

$O_u^+(^3\Pi_u) \leftarrow XO_g^+(\Sigma_g^+)$  transitions in  $Cd_2$  excited in crossed molecular and laser beams

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Excitation spectra of  $Cd_2$  van der Waals molecules produced in a molecular beam employing free-jet supersonic expansion, crossed with a pulsed dye-laser beam, were studied using He, Ne, and Ar as carrier gases. Well-resolved structures, arising from transitions between the vibrational levels of the  $XO_g^+(\Sigma_g^+)$  and  $O_u^+(^3\Pi_u)$  states, were recorded at various translational temperatures. An analysis of the spectra yielded the vibrational constants and bond strengths of the molecule in the two electronic states. The lifetimes of the  $Cd(5^3P_1)$  atoms and  $Cd_2(O_u^+)$  molecules in various vibrational states were also determined.

## I. INTRODUCTION

In recent years there has been a revival of interest in the spectroscopy of group-IIb metal excimers, such as  $Hg_2$ ,<sup>1</sup>  $HgZn$ ,<sup>2</sup>  $Zn_2$ ,<sup>3</sup> and  $Cd_2$ ,<sup>4</sup> perhaps brought about by the hope that these molecules might become vehicles for molecular-dissociation lasers with emission in the blue-green (and shorter) wavelength region of the spectrum. All these excimers have no bound ground states, except for very shallow van der Waals potential wells, and have numerous higher electronic bound states, though most recent calculations of potential-energy (PE) curves assume the ground states to be monotonically repulsive.<sup>5-7</sup> However, the use of experimental techniques involving laser excitation of jet-expanded molecular beams of the metals seeded in noble gases makes it possible to observe molecules of very low bond strengths and obtain details of the ground-state and excited-state PE curves.<sup>8-11</sup> Among the relatively few accounts dealing with the spectroscopy of these excimers, only one was devoted to the  $Cd_2$  molecules<sup>4</sup> and included estimates for the spectroscopic constants associated with the  $XO_g^+(\Sigma_g^+)$  and  $O_u^+(^3\Pi_u)$  states.

In this investigation we have observed an excitation spectrum of  $Cd_2$  molecules produced in a free-jet molecular beam crossed with a laser beam. The purpose of this study was to examine in detail the vibrational structure of the  $O_u^+(^3\Pi_u) \leftarrow XO_g^+(\Sigma_g^+)$  excitation spectrum at various pressures of Ar, Ne, and He as carrier gases and under various cooling conditions, and obtain a reliable estimate of the bond strengths. The lifetimes of the  $O_u^+(^3\Pi_u)$  molecules in several vibrational states, and of  $^3P_1$  Cd atoms, were also determined under conditions under which the collisional quenching of the excited states was suppressed.

## II. DESCRIPTION OF THE APPARATUS AND EXPERIMENTAL PROCEDURE

Figure 1 shows a schematic diagram of the apparatus which was similar to that described in Ref. 4. The expansion chamber was in the form of a cross with each arm

approximately 18 cm long and was connected to an Edwards EH800 Roots pump backed by an Edwards 2M80 rotary pump, which produced an ultimate vacuum of about 1 mtorr. The stainless-steel beam source was water cooled and heated by a differential heating system which maintained the temperature difference between the oven and the nozzle in the range 60–80 K. The temperatures of the nozzle and of various parts of the oven were monitored by means of alumel-chromel thermocouples and digital recorders. The nozzle orifice was 0.15 mm in diameter and the stainless-steel front wall was 0.3 mm thick. The beam source was mounted on an XYZ translation stage which allowed precise alignment of the molecular beam with respect to the laser beam and could be manipulated under vacuum. Tests of the beam source indicated that it was capable of being used at temperatures in the range 290–1120 K without clogging of the orifice or crystallization of metal on the orifice. The Cd metal was of 99.999% purity and the Ar, Ne, and He gases were of research grade. The carrier gases were used at typical backing pressures of 1 atm or less, which resulted in a background pressure of 5–7 mtorr in the expansion chamber.

