

# IS CADMIUM DIMER TRULY A VAN DER WAALS MOLECULE: ROTATIONS AT THE ${}^10_u(5^1P_1) \leftarrow X^10_g$ AND ${}^11_u(5^1P_1) \leftarrow X^10_g$ TRANSITIONS

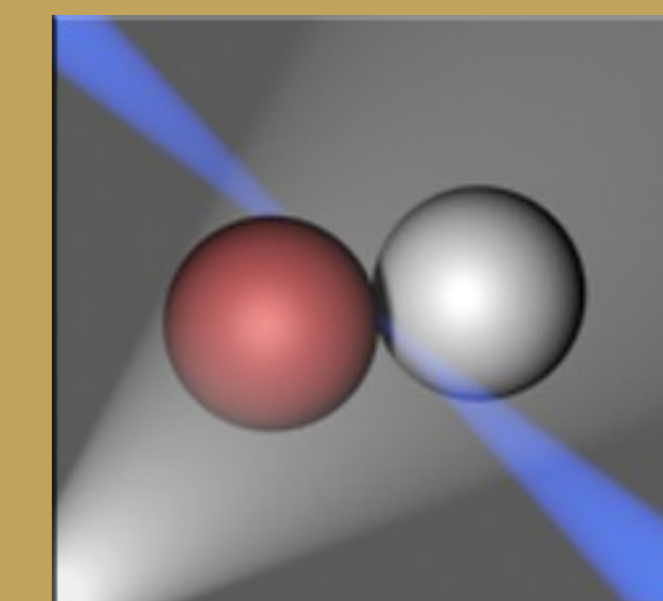


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## ABSTRACT

The supersonic molecular beam method [1] combined with high resolution laser spectroscopy technique has been used for investigation of the rotational structures in the  ${}^10_u(5^1P_1)$  and  ${}^11_u(5^1P_1)$  excited electronic energy states of Cd<sub>2</sub> van der Waals (vdW) molecule. Low resolution spectra of these states were reported by Lukomski et al. [2] and Koperski et al. [3].

In the experiment, the Cd<sub>2</sub> molecules were produced in a supersonic free-jet expansion beam. The dimers were excited with a spectral narrow ( $\Delta\lambda_{\text{las}} \approx 0.08 \text{ cm}^{-1}$ ) dye-laser beam (NarrowScan, Radiant Dyes) in a vacuum chamber and the resulting total laser induced fluorescence in the form of rotationally resolved profiles was recorded with a photomultiplier Fig. 1.

Rotational profiles of the  ${}^{228}\text{Cd}_2$  isotopomer recorded in the  $(v',v'') = (26,0)$ ,  $(27,0)$ ,  $(45,0)$ ,  $(46,0)$ ,  $(48,0)$  vibrational bands of the  ${}^10_u(5^1P_1) \leftarrow X^10_g(5^1P_1)$  transition (Fig. 2) were analysed (in parentheses are Hund's-case-(a) equivalents of Hund's-case-(c) states). This particular isotopomer was chosen considering its relatively high abundance and rotational-levels symmetry properties causing so-called intensity alternation effect Fig. 3. As a direct result, the  $B_{v',v''}$  excited- as well as the  $B_{v',v''}$  ground-state rotational constants (TABLE 1) of the ( ${}^{114}\text{Cd}$ )<sub>2</sub> were determined. A multi-vibrational band and multi-rotational branch analysis together with computer simulations allowed determination of the absolute values for the  $R_e$  and  $R_e^*$  excited- and ground-state bond lengths, respectively. The obtained result - the  $R_e^*$  - distinctly shorter than that obtained with assumption of pure ground-state van der Waals bonding supports a theoretical prediction of a covalent admixture to the bonding [4]. This result clearly indicates that hypothesis of a covalent admixture is plausible, can be supported by our experimental result and, consequently, the ground-state bonding in group-12 M<sub>2</sub> dimers (particularly in Cd<sub>2</sub>) cannot be described as pure vdW interaction. It means that cadmium dimer may be regarded as an intermediate case between a weakly bound van der Waals molecule and a chemically bound species.

Analysis of the partially resolved rotational profile recorded in the  $(v',v'') = (38,0)$  band of the same isotopomer recorded at the  ${}^11_u(5^1P_1) \leftarrow X^10_g$  transition (Fig. 2) allowed estimation of the  $B_{v',v''}$  rotational constant (TABLE 1) in the  ${}^11_u$  state.

