'}$ for various v' of the $0_u^+(5^1P_1)$ electronic state. Red line – a theoretical function $B_{v'}(v')$ assuming a Morse representation for the 1_0^+ state. $B_{v'}(v') = B_e^* - \alpha_e^*(v'+1/2)$ where $\alpha_e^* = \{6[\omega_e^*x_e^*(B_e^*)^2]^{1/2}/\omega_e^* - [6(B_e^*)^2/\omega_e^*]\}$ where $\omega_e^* = 100.5 \text{ cm}^{-1}$, $\omega_e^*x_e^* = 0.325 \text{ cm}^{-1}$ [1] and $B_e^* = 0.0329 \text{ cm}^{-1}$ were fit. As can be seen, the $B_{v'}(v')$ function does not approximate well the experimental points. Another words, a Morse function is not good representation of the 1_0^+ state potential.

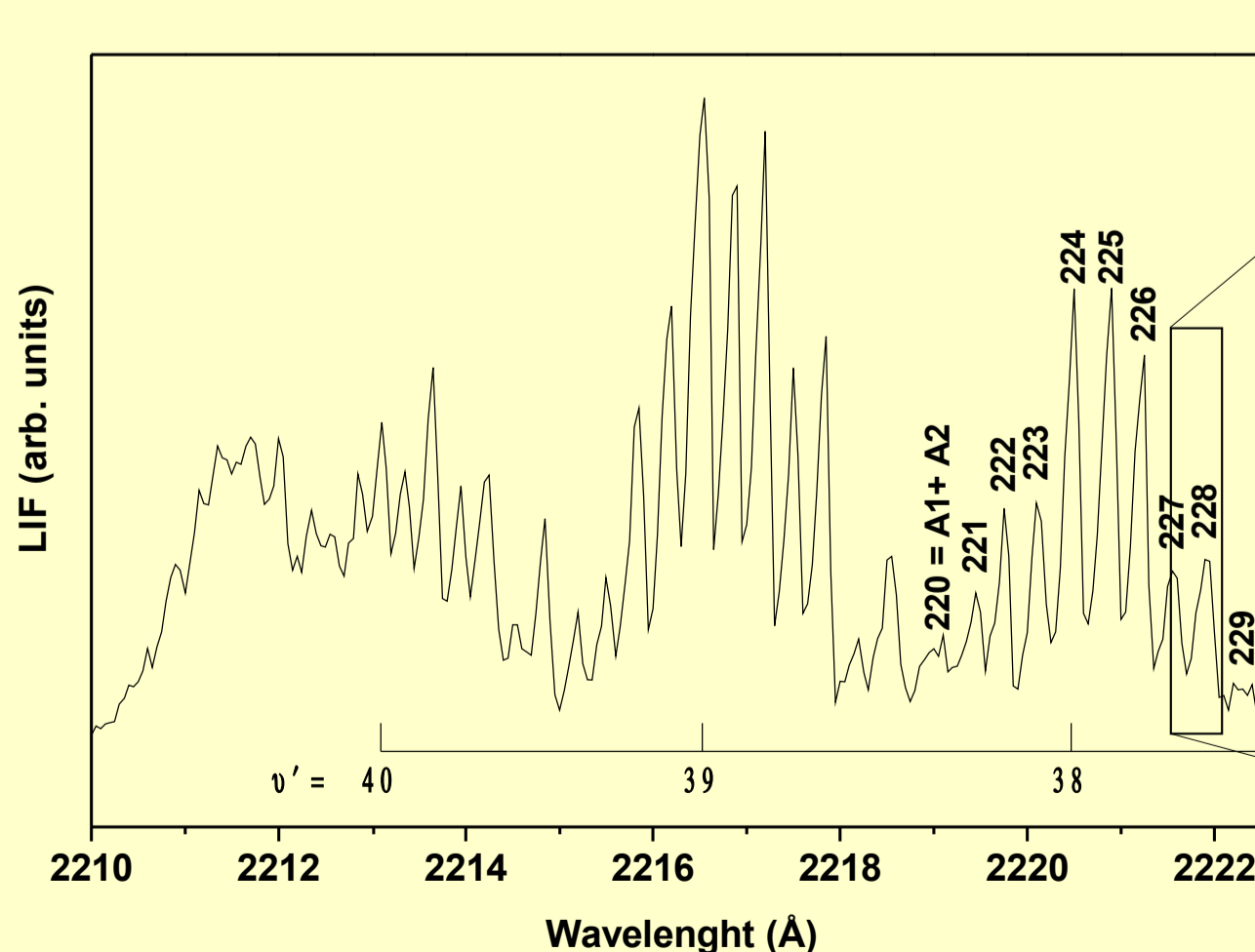


Fig. 8. Excitation spectrum recorded at the $1_u(5^1P_1) \leftarrow X_0^+(5^1S_0)$ transition in Cd₂. Presented example shows “bound-bound” and “bound-free” transition appear together in the same region (short wavelength part). Isotopically-resolved spectrum was possible to record because of relatively high values of v' (38, 39 and part of 40).