The supersonic  $Cd_2$  beam which also contained Cd and noble-gas atoms, was crossed with a beam of laser light emitted from a frequency-doubled  $N_2$ -laser-pumped dye

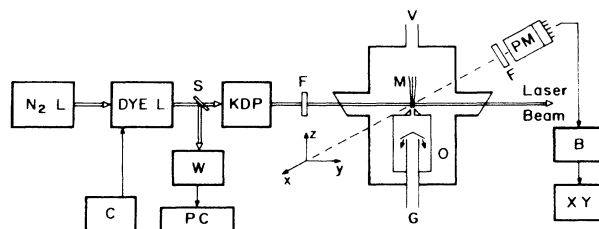


FIG. 1. Schematic diagram of the apparatus: *L*, lasers; *S*, beam splitter; *KDP*, doubling crystal; *W*, wave meter; *PC*, microcomputer; *F*, filters; *O*, oven (source); *G*, carrier gas container; *M*, supersonic beam; *V*, vacuum line; *B*, boxcar amplifier; *XY*, plotter.

laser whose grating was scanned by a stepper-motor-activated sine drive. The scanning of the laser was computer controlled and the lasers (both of which were built in-house) were pulsed at a repetition rate of 10 Hz. The dye laser was operated with 4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4*H*-pyran (DCM) in dimethyl sulfoxide (DMSO), which produced an output with a broad maximum in the 6400–6800 Å range. The second harmonic was produced with a potassium diphosphate (KDP) crystal mounted on a stage which had provision for compensation for the angular walkoff of the second-harmonic component. The first-harmonic component was rejected by a UG-5 absorption filter. The dye laser was frequency calibrated using the Ne optogalvanic spectrum<sup>12</sup> and a wavelength meter.<sup>13</sup> The emitted fluorescence was observed at right angles to the plane of the crossed beams and was focused on the photocathode of an EMR 541-N-03-14 photomultiplier tube whose signal was registered with an EG & G model 162/166 box-car integrator and recorded with an *X-Y* plotter.

To produce a molecular beam, the system was evacuated to a pressure below 1 mtorr, as measured by a thermocouple gauge. The carrier gas was passed through the nozzle at room temperature and the oven heating coils were energized; the upper part containing the nozzle was heated first, and then the lower main body. The temperature of the source continued to be raised while maintaining it at 50–80 K above the oven temperature, until the operating temperature was reached. A  $Cd_2$  molecular beam was produced at above 850 K, a temperature which was normally reached within 60–90 min. The pulsed laser beam, crossed with the molecular beam, was tuned to a wavelength in the vicinity of the atomic Cd  $^3P_1 \leftarrow ^1S_0$  transition and was scanned across the excitation spectrum at the rate of about 1 Å/min.

### III. RESULTS AND DISCUSSION

#### A. Excitation spectrum of $Cd_2$

Figure 2 shows a trace of the excitation spectrum resulting from  $O_u^+(^3\Pi_u) \leftarrow XO_g^+(^1\Sigma_g^+)$  vibronic transitions. The assignment was made in accordance with the PE curves calculated by Bender *et al.*<sup>5</sup> and Hay *et al.*<sup>6</sup> The spectrum which spans the range 3235–3260 Å was obtained with Ar as a carrier gas at a pressure of 700 torr and using an oven temperature of 923 K. A  $v'$  progression has been identified and labeled on the trace which resembles that reported previously,<sup>4</sup> though it contains fewer components due to CdAr molecules and a larger number of  $Cd_2$  vibrational bands extending to  $v'=13$ , which permitted a reliable Birge-Sponer analysis of the spectrum.<sup>14</sup>