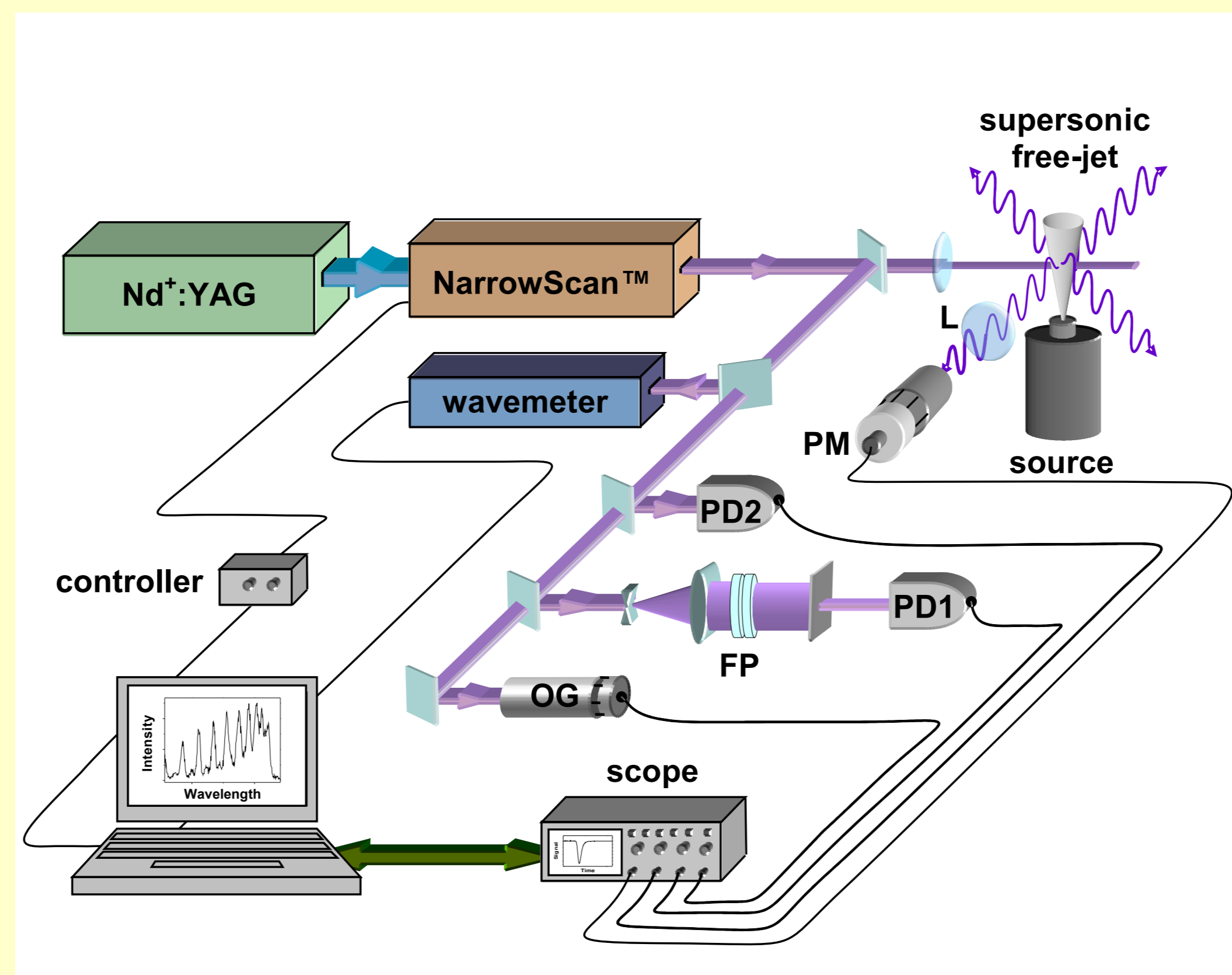


Fig. 1. Scheme of the experimental setup. L - lenses, OG - octagonal cell, PD1, PD2 - photodiodes, FP - Fabry-Perot etalon, PM - photomultiplier tube. Perpendicular directions between laser beam, molecular supersonic expansion beam and direction of observation allow to considerably reduce a Doppler broadening ( $\Delta\lambda_{\text{Dopp}} \approx 0.12 \text{ cm}^{-1}$ ).