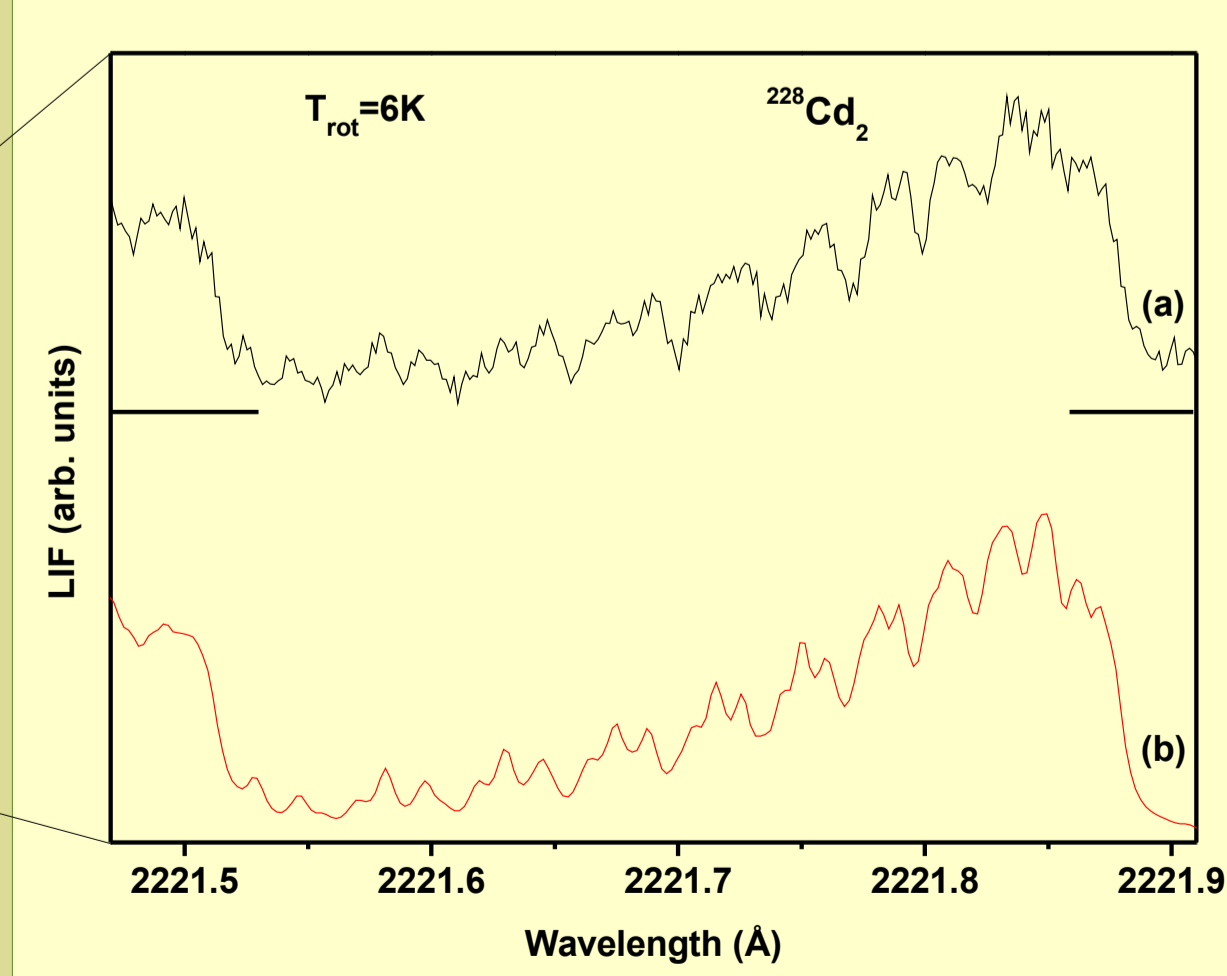


Fig. 9. a) Rotational structure of one isotopic component ²²⁸Cd₂ recorded for $v'=38$ in the $1_u(5^1P_1) \leftarrow X_0^+(5^1S_0)$ transition. In this transition all three branches (P, Q and R) appear therefore intensity alternation effect is not clearly visible. b) Computer simulated profile obtained in the same way as in case above. Rotational temperature $T_{rot}=6\text{K}$ was assumed.