Figure 3 shows a trace of an excitation spectrum of  $Cd_2$  arising from the same transition  $O_u^+(^3\Pi_u) \leftarrow XO_g^+(^1\Sigma_g^+)$  and produced with Ne as the carrier gas. Ne is known to combine easily with Cd atoms and form CdNe molecules<sup>15</sup> whose characteristic excitation spectrum is located close to the Cd resonance line and, consequently, does not overlap the  $Cd_2$  spectrum even at relatively high Ne pressures at which the cooling of the  $Cd_2$  molecules becomes more efficient. The trace in Fig. 3,

and other traces of the  $Cd_2$  spectrum which we produced with Ne, all show some of the vibrational components that had previously been ascribed to CdAr molecules<sup>4</sup> and which are most likely "hot bands" formed by excitation from the  $v''=1$  level of the  $XO_g^+(^1\Sigma_g^+)$  state. This identification considerably facilitated the analysis of the spectrum. The frequencies of the vibrational  $Cd_2$  bands are listed in Table I. Figure 4 shows Birge-Sponer plots of vibrational spacing  $\Delta G$  up to  $v'=14$ . The plots for Ar and Ne are both linear and have intercepts at  $v'=27$  which lead to a value  $D_0=243$  cm<sup>-1</sup>. The spectroscopic constants for the  $O_u^+(^3\Pi_g)$  and  $XO_g^+(^1\Sigma_g^+)$  states, obtained from the analysis of these data, are compared in Table II with the values reported previously.<sup>4</sup> The value of the dissociation energy  $D_0$  for the ground state was ob-

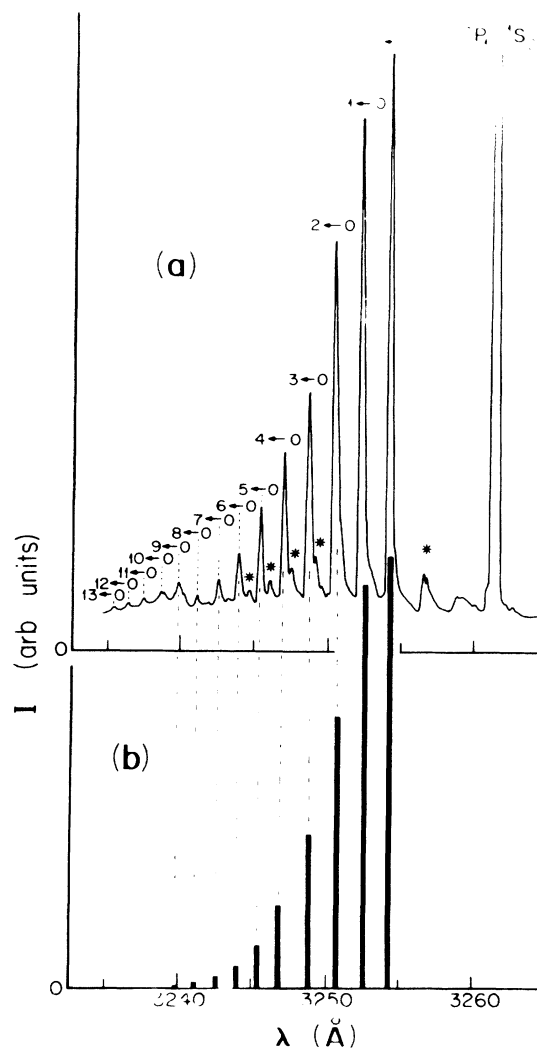


FIG. 2. (a)  $O_u^+(^3\Pi) \leftarrow XO_g^+(^1\Sigma_g^+)$  excitation spectrum of  $Cd_2$ , showing a  $v'$  progression.  $T_0=915$  K,  $D=0.15$  mm,  $X/D=60$ ,  $P_0=760$  torr Ar. The relative intensity scale has been changed above  $v'=8$ . "Hot bands" are indicated by \*. (b) Computer simulation of the excitation spectrum showing relative intensities of the vibrational components.