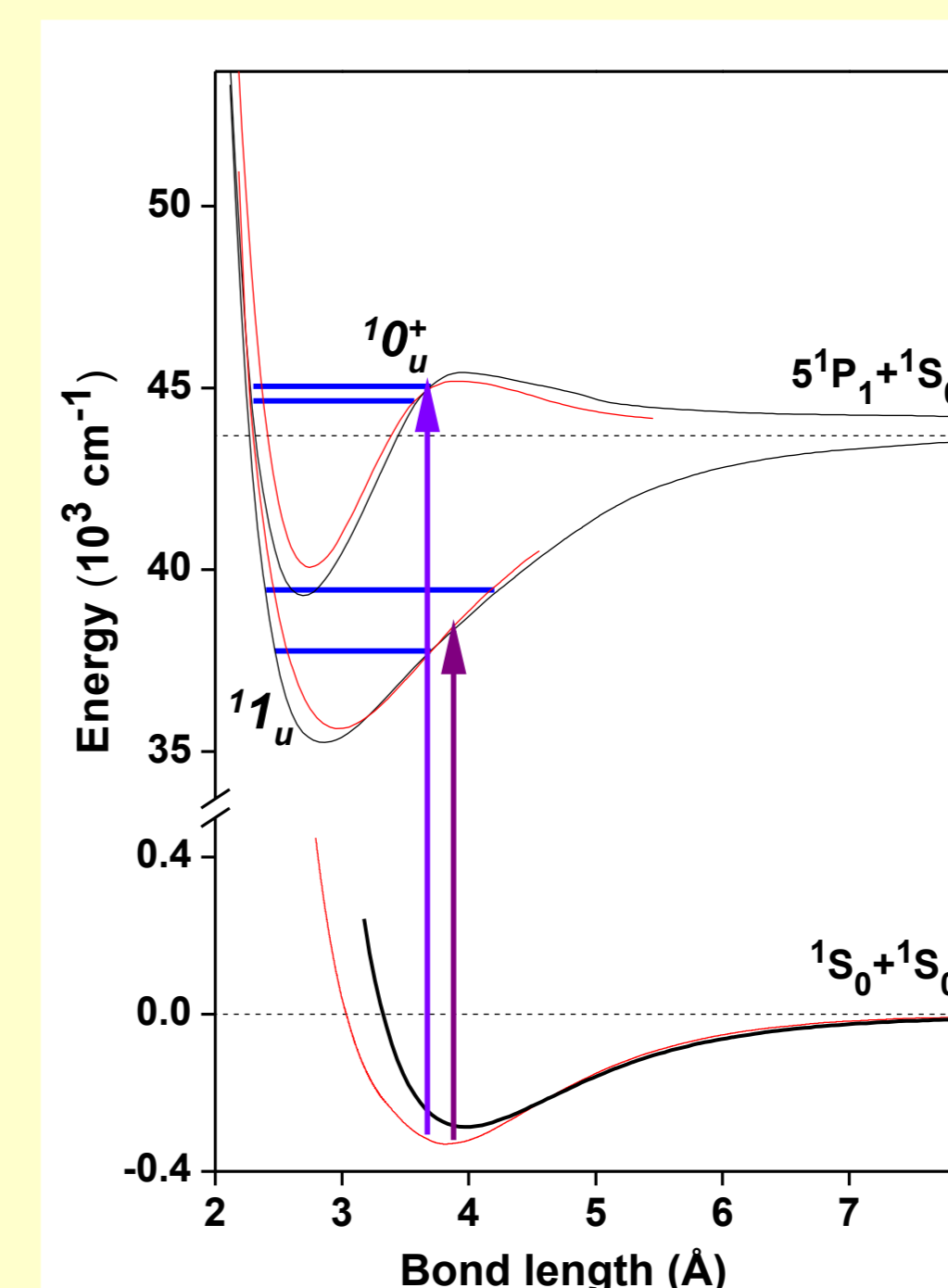


Fig. 2. Interatomic potentials of the Cd<sub>2</sub> for the ground and excited states. Ab initio potentials of Czuchaj [5] (black lines) are compared with result of Łukomski et al. [2] for the ground and for the  ${}^10_u(5^1P_1)$  state as well as for the  ${}^11_u(5^1P_1)$  [3] state (red lines). Ranges of investigated  $v'$  levels in the  ${}^10_u(5^1P_1)$  and  ${}^11_u(5^1P_1)$  potential wells are depicted with horizontal blue lines.

