Interatomic Potentials and the Dipole Moment of the Cadmium Forbidden ($5^3P_2 \rightarrow 5^1S_0$) Transition for the Cd_2 System

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The molecular band appearing at $\Delta V = 770$ cm^{-1} on the blue wing of the intercombination Cd (326.1 nm) line broadened by Cd pressure has been investigated. This band was interpreted as a rainbow satellite accompanying the dipole-forbidden Cd (314.1 nm) line associated with the $5^3P_2 \rightarrow 5^1S_0$ transition. The profile of this band has been calculated using the semiclassical model developed by Szudy and Baylis. To obtain this profile the interatomic potential of the molecular state 1_u and the dipole moment associated with this band have been modified to give the best fit profile with the experimental one.

Key words: Interatomic potentials, Dipole moment, Cadmium.

Introduction

The Cd_2 molecule is representative of a class of excimer molecules. For the Cd dimer, quantitative experimental information on interatomic potentials available only for the lowest excited states (Kowalski *et al* 1985; Helmi *et al* 1996; Czajkowski *et al* 1989 and Bousquet 1986). Moreover, the existing theoretical potentials (Bender *et al* 1979 and Stevens 1979) for Cd_2 may be taken only as a rough guide to the spectroscopy of this system. In a previous paper (Helmi *et al* 1996), we noticed that there are three bands (A, B and C) at about 770, 830 and 1800 cm^{-1} respectively have been observed experimentally on the blue wing of the Cd (326.1 nm) line. The interpretation of these bands have explained in (Grycuk *et al* 1992). The band A was interpreted as a rainbow satellite accompanying the dipole - forbidden Cd line 314.1 nm associated with the $5^3P_2 \rightarrow 5^1S_0$ transition where the potential difference between the upper and lower states has an extremum. As this band has been observed at 770 cm^{-1} on the blue wing of the Cd line 326.1 nm, this means that it's lying at 397 cm^{-1} on the red wing of the forbidden Cd line 314.1 nm.

The aim of this work, is to find the interatomic potential of the state $^3 1_u$ and also the dipole moment variation D(R) that are responsible for the formation of the band A. To do this, the interatomic potential of the excited ($^3 1_u$) state associating with ($5^3P_2 - 5^1S_0$) of Cd transition and its dipole moment D(R) are modified to get the best fit profile of band A with the experimental one measured by (Helmi *et al* 1996).

Materials and Methods

UFC Profile. The unified Frank Condon (UFC) model developed by Szudy and Baylis (Szudy and Baylis 1975) is a quasimolecular treatment of spectral line profiles of collision molecules (Szudy and Baylis 1975, Sando and Wormhoudt 1973. For the case of not two strongly varying dipole transition moments, the reduced molecular absorption coefficient k(v, T) in the line wing region of the atomic line $V_{ij} = E_j - E_i /h$ can be expressed due to UFC theory in the form:

$$K(\nu,T) = \frac{32\pi^{7/2} \nu}{c\, g_o} \sum_i \frac{R_i^2 D^2(R_i)}{|\Delta V(R_i)|} \exp\left[\frac{-Vg(R_i)}{kT}\right] [Z_i]^{1/2} L(Z_i) \quad (1)$$

where g_o is the molecular statistical weight of the initial ground state ($X^1 0_g$) and D(R_i) is the molecular transition moment. The summation extends over all degenerate substates of the initial $X^1 0_g$ and final state $^3 1_u$. R_i denote Condon points, that are complex solutions of:

$$h\nu = \Delta V(R_i) = V_i(R_i) - Vg(R_i) \quad (2)$$

The real R_i represent the transition points, that obey the Frank-Condon principle. Z_i is the reduced frequency given by:

$$Z_i = 0.5\left(\frac{\mu}{kT}\right) \left[\frac{\Delta V'(R)}{h}\right]^{-2} \left|\frac{\Delta V''(R)}{h}\right|^{-4/3} \quad (3)$$

$L(Z_i)$ is the universal line shape function defined and tabulated in (Szudy and Baylis 1975), μ is the reduced mass of the collision molecule and T is the temperature. $\Delta V'$ and $\Delta V''$ are the first and second derivatives of the difference potential $\Delta V(R)$ respectively.