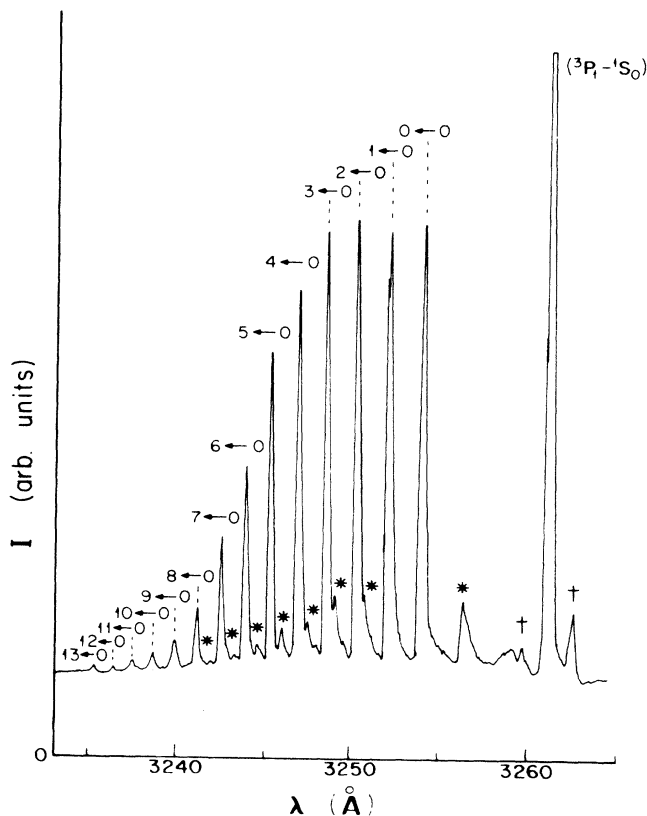


FIG. 3.  $O_u^+(^3\Pi_u) \leftarrow XO_g^+(^1\Sigma_g^+)$  excitation spectrum of  $Cd_2$ , showing a  $v'$  progression.  $T_0=920$  K,  $D=0.15$  mm,  $X/D=60$ ,  $P_0=5$  atm Ne. "Hot bands" are indicated by \*, CdNe bands by †.

tained from the relation

$$D_0(O_g^+) = D_0(O_u^+) + \bar{\nu}_\infty - \bar{\nu}(^3P_1 - ^1S_0) \quad (1)$$

and the values  $\omega_0$  and  $\omega_0 x_0$  were estimated from the "hot" bands using a method described previously.<sup>4</sup> We believe that the differences between the constants determined in this investigation and those reported previously<sup>4</sup>

TABLE I. Frequencies of  $O_u^+(^3\Pi_u) \leftarrow XO_g^+(\Sigma_g^+)$  vibrational bands.

$v' \leftarrow v''$	$\bar{\nu}$ ( $cm^{-1}$ )
0-0	30 724.5
1-0	30 742.6
3-0	30 776.0
4-0	30 791.8
5-0	30 806.3
6-0	30 820.3
7-0	30 833.3
8-0	30 846.2
9-0	30 858.7
10-0	30 870.4
11-0	30 881.7
12-0	30 891.9
13-0	30 901.5
14-0	30 909.8

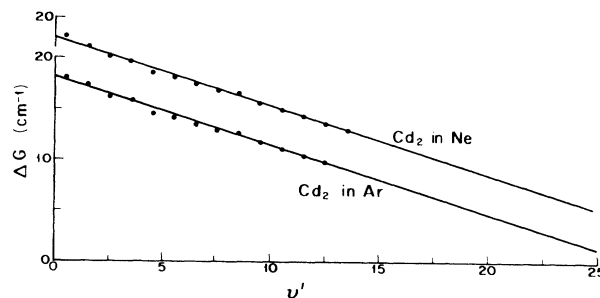


FIG. 4. Birge-Spinner diagrams of the  $v'$  progressions in the  $Cd_2$  spectrum with Ar and Ne as carrier gases.