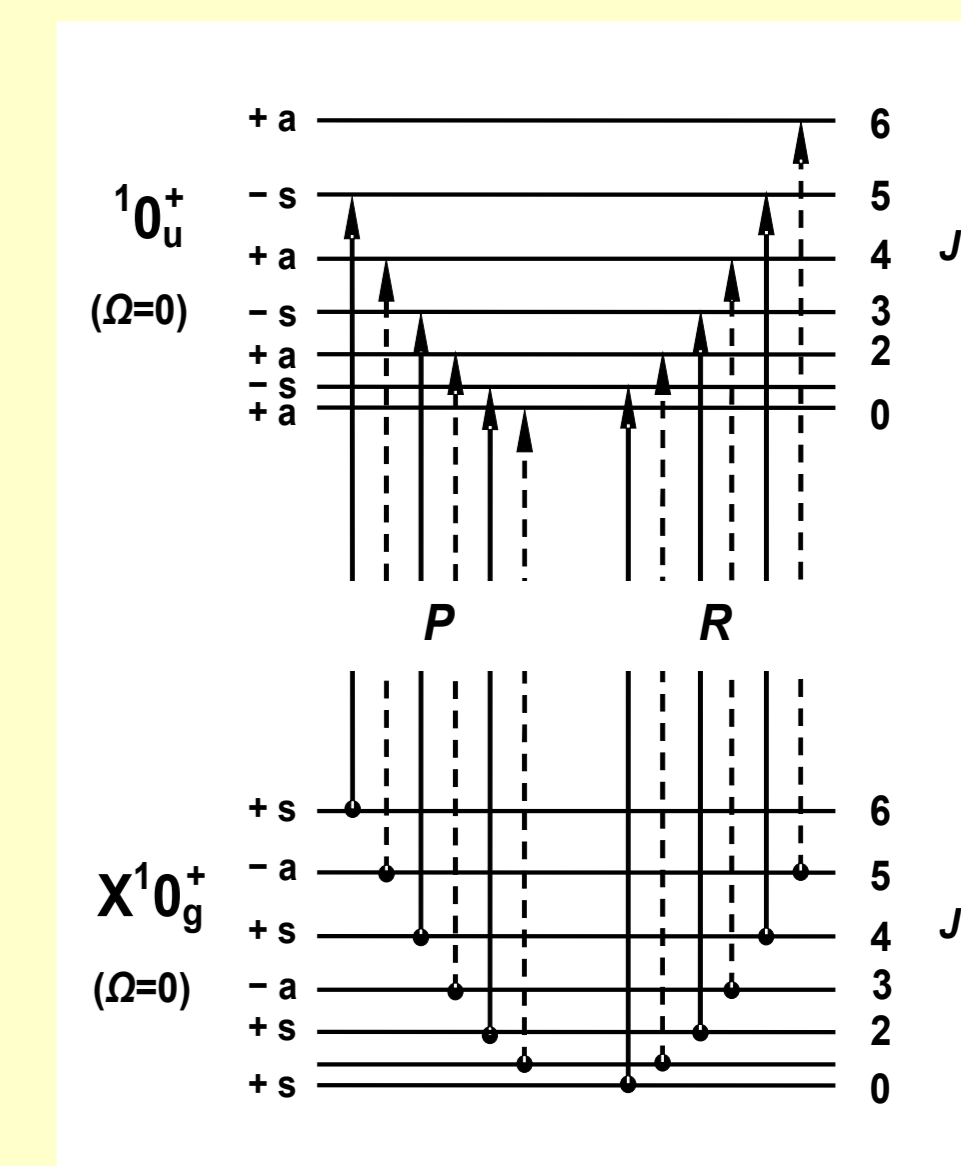


Fig. 3. Schematic diagram of the  ${}^10_u(5^1P_1) \leftarrow X^10_g$  transition for homonuclear isotopomers with  $l = 0$  including appropriate selection rules and rotational-level symmetry properties (every second transition is missing, broken-line arrows). While for homonuclear isotopomers with  $l \neq 0$  instead of missing every second transition there is an intensity alternation of neighbouring transitions caused by statistical weight of these levels. For heteronuclear isotopomers all transitions occur. The nuclear-spin alternation effect together with rotational-levels symmetry properties explain intensities of the different isotopic components.

