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Predissociation spectroscopy of cadmium dimethyl

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The absorption and fluorescence excitation spectra of jet cooled $\text{Cd}(\text{CH}_3)_2$ and $\text{Cd}(\text{CD}_3)_2$ were measured in the structured region between 230 and 200 nm. The symmetric Cd-methyl stretch and methyl umbrella modes in the second excited electronic state of the latter molecule were found to the 304 and 790 cm^{-1} , respectively. Widths of the 0-0 lines (FWHM) were 101 and 25 cm^{-1} , respectively from which lifetimes of 53 and 265 fs were deduced. A weak fluorescence due to CdCH_3 is excited by the absorption of $\text{Cd}(\text{CH}_3)_2$ and an even weaker fluorescence is excited in $\text{Cd}(\text{CD}_3)_2$. The quantum yield of this fluorescence is below 10^{-4} at the electronic origin of the structured band and increases to about 10^{-3} above 2000 cm^{-1} vibrational energy.

I. INTRODUCTION

Cadmium dimethyl was one of the first molecules whose photodissociated fragments were shown to have an anisotropic distribution, peaking perpendicular to the E vector of the polarized dissociating light.¹ As virtually nothing was known about its spectroscopy, theorists adopted the simplest model for the dynamics of its dissociation, namely that of a linear triatomic molecule $A-B-A$.²⁻⁴ It was assumed that the methyl group could be represented as a pseudoatom whose internal structure could be neglected. More recently, it has been found that the photodissociation of $\text{Cd}(\text{CH}_3)_2$ and its neighbors in the periodic table, $\text{Zn}(\text{CH}_3)_2$ and $\text{Hg}(\text{CH}_3)_2$ produce vibrationally hot CH_3 radicals, excited not only in the symmetric bend but in the degenerate antisymmetric stretch as well.^{5,6} The methyl radicals photodissociated from $\text{Zn}(\text{CH}_3)_2$ have been shown to have relatively low kinetic energy.⁷ Chen and Osgood have made a definitive study of the three metal dimethyls and have put forward a convincing theoretical model to explain their spectra.⁸ Briefly put, the first continuous band is a perpendicular transition to a state in which the molecule bends and simultaneously dissociates to CH_3 and MCH_3 in its \tilde{X}^2A_1 ground state. The second, structured spectral band which overlaps the first continuum is another perpendicular transition to a linear E state which correlates with an excited \tilde{A}^2E state of MCH_3 and a ground state methyl. A rather long progression [20 lines for $\text{Cd}(\text{CH}_3)_2$] in all three molecules was explained quantitatively in terms of two frequencies, a metal-methyl stretch around 300 cm^{-1} and a symmetric methyl bend of around 900 cm^{-1} . Recently, $\tilde{A}-\tilde{X}$ fluorescence from ZnCH_3 and CdCH_3 was reported when their parent molecules were excited in the structured region of their spectrum,⁷ thus confirming one aspect of the Chen and Osgood model.⁸

The spectroscopy has several unusual aspects. The first two excited potential surfaces are both dissociative, but the second supports several different vibrations whereas the first does not. It is clear that before it dissociates the molecule spends more time on the upper excited surface than on the

lower. Measuring the absorption spectrum of a cold beam of the target molecules seemed to be a way of determining the actual lifetime on the upper surface. If the vibrational bands would sharpen with decreasing temperature and eventually with sufficient cooling would exhibit rotational structure, this would be evidence for a genuinely metastable state. On the other hand, if cooling produced only a small effect on the linewidth, this would indicate that the line is homogeneously broadened by a short lifetime and was not merely an unresolved superposition of rotational lines. Also, according to the theory of Chen and Osgood, different vibrational bands correspond to excitation of different quantum numbers of vibrations on the upper surface. Are the dynamics of the dissociation different for different vibrational states?