are due to the more accurate wavelength calibration of our dye laser. We measured the width (FWHM) of the laser line with a Fabry-Perot interferometer to be  $0.2$   $cm^{-1}$  and we believe that the positions of the vibrational components in the spectra were measured within  $\pm 0.2$   $cm^{-1}$ . Our value of  $D_0$  is in reasonable agreement with that reported by Su *et al.*<sup>16</sup> for the  $O_g^+$  state ( $383$   $cm^{-1}$ ), though not with the much earlier values determined by Kuhn and Arrhenius<sup>17</sup> ( $768$   $cm^{-1}$ ) and Kuhn and Freudenberg<sup>18</sup> ( $645$   $cm^{-1}$ ).

We have also carried out a computer simulation of the vibrational spectrum. The Franck-Condon factors were calculated assuming the Morse potential<sup>19</sup> for the  $O_u^+$  and  $XO_g^+$  states and using the experimental  $\omega_e$  and  $\omega_e x_e$  values listed in Table I and varying  $r_e' - r_e''$  to fit the data. The simulated spectrum which is shown in Fig. 2, reproduces faithfully the profile of the experimental spectrum, confirming the assignments of the vibrational components. The computer-fitting procedure yielded the difference  $r_e' - r_e'' = 0.265$  Å between the equilibrium internuclear separations in the  $O_u^+$  and  $XO_g^+$  states. Using an empirical law suggested by Morse<sup>19</sup> for the ground state

$$(r_e'')^3 \omega_0'' = 3000 \text{ Å}^3 \text{ cm}^{-1} \quad (2)$$

and the value  $\omega_0'' = 22.5$   $cm^{-1}$ , we obtained the internuclear separations  $r_e'' \approx 5.1$  Å and  $r_e' \approx 5.4$  Å. Figures 2 and 3 shows the vibrational bands to be degraded towards longer wavelengths, confirming that  $r_e' > r_e''$ .<sup>1</sup> Unfortunately there are no calculations of PE curves against which a comparison could be made.

Attempts to register the excitation spectrum using He as the carrier gas over a range of Cd pressures and  $X/D$  parameters (from 30 to 60) indicated that the cooling of the expansion beam was not very efficient. A typical such spectrum containing  $v'$  progressions is shown in Fig. 5, in which the transitions from  $v''=0$  are overlapped by hot bands originating from  $v''=1$  and possibly  $v''=2$ , making a reliable analysis of the spectrum very difficult. This observation is corroborated by theoretical and experimental evidence obtained by Lubman *et al.*,<sup>20</sup> Levy,<sup>21</sup> Ashkenazy and Sherman,<sup>22</sup> and Campargue<sup>23</sup> who found that, in jet expansion of He, quantum effects caused the collision cross sections to increase with decreasing relative energy of the colliding partners, leading to very

TABLE II. Molecular constants of  $Cd_2$  molecules ( $cm^{-1}$ ).

State	$\nu_0$	$\omega_0$	$\omega_0 x_0$	$D_0$	Source
$O_u^+(^3\Pi_u)$	$30\,724.5 \pm 0.2$	$18.0 \pm 0.2$	0.33	$243.3 \pm 0.4$	This work
	30 726.0	17.8	0.34	235	Ref. 4
$XO_g^+(^1\Sigma_g^+)$		$22.5 \pm 0.2$	0.4	$311.7 \pm 0.4$	This work
		22.0	0.4	305	Ref. 4

