# Excited $1_u(5^1P_1)$ state of Cd$_2$ and the dipole moment of the $1_u(5^1P_1)$–$X0_g^+$ electronic transition[†]

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The satellite band of the 228.8 nm Cd line associated with the $1_u(5^1P_1)$–$X0_g^+$ electronic transition in Cd$_2$ is measured in absorption and used for probing and correcting the excited state potential by means of quantum simulations of the spectrum. Best theoretical potential curves available are employed as the initial input data and the spectrum calculated for a single molecule is compared with the experimental spectrum of the absolute absorption coefficient per atom pair. The method yields considerable correction of the upper state potential which, finally, reproduces the experimental spectrum quite well. The dipole transition moment function is roughly determined.

Keywords: Cd$_2$, interatomic potentials, dipole transition moment, absorption spectrum, quantum simulations.

## 1. Introduction

An interaction between the excited state $5^1P_1$, and the ground state $5^1S_0$, cadmium atoms, dominated at long internuclear distances $R$ by resonance forces, leads to the formation of two ungerade molecular states: the $1_u$ and $0_u^+$ ones. The latter, of a regular potential well shape, is relatively strongly bound, whereas the former, being repulsive at large $R$, is characterized by a distinct barrier at intermediate separations [1, 2]. The potential well of this state is considerably shifted towards short distances from the region of the ground state $(X0_g^+)$ potential well, hence the bound–bound (b–b) $1_u$–$X0_g^+$ electronic transitions are ineffective. For such transitions originating from the lowest vibrational levels of the ground state the situation is particularly unfavorable. Therefore, although nowadays a supersonic beam technique allows production and spectroscopy of van der Waals molecules such as Cd$_2$ [3], the above-mentioned excited state $1_u$ is inaccessible via b–b transitions involving the ground state.

However, it is well known [4] that the intensive spectrum observed on the blue wing of the Cd 228.8 nm resonance line, including pronounced diffuse band at about

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[†]In commemoration of the deceased Professor Eugeniusz Czuchaj

221 nm, originates from free–free $1_u$–$X0_g^+$ transitions in Cd diatomics occurring at long and intermediate separations. It is also well known (see [5] and reference therein) that such a spectrum is well described by the quasi-molecular theory of line shape broadened by interatomic interactions. Moreover, based on this theory it is possible to deduce reliable interaction data from the observed intensity distribution, in particular from the profile and spectral position of the satellite band associated here with the existence of a barrier in the potential energy curve of the upper state [4, 6, 7].

In our previous paper [6], and particularly in [7], the absolute absorption coefficient spectrum in the blue wing of the 228.8 nm Cd line has been determined experimentally for several vapour densities. On the other hand, quantum simulations of this spectrum have been performed using recently available theoretical potential energy curves for the upper state derived by CZUCHAJ [1] and later improved [2], and the most accurate experimental and theoretical data for the ground state from comprehensive studies reported in [8]. In those calculations the transition moment function was tentatively assumed to be constant. A comparison of the theoretical predictions with the experimental ones showed, unfortunately, considerable disagreement concerning both the spectral position of the satellite band and the intensity of the total blue wing spectrum. This disagreement was found for all combinations of the potentials available for ground and excited states [7].

The present work extends an experimental study of the spectrum considered by including its temperature dependence. Assuming that the ground state potential is known, the temperature effects enabled us to deduce some information on the excited state potential and the oscillator strength function over the spectral range explored experimentally. These results are taken into consideration in progressive modification of the initial input data used for quantum simulation of the spectrum. The work is mainly aimed at correcting the excited $1_u$ state potential curve.

## 2. Experimental study

The absorption spectrum of the Cd vapour of a constant density $N = 1.93 \times 10^{18}$ cm$^{-3}$, contained in a sealed quartz (spectrosil) cell of 5 cm in length, was measured with a 6-m Rowland spectrometer at several temperatures between 670°C and 990°C. The experimental set-up and procedure were essentially the same as in our recent work [9].