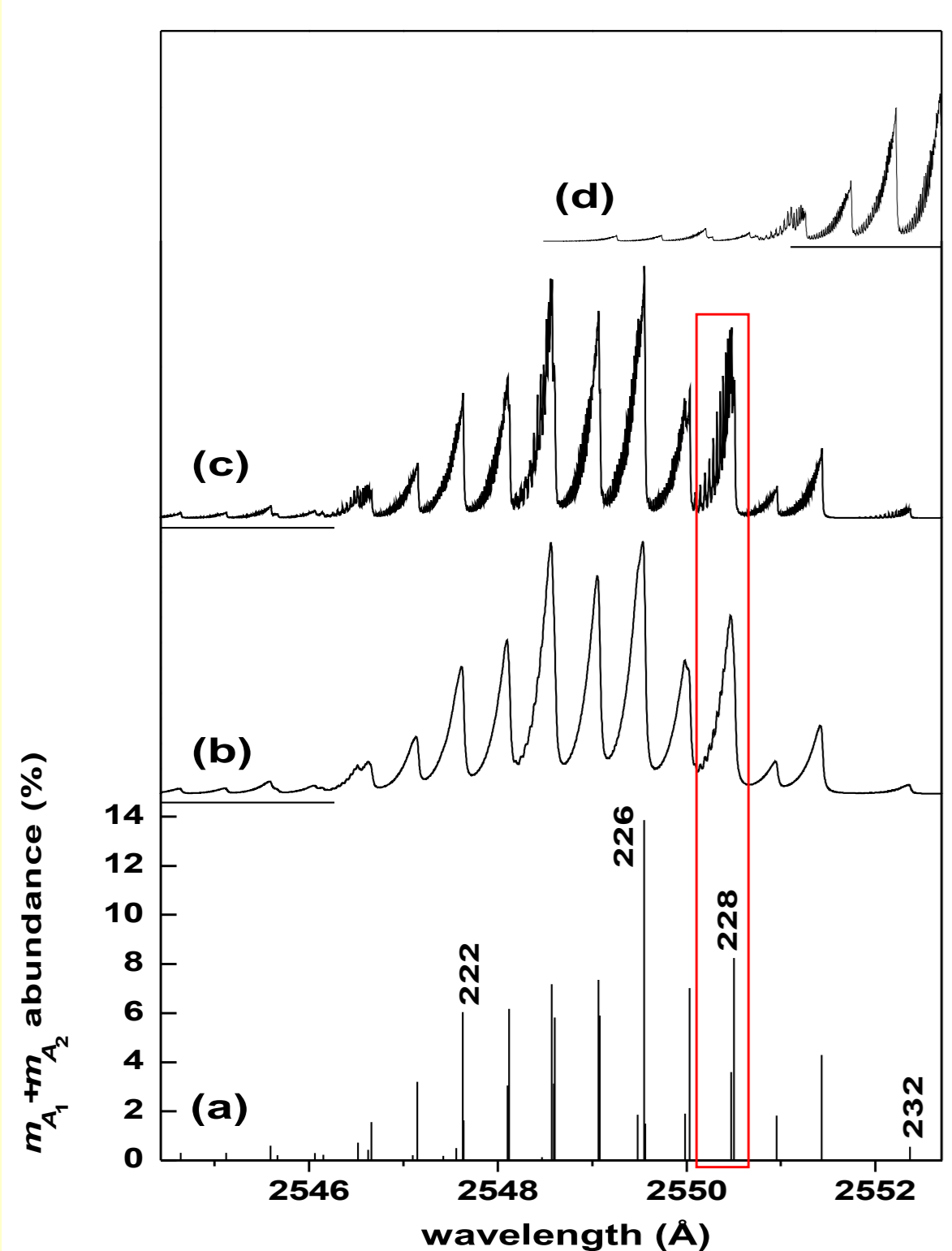


Fig. 4. (a) Isotopic pattern of the  ${}^{228}\text{Cd}_2$  isotopomers in  $(v=45,0)$  vibrational band. Each isotopomer consists of corresponding number of  $(A_1, A_2)$  mass combinations; (b) and (c) simulations showing pattern (a) in which each rotational component within component with different  $m_{A_1} + m_{A_2}$  is convoluted with a Voigt function with  $\text{FWHM} = 0.5 \text{ cm}^{-1}$  (lower-resolution) and  $0.15 \text{ cm}^{-1}$  (higher-resolution), respectively. A part of the neighbouring  $(v'-1,0)$  band is shown in (d) to illustrate an overlap of its isotopic components with those in the  $(v',0)$ .

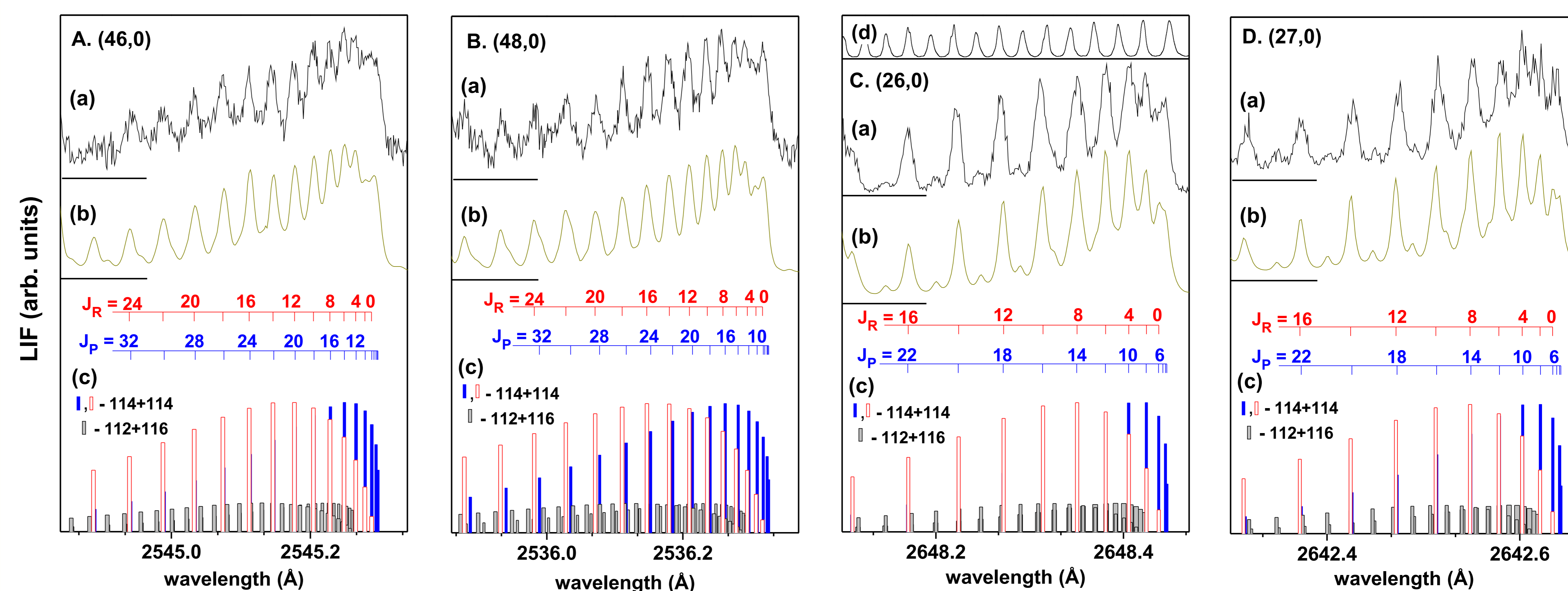


Fig. 5. Details of the rotational profiles of the  ${}^{228}\text{Cd}_2$  isotopomer recorded in (A) (46,0), (B) (48,0), (C) (26,0) and (D) (27,0) vibrational bands (details of band (45,0) are presented elsewhere [6]) of the  ${}^10_u(5^1P_1) \leftarrow X^10_g$  transition. (a) Experimental traces; (b) computer simulated profiles [7] obtained as a result of convolution of every rotational transition with a Voigt function (in the simulations  $\Delta\lambda_{\text{las}} \approx 0.08 \text{ cm}^{-1}$ ,  $\Delta\lambda_{\text{Dopp}} \approx 0.12 \text{ cm}^{-1}$  and rotational temperature  $T_{\text{rot}}$  of (A) 7K, (B) 5K, (C) 13K and (D) 15K were assumed); (c) P-branch (full blue bars) and R-branch (open red bars) of the ( ${}^{114}\text{Cd}$ )<sub>2</sub> isotopomer; P- and R-branches of the  ${}^{112}\text{Cd}{}^{114}\text{Cd}$  isotopomer (grey bars). (d) fringes recorded with a help of Fabry-Perot monitor etalon (FSR=0.2  $\text{cm}^{-1}$ ) for a fundamental dye-laser frequency.