Procedure of calculation. It is seen from Eq.(1) that to calculate the molecular band A profile, we need to know the
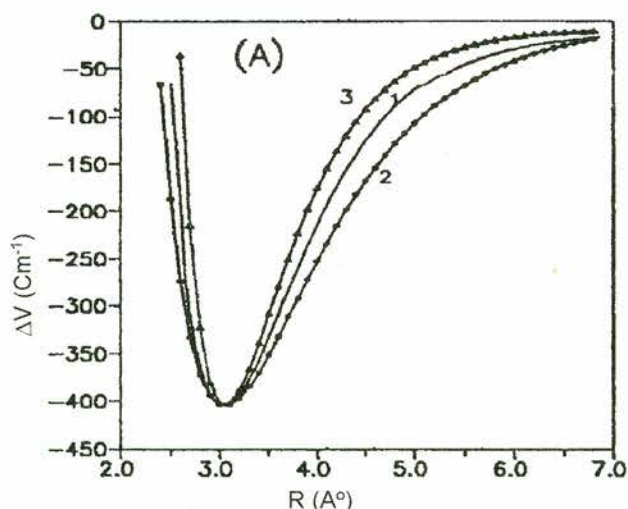
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ground state potential $V_g(R)$ for Cd_2 system, the difference potential $\Delta V(R)$ between the initial and final states and the dipole moment $D(R)$. We have chosen for the ground state potential $V_g(R)$ of the quasimolecule Cd_2, the potential determined experimentally by (Helmi *et al* 1996). This potential is then fitted to the Morse potential by appropriate parameters. The function $\Delta V(R)$ corresponding to the potential difference between [V_g and $^3 1_u$] states leading to the red wing of the Cd line 314.1 nm profile and also the dipole moment $D(R)$ are chosen that give the best fit between the calculated and the experimental profiles measured by (Helmi *et al* 1996 and Grycuk *et al* 1992). As $\Delta V(R)$ and V_g are known, it is easy to obtain the excited state (V_1) potential. This potential is also fitted to the Morse potential by appropriate parameters.

Results and Discussion

The experimental line profiles of the bands A, B and C obtained by (Helmi *et al* 1996 and Grycuk *et al* 1992) for Cd_2 interaction at about 770, 830 and 1800 cm^{-1} on the blue wing from the centre the Cd (326.1 nm) line are presented in Fig 1.

The analytical form of the function $\Delta V(R)$ has been chosen so that its extremity ($\Delta V_m = h\Delta v_m$), where $\Delta v_m = 397$ cm^{-1} is the spectral position of the band A on the red wing of the forbidden Cd (314.1 nm) line. Figure 2 shows the effect of curvature of the function $\Delta V(R)$ near the vicinity of its extrumum (A) on the profile of the band A (B). The sensitivity of the profile to the curvature of $\Delta V(R)$ implies that the shape of the $\Delta V(R)$ is accurately determined, which is not the case for the effect of $D(R)$ as shown in Fig 3 A & B. This is in agreement with the same effects applied on the Cs satellite published in (Visticot *et al* 1981). Figures 4,5 give respec-

tively the functions $D(R)$ and $\Delta V(R)$ that give the best fit calculated profile for band A with the observed one. This is illustrated in Fig 6. The ground state potential $V_g(R)$ for Cd_2 interaction has been taken from the author's papers (Helmi *et al* 1996 ; Roston and Helmi 1998). The fitting parameter β

Table 1

Comparison of our data for the well depth $\varepsilon(cm^{-1})$ and its position R_m (A) of the state $^3 1_u$ with other data

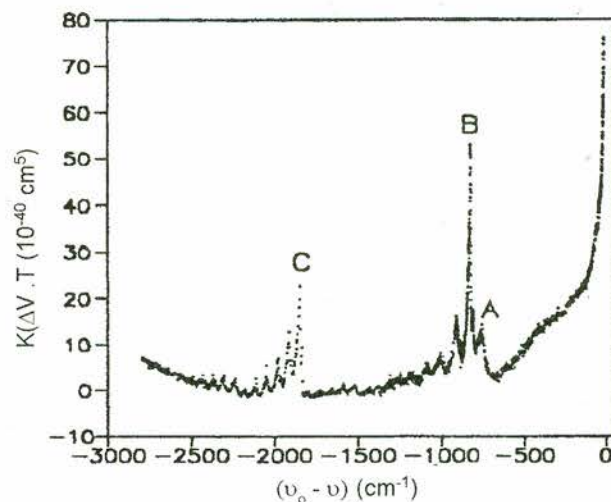| State $^3 1_u$		Reference
$R_m(A)$	$\varepsilon(cm^{-1})$	
3.3	844.5	Grycuk *et al* 1992
3.2	799.5	

