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Interatomic potentials for the ground state X $^1 0^+$ and the two excited states $^3 1$, $^3 0^+$ of the intercombination cadmium line 326.1 nm broadened by Kr pressure

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Abstract

The temperature dependence of the Cd line absorption profile at 326.1 nm perturbed by Kr has been carefully studied over a spectral range extending from 800 cm^{-1} in the blue wing to 1200 cm^{-1} in the red wing using a high-resolution double-beam spectrometer. The atomic densities of krypton (N_{Kr}) and cadmium (N_{Cd}) were $(2.015 \pm 0.07) \times 10^{19}$ and $(3.62 \pm 0.05) \times 10^{18}$ cm^{-3}, respectively. The temperature dependence of the studied line profile was analyzed in the framework of the quasi-static theory. The van der Waals coefficient differences between the ground $^1 0^+$ state and the two excited states $^3 0^+$ and $^3 1$ (ΔC_6^0 and ΔC_6^1) were obtained from the near red wing profile using Kuhn's law. The values of ΔC_6^0 and ΔC_6^1 are found to be equal to 37.8 ± 2 and 58.5 ± 3 eV Å^6, respectively. The ground (X $^1 0^+$), and the excited ($^3 1$, $^3 0^+$) state potentials at the internuclear separations from 3.2 to 6.3 Å were determined. The well depths with their positions for these states are respectively equal to 134 ± 7 cm^{-1}, 3.95 ± 0.2 Å; 72.3 ± 4 cm^{-1}, 4.95 ± 0.3 Å; and 471 ± 12 cm^{-1}, 3.6 Å. The obtained well depths with their allowable errors are in good agreement with the values obtained before for the Cd–Kr system from some theoretical results and molecular beams experiments.

Keywords: Waals potential coefficients; Pressure broadening; Spectral line profile; Potential curves; Spectral line shapes; Interatomic potentials; Cd intercombination line profile

1. Introduction

The Cd-rare gas molecule is representative of a class of excimer molecules. This class is a typical van der Waals diatomic in the ground state and is much more strongly bound in several of the excited states. Such molecules have attracted considerable attention in recent years. In particular, numerous spectroscopic studies of dimers of Group IIb metals have been undertaken, especially regarding the determination of interatomic potentials for the ground and excited states of these systems, experimentally using the temperature dependence of the far wing profile [1–9], the molecular beam [10–14] and theoretically [15–17].

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The temperature dependence of the far wing profile was studied and interpreted in the framework of the unified Frank–Condon (UFC) treatment of pressure broadening of spectral lines developed by Szudy and Baylis [18]. This allows interaction energies to be determined. This work is aimed to obtain the van der Waals coefficient differences ΔC_6^0 and ΔC_6^1, the interatomic potentials for the ground X $^1 0^+$ and the two excited states ($^3 0^+$ and $^3 1$) of the Cd–Kr system. These potentials are derived from experimental studies of the far wing of the Cd 326.1 nm absorption line broadened by krypton pressure.

2. Theoretical

2.1. The quasi-static theory

The UFC treatment of pressure broadening of spectral lines developed by Szudy and Baylis [18] reduces in the appropriate limits to the quasi-static theory in the far wings of the line. Using this theory, the reduced absorption coefficient ($K_n^m(\Delta v,T)$ in cm^5) in the line wings as a consequence of two particle interactions when normalized to the perturbing (N_p) and the radiating (N_r) atom densities is given by

$$K_n^m(\Delta v, T) = \frac{k^m(\Delta v, T)(\mathrm{cm}^{-1})}{N_p N_r} = 4\pi C_m R^2 \left|\frac{dR}{d(\Delta V_m)}\right| \exp\frac{-v_g(R)}{KT} \tag{1}$$

where the symbol $m = 0$ and 1 is assigned to the $^3 0$ and $^3 1$ excited states respectively, R is the internuclear separation, $\Delta V_m(R)$ is the potential difference between the excited $V_m(R)$ and the ground $V_g(R)$ state potentials, given by ($\Delta V_m(R) = V_m(R) - V_g(R) = h\Delta v$), and $\Delta v = v_o - v$ is the frequency separation from the unperturbed line frequency v_o. C_m is the constant which relates the absorption coefficient to the normalized emission intensity. It can be given by

$$C_m = (\pi e^2/mc)(g_m/g_j) f_{eg}$$

where e and m are the electron charge and mass, c is the light velocity, g_j and g_m are the atomic and molecular statistical weights ($g_m = 1$ or 2 for $m = 0$ or 1) and f_{eg} is the oscillator strength for the atomic transition e→g.

2.2. Determination of the van der Waals coefficients

The part of the wings near the line center is arising as a result of electronic transition between the states that are only slightly perturbed by the long-range van der Waals interactions of the form $\Delta V(R) = \Delta C_6 R^{-6}$. In this case for $V_g(R) \ll kT$, Eq. (1) leads to Kuhn's law as

$$K_n^m(\Delta v) = \frac{2\pi C_m}{3} h^{-3/2} (\Delta C_6^m)^{1/2} \Delta v^{-3/2} = A_m (\Delta v)^{-3/2} \tag{2}$$

If $\log K_n^m(\Delta v)$ is plotted versus $\log(\Delta v)$, a straight line with a slope $(-3/2)$ is produced. The ΔC_6^m constant may then be obtained from a measurement of the A_m coefficient.

Generally for Cd-rare gases such a linear dependence on $\log K_n^m(\Delta v)$ is observed in two regions of the near red wing profile [2–6]:

1. The first is due to the transition $^3 0^+ \leftarrow$ X $^1 0^+$, so that

$$A_o = \frac{2\pi C_o}{3} h^{-3/2} (\Delta C_6^o)^{1/2} \tag{3}$$

2. The second is due to the transition from the ground X $^1 0^+$ state to both molecular excited ($^3 0^+$ and $^3 1$) states. In this region the absorption coefficient is given from Eq. (2) as

$$K_n^m(\Delta v) = \sum_{m=0,1} K_n^m(\Delta v) = \frac{2\pi C_o}{3} h^{-3/2} \left[\left|\Delta C_6^0\right|^{1/2} + 2\left|\Delta C_6^1\right|^{1/2} \right] (\Delta v)^{-3/2} = A_1 (\Delta v)^{-3/2} \tag{4}$$