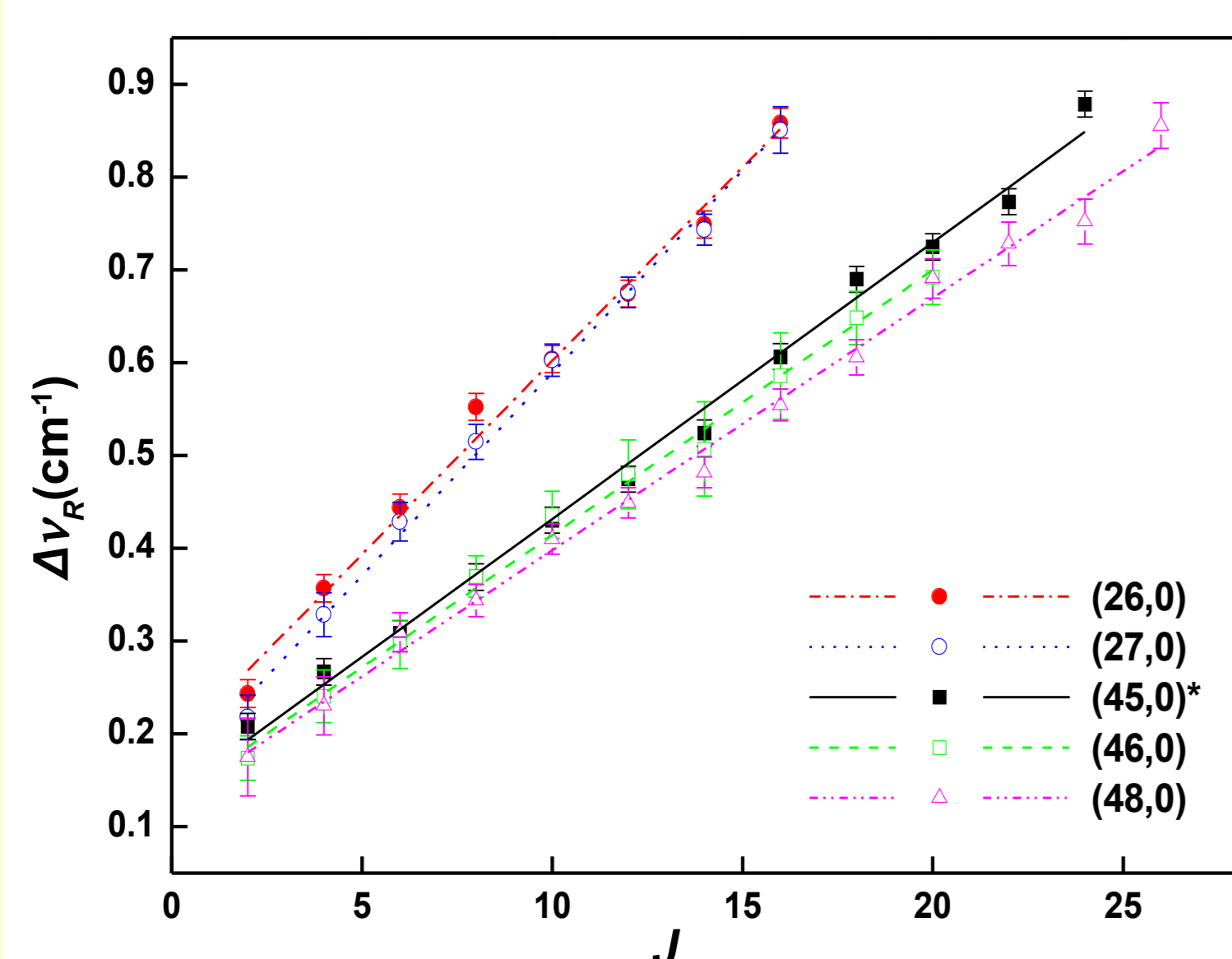


Fig. 6. Result of multi- $(v',0)$ -band and multi-rotational-branch (here presented only for R-branch) fitting. It assumes that the fitting procedure is performed for both R- and P-branches simultaneously. In other words, multiple data sets are simultaneously fitted with appropriate functions [8] of one independent variable ( $J$ ) having common parameters (common  $B_{v',v''}$  for both R- and P-branches of the same  $(v',0)$  band and common  $B_{v',v''}$  for all  $(v',0)$  bands and both R- and P-branches) by minimizing the total WSSR (Weighted by the input data errors Sum of the Squared Residuals between the input data points and the function values) coefficient. The  $\Delta v_r(J)$  plot includes also the (45,0) vibrational band marked with asterisk and analysed in Ref. [6]. Obtained values of the rotational constants  $B_{v',v''}$  and  $B_{v',v''}$  obtained with help of this procedure are collected in TABLE 1.

