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Is Cd_2 truly a van der Waals molecule? Analysis of rotational profiles recorded at the $A0_u^+$, $B1_u \leftarrow X0_g^+$ transitions

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Abstract

Rotational profiles of the $^{228}Cd_2$ isotopomer recorded in the $(\upsilon', \upsilon'') = (26,0), (27,0), (42,0), (45,0), (46,0), (48,0)$ vibrational bands of the $A0_u^+ \leftarrow X0_g^+$ transition were analysed. As a result, the $B'_{\upsilon=26} = 0.0311(5)\ \mathrm{cm}^{-1}$, $B'_{\upsilon=27} = 0.0309(5)\ \mathrm{cm}^{-1}$, $B'_{\upsilon=42} = 0.0279(5)\ \mathrm{cm}^{-1}$, $B'_{\upsilon=45} = 0.0278(5)\ \mathrm{cm}^{-1}$, $B'_{\upsilon=46} = 0.0275(5)\ \mathrm{cm}^{-1}$ and $B'_{\upsilon=48} = 0.0272(5)\ \mathrm{cm}^{-1}$ excited- as well as the $B''_{\upsilon=0} = 0.0207(5)\ \mathrm{cm}^{-1}$ ground-state rotational constants of the $(^{114}Cd)_2$ were determined. The analysis allowed determining the absolute values for the $R'_e(A0_u^+) = 2.71(7)$ Å and $R''_e = 3.76(4)$ Å 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. Analysis of the partially-resolved rotational profile recorded in the $(\upsilon', \upsilon'') = (38,0)$ band of the same isotopomer recorded at the $B1_u \leftarrow X^1 0_g^+$ transition allowed estimating the $B'_{\upsilon=38} = 0.0317(2)\ \mathrm{cm}^{-1}$ rotational constant in the $B1_u$ state.

Keywords: Cadmium dimer; Bond lengths; Rotational constants; van der Waals molecules; Covalent admixture; Interatomic potentials; Supersonic free-jet beam

1. Introduction

Laser spectroscopy of van der Waals (vdW) molecules produced and ro-vibrationally cooled in supersonic free-jet expansion is one of methods for investigation of molecular energy structure and geometry [1]. It was applied in low-resolution experimental studies of the $a1_u\ ^3\Sigma_u^+(5^3P_1)$ [2], $b0_u^+\ ^3\Pi_u(5^3P_1)$ [3–5], $c1_u\ ^3\Pi_u(5^3P_2)$ [6], $A0_u^+\ ^1\Sigma_u^+(5^1P_1)$ [7] and $B1_u\ ^1\Pi_u(5^1P_1)$ [8] excited as well as the $X0_g^+\ ^1\Sigma_g^+(5^1S_0)$ ground [7,8] Cd_2 electronic-energy states (see Fig. 1). In the investigation of the singlet states [7,8], the $A0_u^+$ state was characterized using a Morse–vdW function, whereas sets of turning points resulted from an inverse perturbation approach (IPA) procedure was applied in characterization of both $A0_u^+$ and $B1_u$ states. One of the straightforward conclusions was that the R''_e ground-state bond length is larger than those of the $R'_e(A0_u^+)$ and $R'_e(B1_u)$ excited-state bond lengths. In addition, presence of a potential barrier in the $B1_u$ state was determined in agreement with *ab initio* calculations [9]. Characterisation of the $X0_g^+$ state was reported by Czajkowski and Koperski [10]. The study was based on a detection of so-called "hot" bands recorded at the $b0_u^+ \leftarrow X0_g^+$ transition. Studies of Łukomski et al. [7] concluded with Morse–vdW and Born–Mayer representations of the $X0_g^+$-state bound well and repulsive wall, respectively. Among other results of characterization of the $A0_u^+$, $B1_u$ and $X0_g^+$ singlet states performed using different methods are those of Eden and co-workers [11,12], Bousquet [13] and Grycuk et al. [14]. However, none of them presented a high-resolution (e.g., rotational) spectroscopy of Cd_2. It should be mentioned, though, that Tran and Eden [12] claimed a partial resolution of a rotational structure while investigating the

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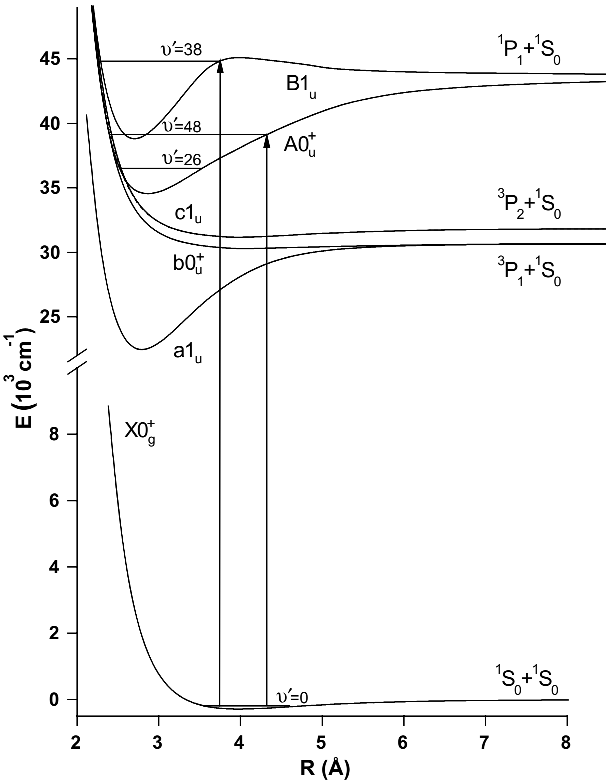

Fig. 1. Interatomic potentials of Cd$_2$ shown for the $X0_g^+$ $^1\Sigma_g^+$ ground and $a1_u$ $^3\Sigma_u^+$, $b0_u^+$ $^3\Pi_u$, $c1_u{}^3\Pi_u$, $A0_u^+$ $^1\Sigma_u^+$ and $B1_u{}^1\Pi_u$ excited states directly accessible in the excitation from the ground state [2–8]. Potentials are drawn according to results of *ab initio* calculations of Czuchaj [9]. Vibrational levels $\upsilon' = 26, 48$, $\upsilon' = 38$ and $\upsilon'' = 0$ in the $A0_u^+$, $B1_u$ and $X0_g^+$ electronic energy states, respectively, investigated in this article are depicted with horizontal solid lines. Levels $\upsilon' = 27, 42, 45, 46$ in the $A0_u^+$ state were also investigated but they are not shown.