Fig 1. Exeprimental blue wing profile of Cd line 326.1 nm (Helmi et al 1996 and Grycuk et al 1992).
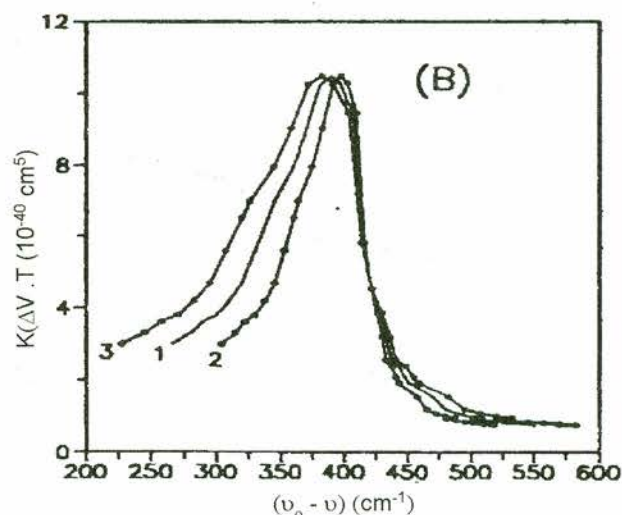

Fig 2. The calculated profile of the band A(B) corresponding to the curvature variation function of $\Delta V(R)$ (A), at the same extremum of $\Delta V(R)$ and the dipole moment.
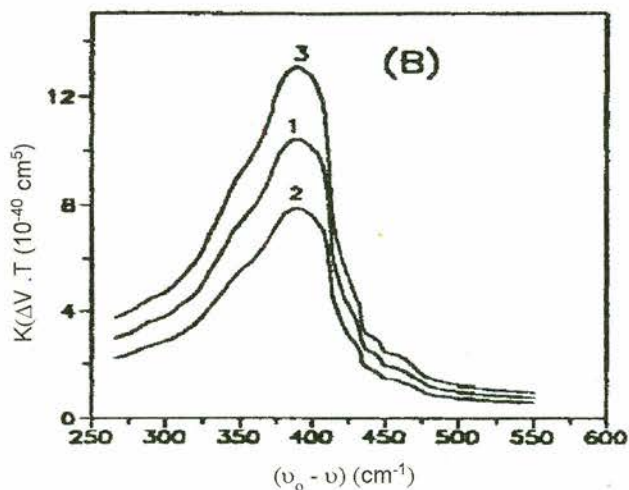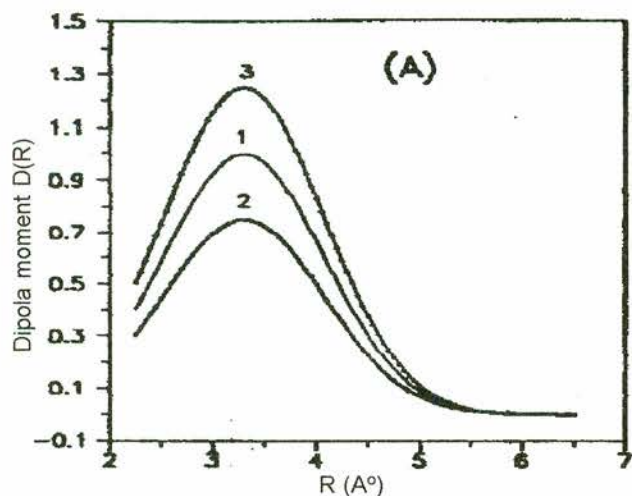
Fig 3. The calculated band profile (B) corresponding to the variation of the dipole moment D(R) (A), at the same curvature and extremum of V(R).
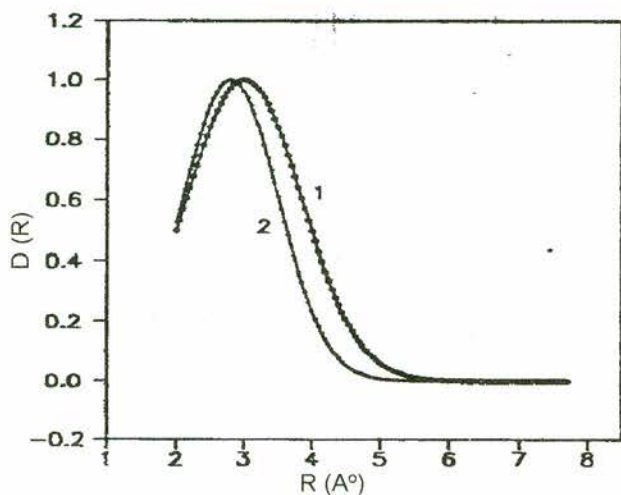
Fig 4. The obtained induced dipole moments (1) this work, (2) by quantum calculations.
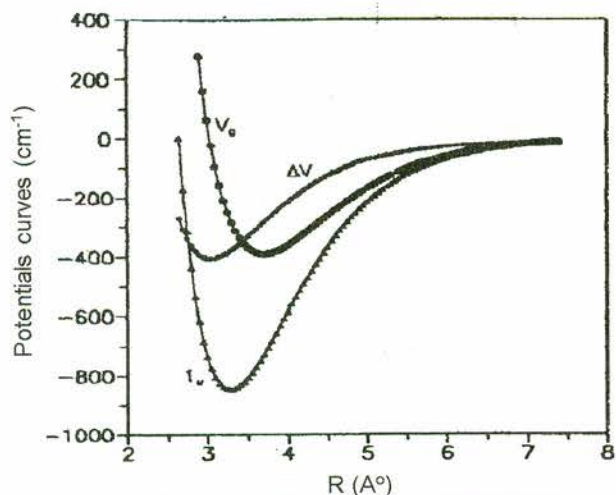
Fig 5. The difference $\Delta V(R)$ with the excited potentials obtained in this work and the ground (V_g) state potential taken from (Helmi et al 1996, Roston and Helmi 1998).
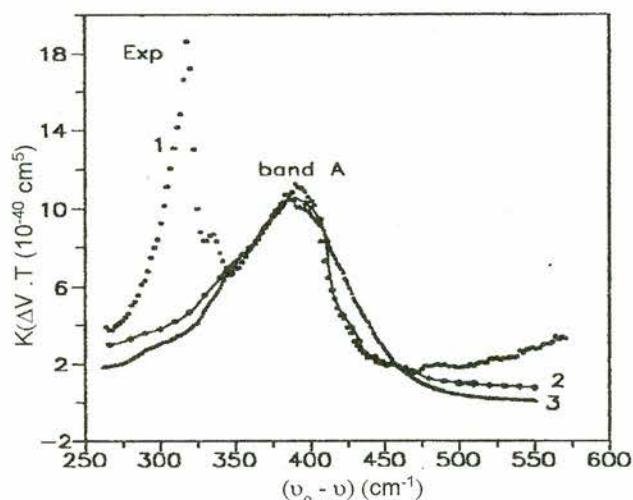
Fig 6. (1) The experimental band A profile obtained by (Helmi et al 1996 and Grycuk et al 1992) and (2,3) are respectively the calculated profiles by the authors and that obtained by (Grycuk et al 1992 using quantum calculation.