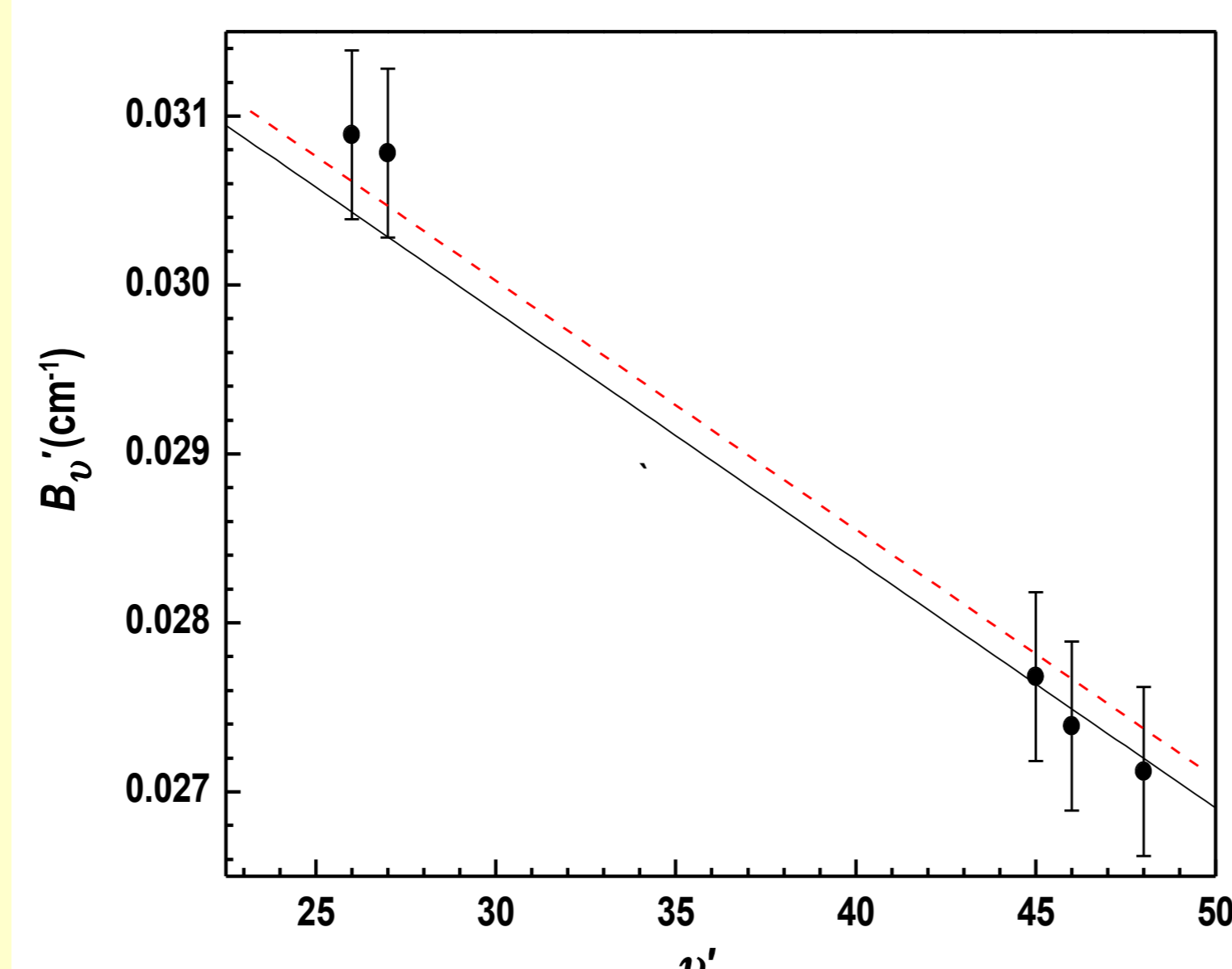


Fig. 7. The rotational constants  $B_{v'}$  obtained for the  ${}^10_u(5^1P_1)$  excited state plotted against  $v'$ . Theoretical function plotted according to  $B_{v'} = B_e - a_e(v + 1/2)$  (solid line) assuming a Morse representation of the excited state. A linear fit (dashed red line) obtained with the  $R_e^*$  as a free parameter (according to  $R_e^* = (h/8\pi^2 \mu B_e)^{1/2}$ ) allowed approximation of the excited-state bond length (TABLE 1).