It is now clear that the internal vibrations of the methyl groups play a role in the dynamics of $\text{M}(\text{CH}_3)_2$ on its excited surfaces. In this paper we report (i) the spectra of $\text{Cd}(\text{CH}_3)_2$ and $\text{Cd}(\text{CD}_3)_2$ in a nozzle beam cooled to ~ 20 K, and (ii) the fluorescence excitation spectrum of the cold $\text{Cd}(\text{CH}_3)_2$ molecules, the CdCH_3 being the emitter. The model of Chen and Osgood is further confirmed, the lifetime of the upper excited state is estimated and it is shown that in this second excited state, level crossing to the "dark" lower excited state is about three orders of magnitude faster than dissociation to the fluorescent \tilde{A}^2E CdCH_3 .

II. EXPERIMENTAL

Our apparatus and techniques for measuring absorption spectra, lamp induced fluorescence spectra and fluorescence quantum yield are described elsewhere.¹¹⁻¹⁴ Briefly, the absorption spectra and the fluorescence excitation spectra of cadmium dimethyl seeded in an argon pulsed planar supersonic expansion were simultaneously determined using a pulsed xenon lamp and a monochromator. Cadmium dimethyl was placed in a sample chamber outside the apparatus and its vapor pressure was separately controlled by its temperature. It was mixed with argon at ~ 60 Torr stagna-

tion pressure and expanded through a slit nozzle. The nozzle dimensions¹⁴ were 0.22×35 mm and its repetition rate was 9 Hz resulting in a gas pulse width of ~ 200 μ s. The nozzle temperature was ~ 25 °C.

Light from a pulsed simmered xenon flashbulb (pulse duration 24 μ s) was focused and passed through a 0.75 m SPEX-1500 monochromator with a 2400 lines/mm grating and ~ 0.06 nm resolution with a 100 μ slit width. The pulsed light was focused onto a jet parallel to the slit at a distance of 16 mm from it. The light beam was split by a sapphire window and monitored by two vacuum photodiodes. The attenuation ΔI of the light beam due to absorption was determined from the difference in the light intensity before and after crossing the planar jet. The lamp induced fluorescence intensity I_F was monitored by a photomultiplier sometimes with a long pass filter before it. (300 or 385 nm filters were used). The pulse repetition rate of the flash lamp was twice the nozzle pulse rate and a second subtraction was performed of the light pulses measured with and without the intervening pulsed jet. This procedure ensured the elimination of any stray absorption and produced a flat, wavelength independent zero baseline. The absorption signal ΔI and the lamp induced fluorescence signal I_F were normalized to the incident light intensity I_0 . A small long term instability of the sample chamber however slightly affected the relative intensities of the spectral features. Relative emission quantum yields were obtained by dividing I_F by ΔI . The absolute values of the emission quantum yields were not measured but are estimated to be in the range of 10^{-4} – 2×10^{-3} from the relative normalized fluorescence intensities.¹³ The effect of the nozzle stagnation pressure was briefly studied and 60 Torr was found to be a good compromise to avoid cluster formation. The rotational temperature is estimated to be 20 K under these conditions.¹¹ $\text{Cd}(\text{CH}_3)_2$ was a commercial sample from Alfa Inorganics. $\text{Cd}(\text{CD}_3)_2$ was synthesized from CD_3I and anhydrous CdBr_2 using the Grignard reaction.¹⁵

III. RESULTS

Figure 1 presents an overall view of the first 15 vibrational lines of $\text{Cd}(\text{CH}_3)_2$ in the region 230–207 nm. There is a substantial but not dramatic improvement in the resolution as compared to the spectrum at 243 K measured by Chen and Osgood. Table I lists the first seven lines and their assignments. Figure 1 also shows the spectrum of jet cooled $\text{Cd}(\text{CD}_3)_2$. At first glance the spectrum of $\text{Cd}(\text{CH}_3)_2$ seems simple as if it were a progression in one vibration, whereas that of $\text{Cd}(\text{CD}_3)_2$ seems more complex. Figure 2, however, shows on an expanded scale the first six peaks of $\text{Cd}(\text{CH}_3)_2$ and certain peaks of $\text{Cd}(\text{CD}_3)_2$. It is clear that the widths of the first three lines are about half that of the next three which are also nonsymmetric. In $\text{Cd}(\text{CH}_3)_2$ there is an unfortunate degeneracy in that one frequency of 1008 cm^{-1} is close to three times the other frequency of 326 cm^{-1} . Thus, all bands after the first three which are labeled (0,0), (0,1), and (0,2) are unresolved combinations. On the other hand, the $\text{Cd}(\text{CD}_3)_2$ spectrum is fitted by a high frequency of 790 cm^{-1} with an anharmonic term of -7.6 cm^{-1} and a low