much larger Mach numbers than those predicted by the expression

$$M_{\text{eff}} = A \left[ \frac{X}{D} \right]^{\gamma-1}, \quad (3)$$

where  $X$  is the distance of the region of observation from the nozzle,  $D$  is the nozzle diameter,  $A = 3.26$  for monatomic gases (except He), and  $\gamma = C_p/C_v$ . Equation (3) describes the increase in the Mach number in the region where the density of the gas is sufficiently high to make possible the two-body collisions that are required for cooling. At some point downstream the density becomes sufficiently low that there are no collisions and the Mach number and temperature remain constant. The terminal Mach number  $M_T$  was found to be given by

$$M_T \cong 133 (P_0 D)^{0.4}, \quad (4)$$

where  $P_0$  is the pressure in the source in atm and  $D$  is the diameter of the nozzle in cm.<sup>20,21</sup> In this investigation  $M_T$  ranges from 25 ( $X = 0.37$  cm) to 62 ( $X = 0.93$  cm) but, when making observations in the range  $X = 0.8$ – $1.0$  cm, we were not able to produce sufficient cooling of the gas; this confirmed the various reports on the behavior of He in jet-expansion experiments.<sup>20–23</sup> Equation (4) is believed to describe correctly the behavior of Ne, Ar, Kr, and Xe, but the  $M_T$  values for He were found to be much larger than predicted by Eq. (4).<sup>21</sup> The results of this experiment suggest that, in the case of He, it is not sufficient to make observations at  $60D$  from the jet orifice to have a collision-free beam. On the other hand, at larger distances no observations were possible because of vanishing LIF intensities.

### B. Measurements of the $Cd\ ^3P_1$ lifetime

The lifetime of the  $Cd\ ^3P_1$  state was measured in the supersonic beam by exciting the Cd atoms with 3261-Å laser radiation and observing the decay of the fluorescence through a UG-5 filter along a direction perpendicular to both beams. The excitation took place at  $X = 8$  mm from the nozzle, corresponding to  $X/D = 54$ , and using an Ar backing pressure of 760 torr. The oven temperature  $T_0$ , was varied in the range 820–950 K. As pointed out by Lubman *et al.*,<sup>20</sup> the particles in the beam are never completely isolated from one another and the collision rate depends on the velocity spread, the beam density, and the deexcitation cross section. Changes in  $T_0$  caused corresponding changes in Cd density in the constant-pressure carrier gas and, consequently, any changes in nonradiative depopulation must have been associated with changes in Cd density. The number density  $n$  of Cd atoms in the beam is given by<sup>20</sup>

$$n = n_0 \left[ 1 + \frac{1}{2}(\gamma - 1)M_{\text{eff}}^2 \right]^{-1/(\gamma-1)}, \quad (5)$$

where  $n_0$  is the number density in the source at  $T_0$  and  $M_{\text{eff}}$  is the effective Mach number given by Eq. (3). In our experiment we used  $X = 8$  mm,  $D = 0.15$  mm, and  $M_{\text{eff}} = 47$ , resulting in  $n = 5.4 \times 10^{-5} n_0\ cm^{-3}$ . Figure 6 shows a plot of  $\tau^{-1}$  (the reciprocal of the measured mean effective lifetime) against  $n$ . Since

$$\frac{1}{\tau} = \frac{1}{\tau_0} + nv_r Q, \quad (6)$$

where  $\tau_0$  is the mean radiative lifetime and  $Q$  the depopulation cross section, the intercept of the plot yielded  $\tau_0 = (3.0 \pm 0.1) \times 10^{-6}$  s, a value which is compared in Table III (Refs. 24–28) with some results reported elsewhere. The radiative lifetime determined in the course of