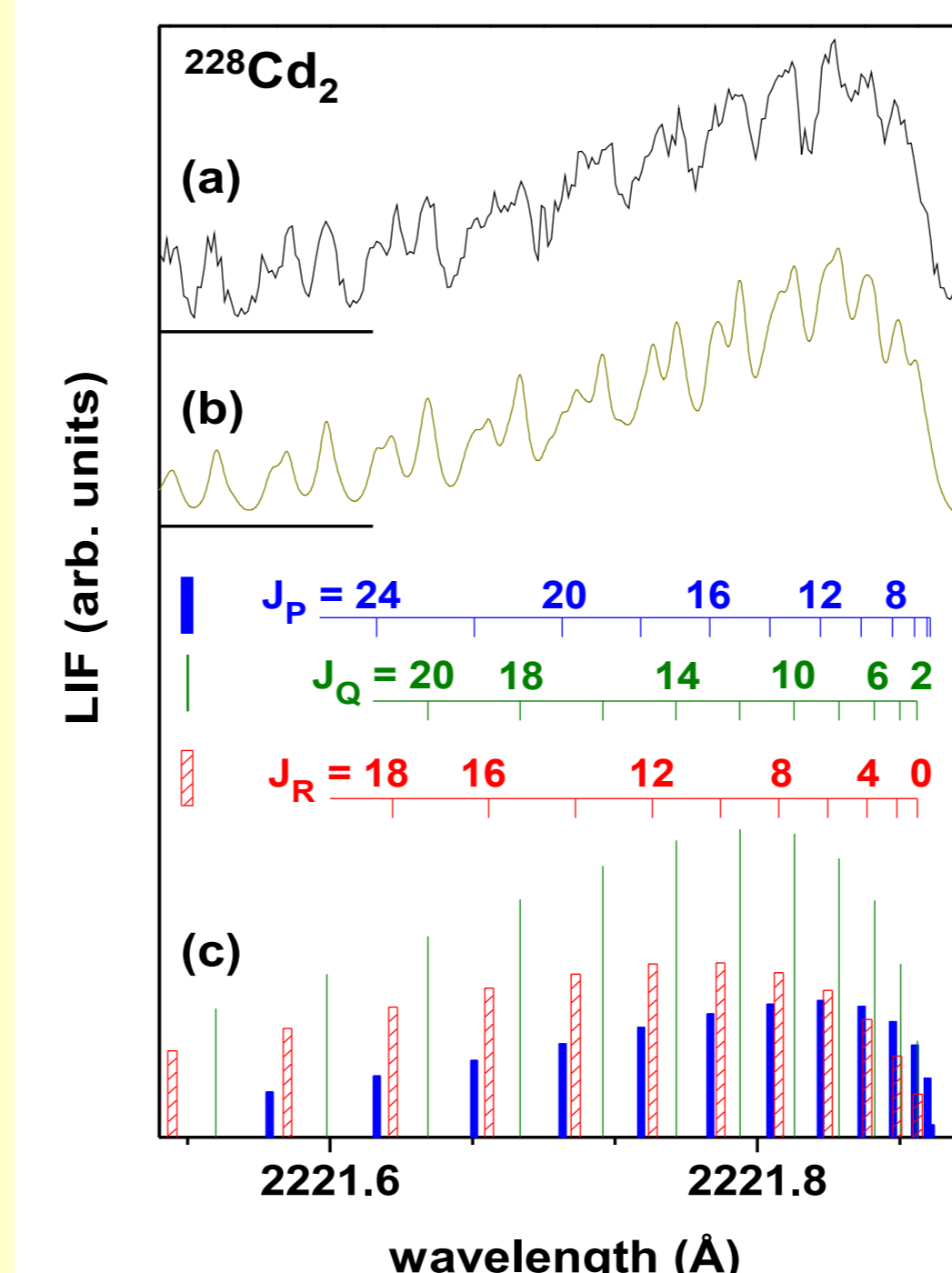


Fig. 8. Details of the rotational profile of the  ${}^{228}\text{Cd}_2$  isotopomer recorded in the  $(38,0)$  vibrational band of the  ${}^11_u(5^1P_1) \leftarrow X^10_g$  transition. (a) Experimental trace; (b) computer simulated profile [7] obtained as a result of convolution of every rotational transition with a Voigt function (assuming  $\Delta\lambda_{\text{las}} \approx 0.08 \text{ cm}^{-1}$ ,  $\Delta\lambda_{\text{Dopp}} \approx 0.12 \text{ cm}^{-1}$  and  $T_{\text{rot}} \approx 8 \text{ K}$ ); (c) P-, Q- and R-branches shown for the ( ${}^{114}\text{Cd}$ )<sub>2</sub> isotopomer with corresponding vertical bars. The  ${}^{112}\text{Cd}{}^{114}\text{Cd}$  isotopomer is not shown, however, it was taken into consideration during the simulation.

TABLE 1.

Rotational constants obtained for the  $X^10_g$  ground, and  ${}^10_u(5^1P_1)$  and  ${}^11_u(5^1P_1)$  excited states.

state	$v'$	$B_{v',v''}(\text{cm}^{-1})$	$B_e(\text{cm}^{-1})^a$	$R_e(\text{Å})$
${}^10_u^+$	48	$0.0271 \pm 0.0005$		$2.93 \pm 0.01^a$
	46	$0.0274 \pm 0.0005$		$2.94 \pm 0.03^b$
	45	$0.0277 \pm 0.0005$	$0.0343 \pm 0.0007$	$3.03 \pm 0.01^c$
	27	$0.0308 \pm 0.0005$		$2.86^d$
	26	$0.0309 \pm 0.0005$		$3.24^e$
${}^11_u$	38	$0.0317 \pm 0.0002$	$0.0415 \pm 0.0003$	$2.67 \pm 0.05^a$
				$2.69^f$
$X^10_g^+$				$3.77 \pm 0.04^{a,b}$
				$3.98^d$
				$3.915^g$
				$4.05^h$
				$4.07^i$

<sup>a</sup> this work (expt), for ( ${}^{114}\text{Cd}$ )<sub>2</sub>  
<sup>b</sup> Ref. [6] (expt), for ( ${}^{114}\text{Cd}$ )<sub>2</sub> (preliminary determination for  $v'=45$ )  
<sup>c</sup> Ref. [2] (expt), for ( ${}^{114}\text{Cd}$ )<sub>2</sub>; <sup>d</sup> Ref. [2] (ab initio);  
<sup>e</sup> Ref. [9] (ab initio); <sup>f</sup> Ref. [5] (ab initio); <sup>g</sup> Ref. [10] (ab initio); <sup>h</sup> Ref. [11] (ab initio); <sup>i</sup> Ref. [12]

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