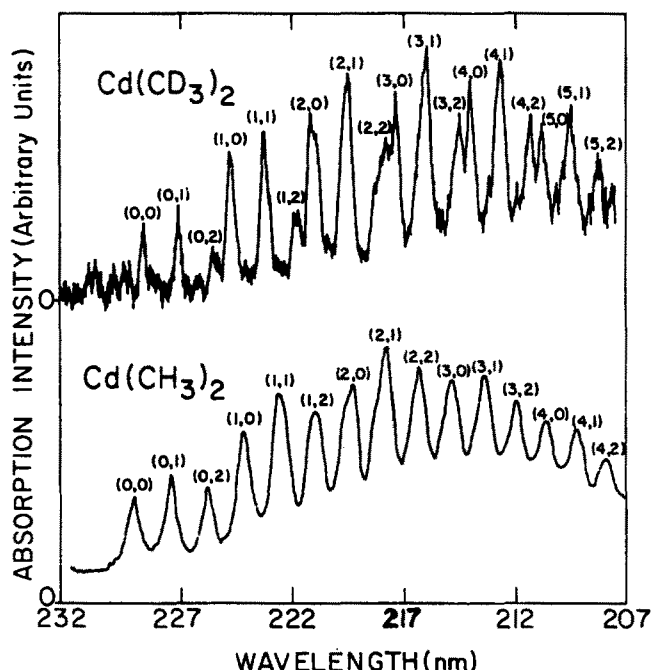


FIG. 1. Absorption spectra of jet cooled $\text{Cd}(\text{CH}_3)_2$ and $\text{Cd}(\text{CD}_3)_2$. Bands are labeled (n,m) where n,m are the vibrational quantum numbers of the symmetric umbrella vibration of the methyl group and the symmetric methyl-metal atom stretch. Spectra were generally recorded with 15 cm^{-1} resolution. The zero of absorption is indicated on the spectra.

TABLE I. Wavelengths, frequencies, and assignments of vibrational bands.^a

(n,m)	$\lambda(\text{nm})$	$\bar{\nu}(\text{cm}^{-1})$	$\bar{\nu}(n,m) - \bar{\nu}(0,0)$ (obs)	calc)
$\text{Cd}(\text{CH}_3)_2$				
(0,0)	229.16	43 638	0	0
(0,1)	227.50	43 956	318	326
(0,2)	225.84	44 279	641	652
(0,3)	224.28	44 587	949	978
(1,0)	224.08	44 627	989	1008
(0,4)	222.76	44 891	1253	1304
(1,1)	222.38	44 968	1330	1334
$\text{Cd}(\text{CD}_3)_2$				
(0,0)	228.76	43 714	0	0
(0,1)	227.14	44 026	312	303
(0,2)	225.59	44 328	614	607
(1,0)	224.89	44 466	752	775
(1,1)	223.38	44 767	1053	1078
(1,2)	221.81	45 084	1370	1382
(2,0)	221.15	45 218	1504	1534
(2,1)	219.49	45 560	1846	1838
(2,2)	218.01	45 870	2156	2141
(3,0)	217.34	46 011	2297	2278
(3,1)	216.00	46 296	2582	2582
(3,2)	214.50	46 620	2906	2885
(4,0)	213.97	46 736	3022	3007
(4,1)	212.65	47 026	3312	3311
(4,2)	211.32	47 322	3608	3614
(5,0)	210.80	47 438	3724	3721
(5,1)	209.48	47 737	4023	4024
(5,2)	208.24	48 022	4308	4328

^a The numbers n,m are quantum numbers of vibrations on the upper surface. All frequencies are given in cm^{-1} .