The measured quantity was, finally, the absorption coefficient of the vapour reduced to one atom pair, $k_r(\Delta v) = k(\Delta v)/N^2$, as a function of the difference frequency $\Delta v = v - v_0$ with $v_0 = 43692.47$ cm$^{-1}$ being the frequency of the line center. Under the experimental conditions $\Delta v$ was limited to the range of 800–1300 cm$^{-1}$ and up to about 1100 cm$^{-1}$ the quasi-static inversion method seemed to be applicable to this spectrum. Similarly, as has been done and described in detail in [9], it was assumed that the ground state potential is known. For this reason we accepted the theoretical

potential derived from *ab initio* calculations in [8], characterized by the following main parameters: well depth $D''_e = 287.3$ cm$^{-1}$ and equilibrium distance $R''_e = 3.98$ Å. Using this potential the quasi -static inversion approach yielded the following information:

i) The maximum of the potential energy barrier in the $1_u$ state is expected to be slightly shifted towards short distances relative to the equilibrium distance $R''_e$;

ii) The oscillator strength $f$ for the transition $1_u$–$X$ decreases considerably for $\Delta v$ greater than 800 cm$^{-1}$, *i.e.*, for distances R < 4.7 Å. In particular, it was found that $f(R = 4)/f(R = 4.7) = 0.6 \pm 0.05$.

In addition, the spectral position of the satellite band with its maximum at about 1470 cm$^{-1}$ indicated that the barrier of the excited $1_u$ potential determined in [1] as well as in [2] is too high.

## 3. Quantum simulations of the absorption profile of the 221 nm $Cd_2$ band

Taking into account the above-mentioned remarks and assuming that the ground state potential curve determined in [8] is more accurate than that for the excited state $1_u$ even that from [2], we made an attempt at correction of the latter in order to improve the consistency between theoretical and experimental spectra.

The absorption coefficient for a single $Cd_2$ collision molecule was calculated accounting for free–free (f–f) and bound–free (b–f) transitions and assuming that population of the free states as well as the bound rovibrational states is thermalized. Calculations employ the theoretical formulation presented in our earlier paper [10], where the details concerning all the numerical problems were also described.

In the first step, the dipole transition moment $D$ was assumed to be independent of $R$ and a barrier in the excited state potential was modified until the position and width of the band predicted agreed reasonably with the experiment. In the next step, the intensity of band calculated was slightly corrected by taking into account a variable $D(R)$ deduced partly from $f(R)$ behaviour mentioned in ii) of the previous section and partly from the only known theoretical data derived earlier by CZUCHAJ *et al.* [11] together with potential energy curves for several electronic states of $Cd_2$. However, the theoretical approach used in [11] was much less accurate than the one employed later by CZUCHAJ in [2] and spin-orbit coupling was neglected altogether, therefore the function $D(R)$ deduced can only be considered as a first approximation.

## 4. Results and discussion

Figure 1 shows the interaction data used for simulation of spectra and includes the ground state potential $X$ from [8] and the initial excited state potential $E$ after [2] as well as the corrected one $E_{corr}$. It is surprising that the corrected curve proved to
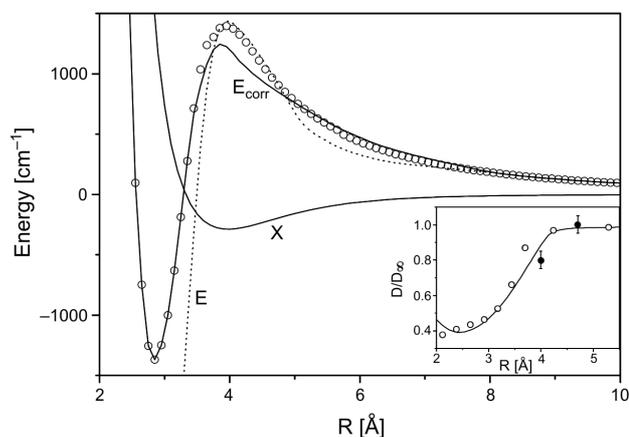
Fig. 1. The potential energy curves $X$ [8], $E$ [2], and $E_{corr}$ (this work), used for simulations. The bottom of the well in $E$ reaches about –4900 cm$^{-1}$. The markers ○ represent theoretical data from [1]. Inset: the transition moment function $D(R)/D_\infty$ (line); our experimental (●) and theoretical data (○) from [11].

be closer to the one derived earlier by CZUCHAJ [1], which is also presented in Fig. 1. The dipole transition moment function deduced in the above-mentioned way is shown in the inset of Fig. 1. The numerical data for $E_{corr}(R)$ and $D(R)$ are available upon request from the authors.