of this potential to the Morse potential with its depth $\varepsilon_g = 386$ cm^{-1} (Helmi *et al* 1996) and depth position $R_g = 3.7$ A [12] is obtained as $\beta = 1.1$.

As the ground state potential $V_g(R)$ and $\Delta V(R)$ are known, then the excited state potential V_1 for the molecular state ^31_u of the ($5^3P_2 \rightarrow 5^1S_o$) transition for Cd$_2$ system can be obtained using the relation:

$$V_1(R) = V_g(R) + \Delta V(R)$$

The Morse potential parameters of the obtained excited state potential $V_1(R)$ are found to be equal to $\varepsilon_1 = 844.5$ cm^{-1}, $R_1 = 3.3$ A and $\beta=1.3$. The ground $V_g(R)$ and the excited $V_1(R)$ state potentials with the difference potential $\Delta V(R)$ are presented in Fig 5. Figure 4 shows the induced dipole

moment D(R) for the molecular transition $(X^1 0_g \rightarrow {}^3 1_u)$ obtained by the authors that gives the best fit for the calculated and experimental profiles of the band A and dipole moment for that transition obtained by (Grycuk *et al* 1992). The obtained D(R) has an exponential form given by:

$$d(r) = A \exp^{\left(\frac{R-R_o}{b}\right)^2}$$

where A, b and R_o are respectively equal to 1, 0.8, 3.

Conclusion

The band A appearing at $\Delta v = 770$ cm^{-1} on the blue wing of the Cd (326.1 nm) line broadened by cadmium pressure has been analysed using (UFC) model of Szudy and Baylis (1975). This analysis has led to the following conclusions.

i)The shape of the band A is strongly affected by the curvature of the difference potential $\Delta V(R)$ in the vicinity of its extrumum, while it is little affected by the dipole moment variation D(R).

ii) The dipole moment variation D(R)obtained by the authors is in close agreement with D(R) obtained before by (Grycuk *et al* 1992) using quantum calculations.

iii) The obtained interatomic potential of the excited state $({}^3 1_u)$ resulting from $({}^3 P_2 - {}^1 S_0)$ for Cd$_2$ interaction using this analysis is in close agreement with the potential of that state obtained by (Grycuk et al 1992) using quantum calculations. This is shown in the Table 1.

iv) From the foregoing discussion it is seen that the analysis of the molecular spectrum using (UFC) model gives reasonable results for the interatomic potential of the molecular excited state $({}^3 1_u)$ comparing with other procedures for obtaining such potential.

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