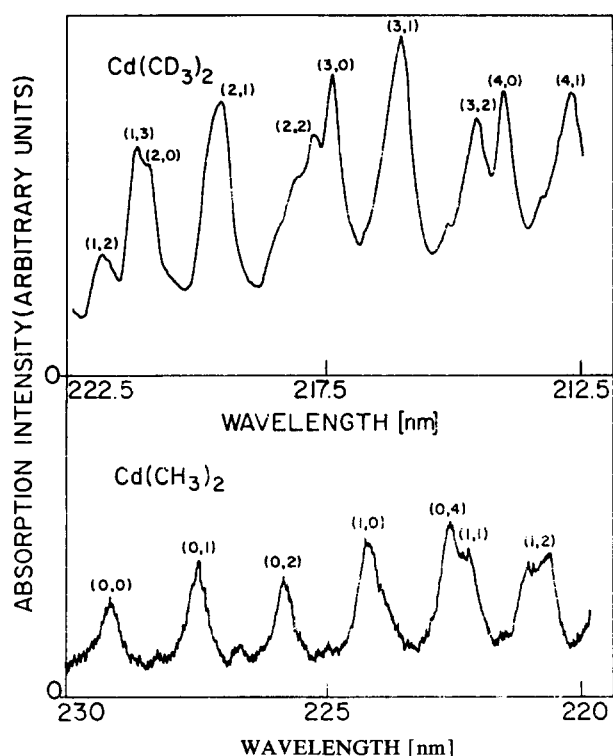


FIG. 2. Spectra on expanded scale of certain peaks of $\text{Cd}(\text{CD}_3)_2$ and the first six peaks of $\text{Cd}(\text{CH}_3)_2$.

frequency of 304 cm^{-1} . Frequencies and assignments of the first eighteen transitions are listed in Table I. The rms deviation of the frequencies is 15 cm^{-1} which is just the resolution of the monochromator.

We have observed that the individual transitions of $\text{Cd}(\text{CD}_3)_2$ are intrinsically much sharper than those of $\text{Cd}(\text{CH}_3)_2$. In Fig. 3 the 0-0 bands of the two molecules are compared and it is seen that the $\text{Cd}(\text{CD}_3)_2$ band is four times narrower. As the quantum numbers of the excited state increase, the lines become somewhat broader. One reason may be the overlapping of transitions. However while excitation of the low frequency mode causes no noticeable change in the line breadth, the high frequency mode has a distinct effect. Note that each of the two lines of the (0,0),(0,1) and the (1,0),(1,1) pairs have very similar widths but the latter pair are broader than the former. Also, in the progression (0,1),(1,1),(2,1), and (3,1) the lines become distinctly broader as the high frequency quantum number increases. Jet cooling to $\sim 20\text{ K}$ improves resolution but does not entirely eliminate the continuous background. This background which originates from the lower energy spectrally unresolved S_1 excited state extends to the red of our measured spectral range. It is more noticeable in $\text{Cd}(\text{CH}_3)_2$ than $\text{Cd}(\text{CD}_3)_2$ as the former has broader and therefore smaller peak absorptions.