The experimental profile of the Cd$_2$ $(1_u(5^1P_1)–X0_g^+)$ band at a temperature $T = 846$ K (vapour density [Cd] = $6.174 \times 10^{17}$ cm$^{-3}$) is compared with the simulated spectrum in Fig. 2. Both experimental and theoretical spectra are expressed in absolute units without any fitting parameters. In Fig. 2**a** the calculated spectrum was obtained for the best theoretical potential $E$ from [2] and for $D(R)$ = const = 3.2667 au deduced from $f = 1.416$ accepted after [12]. For comparison with Fig. 2**a**, Fig. 2**b** presents the calculated spectrum obtained using the presently corrected excited state potential $E_{corr}$ for the same constant value of $D$ and for $D(R)$ function presented in Fig. 1. It is clearly seen that the hereby suggested modification of the excited $1_u(5^1P_1)$ state leads to the correct position of the band while $D(R)$ function influences only its intensity.

It is worth noting that in the spectral range 800–1300 cm$^{-1}$ of the experimental spectrum characteristic undulations appear which are also reproduced in the calculated spectrum (see inset of Fig. 2**b**). These spectral features, associated with purely f–f transitions, are due to interference between contributions to the spectrum at the same frequency from different Condon points [5]. The undulation structure is very sensitive to the width of the barrier in the difference potential between the upper and lower states of the transition which in our case is determined by the width of the barrier in the excited state.

Summarizing, the consistency between the experimental and theoretical spectra observed also for the undulation structure indicates that both the height and the width
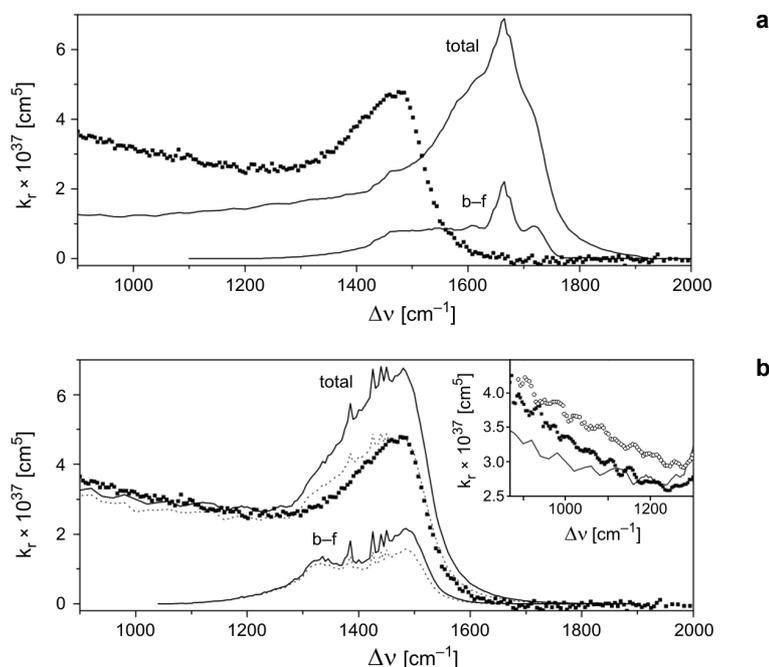
Fig. 2. The experimental profile of the Cd$_2$ band associated with the $1_u(5^1P_1)$–$X0_g^+$ transition at $T = 846$ K and [Cd] $= 6.174 \times 10^{17}$ (●) versus the simulated total spectrum and its b–f component (lines). The simulation employs the $X$ and $E$ potential curves – **a**. The simulation employs $X$ and $E_{corr}$ potential curves and is performed for $D = $ const (solid line) and for $D(R)$ function deduced in this work (dotted line) – **b**. Inset: undulations in the experimental spectrum derived for [Cd] $= 1.93 \times 10^{18}$ at two different temperatures: 940 K (○) and 1260 K (●) and the f–f component of the spectrum simulated at $T = 1260$ K (line).

of the barrier in the excited $1_u(5^1P_1)$ state of Cd$_2$ established in this work are close to the real value. Contrary to this, the dipole transition moment data presented in the inset of Fig. 1 are less accurate and the problem needs further study.

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