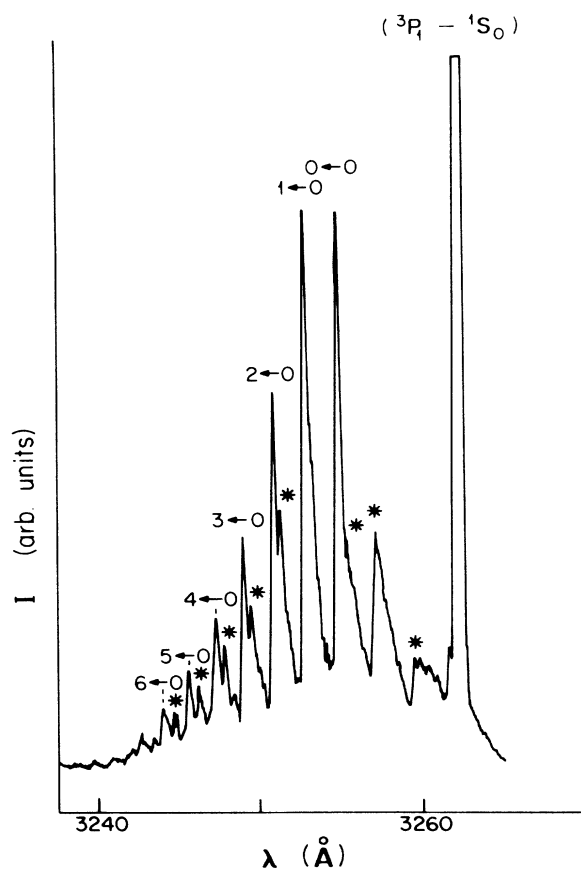


FIG. 5.  $O_u^+(^3\Pi_u) \leftarrow XO_g^+(^1\Sigma_g^+)$  excitation spectrum of  $Cd_2$ , showing a  $v'$  progression.  $T_0 = 980$  K,  $D = 0.15$  mm,  $X/D = 34$ ,  $P_0 = 760$  torr He. "Hot bands" are indicated by \*.

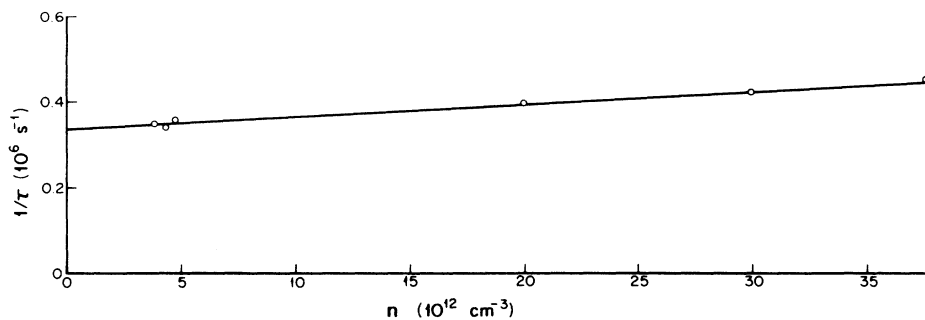
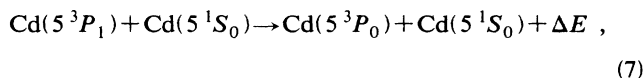


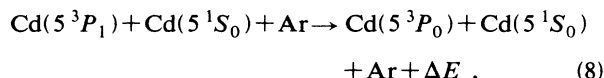
FIG. 6. Plot of  $1/\tau$  against  $n$ , the density of Cd atoms, representing the decay of the  $5^3P_1 \rightarrow 5^1S_0$  fluorescence.

this investigation is in remarkably good agreement with a recent theoretical value derived from an oscillator strength calculation employing a multiconfiguration relativistic Hartree-Fock method.<sup>24</sup> The discrepancies with earlier experimental results we ascribe to the fact that these experiments were carried out in vapor cells and were subject to wall effects and errors due to collisions with impurities.