A weak fluorescence was observed from irradiated $\text{Cd}(\text{CH}_3)_2$ whose yield is roughly estimated as $\sim 10^{-3}$ from comparison with emission strengths from other molecules. Figure 4 shows the excitation spectrum which is noisier than the absorption spectrum but matches it peak for peak. How-

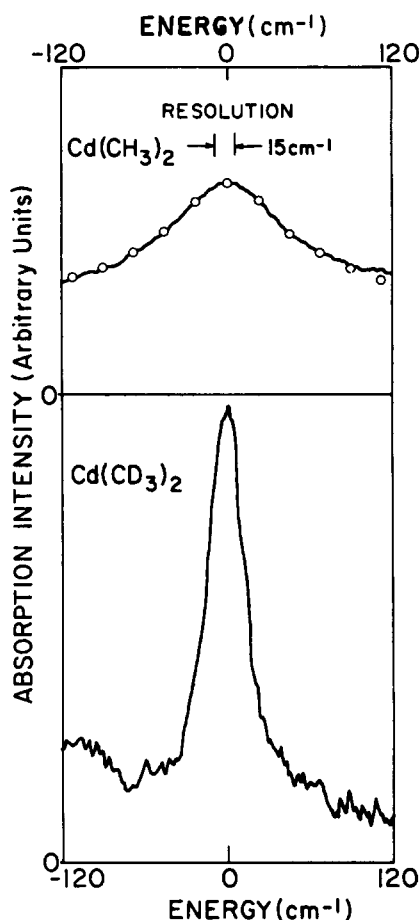


FIG. 3. The 0-0 band of the second structured electronic state of $\text{Cd}(\text{CH}_3)_2$ and $\text{Cd}(\text{CD}_3)_2$. The 0-0 band of the deuterated molecule is approximately four times narrower than that of the protonated molecule. The open circles are a fit to a Lorentzian line shape with 101 cm^{-1} FWHM. The baseline slope in the $\text{Cd}(\text{CD}_3)_2$ spectrum is an artifact due to a change in the $\text{Cd}(\text{CD}_3)_2$ partial pressure.

ever as shown in Fig. 5 the quantum yield is not the same for all vibrational bands being close to zero in the 0-0 band and reaching a plateau only at the eighth band. An even weaker fluorescence was seen from the deuterated molecule with the

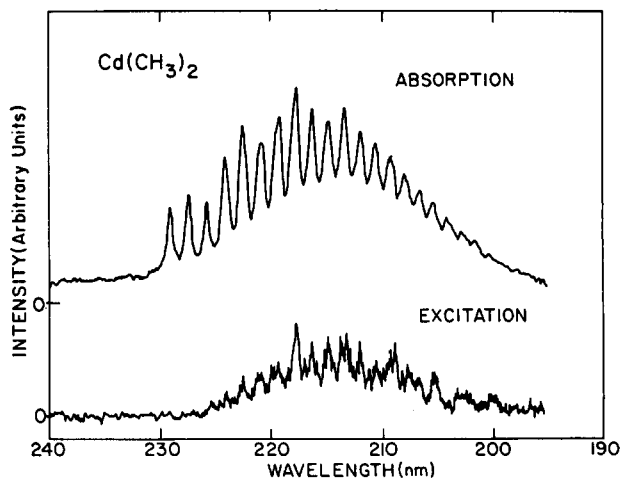


FIG. 4. Absorption and fluorescence spectra of $\text{Cd}(\text{CH}_3)_2$ in the range from 230 to 195 nm.

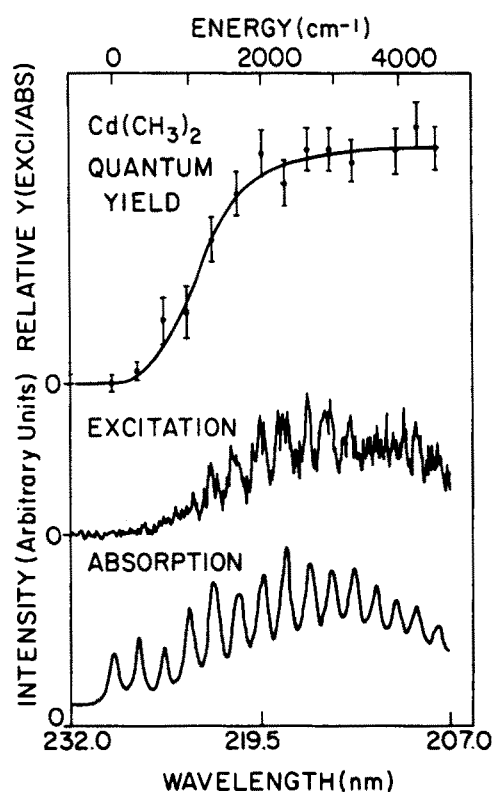


FIG. 5. Absorption and fluorescence excitation spectra and, in the upper plot, relative quantum yield of fluorescence (fluorescence intensity divided by the absorption intensity at each peak of the latter).