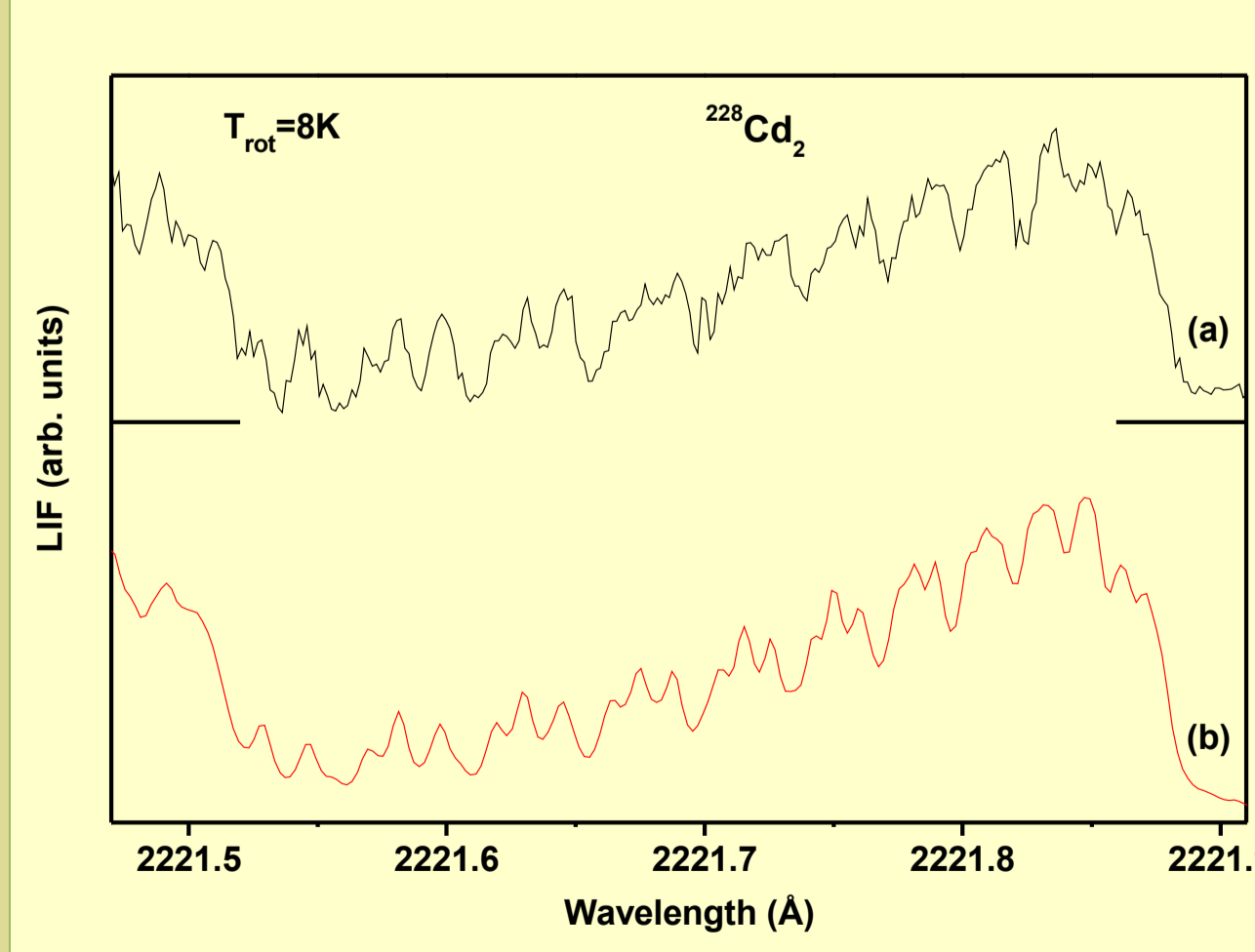


Fig. 10. a,b) The same as in Fig. 9 except a higher rotational temperature. In the simulation $T_{rot}=8\text{K}$ was assumed.

	B_e (cm ⁻¹)	B_e (cm ⁻¹)	R_e (Å)
$1_0^+ v'=26$	0.0301		
$1_0^+ v'=27$	0.0297		
$1_0^+ v'=45$	0.0269	-0.033 ^a	-3.0 ^a
$1_0^+ v'=46$	0.02655		
$1_0^+ v'=48$	0.02645		
$1_1 v'=38$	0.03055	-0.0398 ^b	-2.7 ^b
$X_0^+ v'=0$	0.0195	0.0197	3.88

Table 1. Rotational constants for the investigated states of Cd₂.

a) The $1_0^+(5^1P_1)$ electronic state is only approximately represented by a Morse function (see plot in Fig. 7).
b) The $1_1(5^1P_1)$ electronic state can not be represented by a Morse function; in addition $B_{v'}$ was measured only for high v' close to the top of the potential barrier.

Bibliography:

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