The slope of the plot in Fig. 6 yields the cross section  $Q = (4.6 \pm 0.3) \times 10^{-14} \text{ cm}^2$  for depopulation of the  $5^3P_1$  state. We believe that the collisional depopulation may result from the following processes:

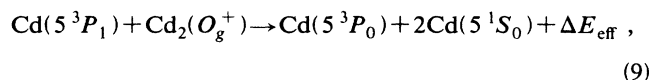


where  $\Delta E = 542 \text{ cm}^{-1}$  is the  $5^3P_1 - 5^3P_0$  energy defect. This cross section is rather large even for collisions of atoms of the same species. The  $6^2P$  fine-structure mixing cross section for Cs was found to be  $3.1 \times 10^{-15} \text{ cm}^2$ , with  $\Delta E = 554 \text{ cm}^{-1}$ .<sup>29</sup> The much larger cross section for fine-structure mixing in Cd may be due to the participation of Ar as a third body in the collision



with the energy defect divided among three collision partners, making the transfer process more efficient. An

alternative and less likely mechanism would involve collision with ground-state  $\text{Cd}_2$  molecules,



where  $\Delta E_{\text{eff}} = \Delta E - D_0 = 231 \text{ cm}^{-1}$ . Here a part of the released excitation energy is used for the dissociation of the  $\text{Cd}_2$  molecules and the remaining balance is released into the continuum. This is not a likely mechanism because the quenching effect was detected well below 770 K, a temperature region in which the probability of  $\text{Cd}_2$  formation is negligible though fluorescence from  $\text{Cd}(5^3P_1)$  atoms could be observed quite easily.

### C. Measurement of $\text{Cd}_2$ lifetimes

When the laser was tuned to excite a particular vibrational level of the  $O_u^+(^3\Pi_u)$  state, it was possible to determine the persistence time of the fluorescence emitted in the decay of each level and thus find the radiative lifetimes of the individual vibrational levels. The measured lifetimes which are tabulated in Table IV, correspond to a source temperature  $T = 923 \text{ K}$ , Ar pressure of 760 torr, and  $X/D = 54$ . The table also shows the effective lifetime of  $\text{Cd}(5^3P_1)$  atoms which was measured at the same time and is in agreement with the value read off the graph in Fig. 6. As may be seen in Table IV,  $\tau(\text{Cd}_2)$  increases with

TABLE III. Radiative lifetime of  $\text{Cd}(5^3P_1)$ .

$\tau$ (ns)	Source
$3000 \pm 100$	This investigation
3000	Migdalek and Baylis <sup>a</sup>
$2490 \pm 130$	Schaefer <sup>b</sup>
$2500 \pm 250$	Koenig and Ellet <sup>c</sup>
$2390 \pm 40$	Byron <i>et al.</i> <sup>d</sup>
$2050 \pm 50$	Matland <sup>e</sup>

<sup>a</sup>Reference 24.

<sup>b</sup>Reference 25.

<sup>c</sup>Reference 26.

<sup>d</sup>Reference 27.

<sup>e</sup>Reference 28.

TABLE IV. Lifetimes of  $\text{Cd}_2$  molecules in various vibrational  $O_u^+$  states  $X/D = 54$ ,  $P(\text{Ar}) = 760 \text{ torr}$ ,  $T = 923 \text{ K}$ .

Vibrational level $v'$	$\tau$ ( $\mu\text{s}$ )
0	$0.84 \pm 0.02$
1	$0.91 \pm 0.02$
2	$0.90 \pm 0.03$
3	$1.00 \pm 0.02$
6	$1.07 \pm 0.02$
7	$1.18 \pm 0.02$
Atomic state	$\tau$ ( $\mu\text{s}$ )
$5^3P_1$	$1.66 \pm 0.02$

the vibrational quantum number up to  $v'=7$ , the highest level accessible in this experiment. The increase in  $\tau(Cd_2)$  (and decrease in transition probability) appears to be monotonic and tends to the value of transition probability for the atomic  $^3P_1-^1S_0$  transition. We believe this trend to be due to the fact that, in general, for higher vibrational states the transition moment or the overlap integral of the vibrational wave functions of the upper and lower states decreases as the separation  $r'_e-r''_e$  increases.<sup>14</sup>

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