same increase of quantum yield with the increasing photon energy. Use of a 385 nm long pass filter did not change the emission intensity showing that the emission is in the visible.

IV. DISCUSSION

A. Assignment of the first excited electronic state

The UV spectrum of $\text{Cd}(\text{CH}_3)_2$ consists of a continuous absorption of moderate strength joining on to a higher energy somewhat stronger and structured transition. The continuous absorption was interpreted by Chen and Osgood as a transition to a bent repulsive state which dissociates into CH_3 and $\text{CdCH}_3(\tilde{X}^2E_{1/2})$. The latter molecule has enough energy to further dissociate into $\text{Cd}(^1S_0)$ and the CH_3 . These, however, are the same dissociation products as those of the singlet ground state. Indeed, at the beginning of the continuous absorption near 280 nm there is not enough energy to produce electronically excited CdCH_3 . Therefore, it must follow that the bent repulsive state is a triplet. The relatively strong continuous absorption must mean that the first excited state is a triplet with considerable singlet character. This is not unreasonable considering that cadmium is a heavy atom with strong spin-orbit coupling. The cadmium dimethyl molecules were cooled in an expansion in order to simplify the structured spectrum and to see how far the continuous absorption extends. The spectra of both the hydrogenated and deuterated molecules show that there is considerable overlap between the continuous and structured absorption which is the same conclusion drawn by Chen and Osgood.

B. Assignment of the second excited electronic state

In the Chen-Osgood model the second excited state potential surface has a saddle point at the linear structure which can dissociate into CH_3 and $\text{CdCH}_3(\tilde{A})$. The latter molecule is fluorescent. Yu *et al.*⁷ reported the observation of fluorescence by two excitation methods. One was by using synchrotron radiation from the Brookhaven storage ring; weak fluorescence was observed by excitation throughout the VUV region and the structured UV absorption region but could not be excited by light in the region of continuous absorption. The other method was an excimer laser at 193 nm which produced emission from both $\text{Cd}(\text{CH}_3)_2$ and $\text{Zn}(\text{CH}_3)_2$. Together these findings seemed to confirm the assignment of the second state. However, Suto *et al.*⁹ did not detect fluorescence when exciting in the structured region (200–249 nm) using synchrotron radiation from the Wisconsin storage ring. They also gave evidence that the emission excited by the 193 nm laser was due to a multiphoton (two are sufficient) absorption which produced $\text{CH}(A^2\Delta)$. The experiments reported here were carried out with 100 pJ light pulses of 24 μs duration and 15 cm^{-1} resolution. The fluorescence excitation curve clearly follows the absorption peaks although the quantum yield is not the same for each peak. The pulsed UV light source used in the present experiments is much weaker in photons/s/steradian than an excimer laser and thus nonlinear effects can be excluded. As mentioned in Sec. III, the quantum yield for the CdCH_3 emission is $\sim 10^{-3}$ and that from CdCD_3 is even less. Thus, we conclude that the second excited state of $\text{Cd}(\text{CH}_3)_2$ correlates with $\text{CdCH}_3(\tilde{A})$ and CH_3 but almost all of the dissociations are preceded by level crossing either to the adjacent triplet state or to the ground state. One argument for the ground state rather than the repulsive triplet state is that rather little energy is released into translational energy of the methyl radicals.⁷ One might expect that a slide down a repulsive surface would liberate considerable kinetic energy but that the opposite would be true for escape from the attractive ground state.