$^1\Sigma_u^+ \leftarrow \tilde{a}^3\Pi_g(5^3P_1)$ transition in the $(^{114}\mathrm{Cd})_2$ isotopomer. However, no analysis and/or values for rotational constants were reported.

First-time performed rotational spectroscopy of Cd$_2$ was reported from our laboratory by Łukomski et al. [15]. We studied one of the rotational profiles in a single $(\upsilon', \upsilon'') = (45, 0)$ vibrational band of the $A0_u^+ \leftarrow X0_g^+$ transition in the ^{228}Cd$_2$ isotopomer. From the analysis of the *R*-branch, the $B''_{\upsilon=0}$ and $B'_{\upsilon=45}(A0_u^+)$ rotational constants of the $(^{114}\mathrm{Cd})_2$ were determined. This allowed estimating the R''_e and $R'_e(A0_u^+)$ ground- and excited-state bond lengths. In this article, we present a complex multi-vibrational-band (i.e., for the $(\upsilon', \upsilon'') = (26, 0), (27, 0), (42, 0), (45, 0), (46, 0), (48, 0)$) and multi-rotational-branch (i.e., for the *P*- and *R*-branches) rotational analysis of the $A0_u^+ \leftarrow X0_g^+$ transition in ^{228}Cd$_2$ isotopomer. This way, the accuracy of determination of the rotational constants as well as the bond lengths increased, and the obtained results supersede those of Łukomski et al. [15]. Moreover, a rotational profile recorded in the (38,0) band of the $B1_u \leftarrow X0_g^+$ transition in the same isotopomer enabled estimating the $B'_{\upsilon=38}(B1_u)$ and $R'_e(B1_u)$. The rotational analysis and new value for the R''_e permitted an experimental corroboration of a theoretical hypothesis of a covalent admixture to the dominating ground-state vdW bonding in Cd$_2$. Such a corroboration was recently reported in low- [16] and high- [17] resolution investigation of Hg$_2$ and – preliminarily – in low-resolution study of Zn$_2$ [18]. With further rotational spectroscopy of Zn$_2$ it may complete the ongoing discussion on a bond characterization in the group-12 M$_2$ homoatomic molecules (M = Zn, Cd, Hg).

Results of *ab initio* calculations related to the Cd$_2$ interatomic potentials are those of Bender et al. [19], Czuchaj et al. [9,20], Schautz et al. [21], Yu and Dolg [22] and Łukomski et al. [7]. In a very weakly bound ground state of the group-12 molecules, the long-range interaction is dominated by pure dispersion forces as expected from a simple consideration of the closed-shell atomic configurations [1]. *Ab initio* calculations of the interaction-energy components in the ground state of Hg$_2$ [23] showed that short-range induction effects play a significant role in the stabilization of Hg$_2$. Therefore, the Hg$_2$ may be regarded as an intermediate case between a weakly bound vdW molecule and a chemically bound species. The same behavior has been inferred from *ab initio* calculations of Zn$_2$ and Cd$_2$ [22,24]. Studies of Dolg and coworkers [21,22,24,25] resulted in a clear conclusion that the group-12 homoatomic molecules, besides a vdW-type interaction, exhibit the presence of significant covalent contributions to the bonding.

2. Theoretical analysis

For the experimental study, in both of the $A0_u^+ \leftarrow X0_g^+$ and the $B1_u \leftarrow X0_g^+$ singlet–singlet transitions the ^{228}Cd$_2$ isotopomer was selected [15], mainly because of its relatively high abundance (11.85%) and its dominating homonuclear ^{114}Cd^{114}Cd (8.25%) over heteronuclear ^{112}Cd^{116}Cd (3.6%) composition.

In case of both $A0_u^+ \leftarrow X0_g^+$ and $B1_u \leftarrow X^10_g^+$ transitions, the vibrational progressions extend for considerably high υ' (i.e., from $\upsilon' = 19$ to 53 and $\upsilon' = 34$ to 40 [26] for the former and latter, respectively). This assures a large isotope shift, very advantageous in the present study (see Eq. (1) below and Fig. 2). The vibrational and isotopic structure of the first transition considered here ($A0_u^+ \leftarrow X0_g^+$) was thoroughly characterized in low-resolution study of Łukomski et al. [7]. Thus, the higher-resolution spectroscopy and complex analysis of rotational profiles would complete investigation of [7]. An introductory study of one of the rotational profiles in the (45,0) vibrational band in the ^{228}Cd$_2$ was recently published [15].

As the $A0_u^+ \leftarrow X0_g^+$ transition takes place between two Hund's-cases-(c) singlet states, both with $\Omega = 0$, there are only *P*- and *R*-branches present (*Q*-branch is not). This offers a simplification of the recorded rotational profiles and their improved analysis. As for the second $B1_u \leftarrow X0_g^+$ transition considered in this study, it was previously characterized by Koperski et al. [8] and Ruszczak et al. [26] in a low-resolution study. In that case (i.e.,