C. Time scale for dissociation

Let us now consider the time scale for the dissociation. The anisotropy of the photofragment angular distribution showed that the mean lifetime for dissociation had to be substantially shorter than the average period of rotation of $\text{Cd}(\text{CH}_3)_2$ about axes perpendicular to its threefold axis. This average period, $2\pi(I/kT)^{1/2}$ where I is the perpendicular moment of inertia,¹⁰ has the numerical value of 4.8 ps at room temperature. The widths of the 0–0 bands should provide us with the lifetimes of the excited molecule. The 0–0 band of $\text{Cd}(\text{CH}_3)_2$ is Lorentzian in shape but the 0–0 band of $\text{Cd}(\text{CD}_3)_2$ is not quite Lorentzian (see Fig. 3). These bands have full widths at half-maximum (FWHM) of 101 and 25 cm^{-1} , respectively. Inasmuch as the spectral resolution is 15 cm^{-1} , the widths have to be deconvoluted to 100 and 20 cm^{-1} . These bands show little or no change in width when the stagnation pressure is raised and we therefore assume that the intrinsic width is due to lifetime broadening. From the equation $\Delta\omega\tau = 1$ where $\Delta\omega$ is the angular frequency

corresponding to the FWHM, one finds $\tau = 53$ and 265 fs for the two molecules. The latter time is a lower limit for the dissociation time because the line is not a perfect Lorentzian. Nevertheless recalling that a 1000 cm^{-1} vibrational frequency has a period of 33 fs only a few vibrations occur before level crossing.

Finally, one might ask, is the fluorescent emitter $\text{CdCH}_3(\tilde{A})$ or the parent $\text{Cd}(\text{CH}_3)_2$ molecule? That it is not the latter follows from the fact that the lifetime of the upper state is not 10^{-3} of a typical radiative lifetime but around 10^{-6} . In other words, the molecule does not hold together long enough to radiate. Once released, however, the $\text{CdCH}_3(\tilde{A})$ fragment can radiate at its leisure.

D. Assignment of the vibrations on the second excited electronic surface

Chen and Osgood fitted the $\text{Cd}(\text{CH}_3)_2$ structured spectrum with two frequencies 326 and 1008 cm^{-1} which they assigned to a $\text{CH}_3\text{-Cd}$ atom stretch and a symmetric bend (umbrella motion) of the CH_3 group. We have fitted the first 18 lines of the structured $\text{Cd}(\text{CD}_3)_2$ spectrum by least squares to the equation

$$G(v_1, v_2) = G(0,0) + \omega_1 v_1 - \omega_1 x_1 v_1 (v_1 + 1) + \omega_2 v_2, \quad (1)$$

where $G(0,0)$, ω_1 , $\omega_1 x_1$, and ω_2 are 43714, 790, 7.6, and 304 cm^{-1} , respectively. The square root of the ratio of the reduced mass of the CH_3 and ^{112}Cd to the reduced mass of the CD_3 and the ^{112}Cd atom is 0.9236. The square root of the ratio of the reduced mass of H_3 and a ^{12}C atom to the reduced mass of the D_3 and a ^{12}C is 0.7746. Assuming that the deuterated molecule frequencies differ from the protonated molecule frequencies by only these reduced mass factors, one obtains 781 and 301 cm^{-1} , respectively, for the umbrella mode and metal-methyl stretch frequencies in the deuterated molecule. This nice agreement confirms Chen and Osgood's interpretation of the two frequencies. The only excited state frequencies which should be seen in the absorption of a vibrationally cold linear centrosymmetric molecule to a linear centrosymmetric upper state are symmetric vibrations. (The upper state, although of u symmetry, still has a centrosymmetric saddle point.) There are only three such modes in this molecule, the in phase metal atom-methyl radical stretches, the in phase umbrella motion of both methyl radicals and the in phase symmetric C-H stretch of both methyl radicals. The only sign of this latter mode in the entire spectrum of $\text{Cd}(\text{CD}_3)_2$ is a weak shoulder near 2100 cm^{-1} on the low energy side of the complex peak which is assigned to both (3,0) and (2,2). All other peaks in the spectrum have been interpreted in terms of Eq. (1).

The symmetric cadmium-methyl stretch in the electronic ground state of $\text{Cd}(\text{CH}_3)_2$ is 473 cm^{-1} and the methyl umbrella vibration is 1158 cm^{-1} .¹⁷ Comparing these with the excited state frequencies, the stretching force constant in the excited state is half of its value in the ground state and the bending force constant is three quarters of its value in the ground state. In other words the molecule in its excited state is more easily deformable.

E. Competition between electronic and vibrational predissociation

With the vibrational features of the spectrum firmly determined we can now try to understand the effect of these vibrations on both radiative and nonradiative processes. Most remarkable we think is the fact that excitation in the first two bands, i.e., the (0,0) and the (0,1) band which places one quantum in the symmetric methyl-Cd stretch produces no observable fluorescence; on further excitation (see Fig. 4) there is a gradual increase in fluorescence until a plateau is reached. The same effect was seen with the deuterated compound except with even poorer signal/noise.

We now have to explain why (a) the fluorescence yield increases with increasing vibrational energy, (b) the excited deuterated molecule has a longer lifetime, and (c) the deuterated molecule fluorescence yield is less than that of the protonated one.

It is possible that the delayed onset of fluorescence is due to a coincidence, that the energetic threshold for producing electronically excited CdCH_3 is at $229 \pm 4\text{ nm}$, thus preventing excitation of fluorescence in the first few transitions. However a more interesting possibility is that the rate of dissociation depends on the vibrational state. The rate constant for leaving the upper excited state, S_1 can be written

$$k(\text{H}) = 1/\tau(\text{H}) = k_{\text{LC}}(\text{H}) + k_{\text{DISS}}(\text{H}), \quad (2)$$

where k_{LC} , the rate constant for electronic predissociation, that is, crossing to a lower electronic state is about three orders of magnitude greater than the rate constant, k_{DISS} for vibrational predissociation on the excited state surface to give the emitting species $\text{CdCH}_3(\tilde{A})$. In other words, the quantum yield for fluorescence is $k_{\text{DISS}}/k_{\text{LC}}$. An equation of the same form will hold when H is replaced by D. The observations to be explained can be restated as follows. k_{LC} and $k_{\text{DISS}}/k_{\text{LC}}$ increase with increasing vibrational energy and $k_{\text{LC}}(\text{D}) < k_{\text{LC}}(\text{H})$ and

$$\frac{k_{\text{DISS}}(\text{H})}{k_{\text{LC}}(\text{H})} > \frac{k_{\text{DISS}}(\text{D})}{k_{\text{LC}}(\text{D})}. \quad (3)$$

Nonradiative transitions in general increase in rate with increasing vibrational energy because of the increased density of final states. The upper state potential energy is a function of the metal-carbon separations. However the symmetric metal-methyl stretch coordinate is, in a literal way, orthogonal to the reaction coordinate and therefore its excitation does not strongly accelerate dissociation. The upper state potential energy is also a function of the shapes of the two methyl groups. The more they are bent the greater is the internal energy of the departing methyl groups. Indeed, one may think of the excited cadmium dimethyl as being trapped in a well when the methyl group is pyramidal but being able to escape when the methyl groups are flatter. Increasing the vibrational energy will clearly increase k_{DISS} and probably faster than k_{LC} increases thus increasing $k_{\text{DISS}}/k_{\text{LC}}$.

The decrease of k_{LC} with deuteration is the normal trend in deuterated molecules and is explained in terms of Franck-Condon factors for the transition.¹⁶ For the same size energy gap these are smaller for an accepting C-D vibration because its final vibration quantum number must be

higher and its value function is more oscillatory. Thus, radiationless transitions are slowed down. At first sight a greater fluorescence quantum yield would be expected because the molecule remains longer on the upper surface. However the decreased amplitude of D atom vibration causes k_{DISS} to decrease appreciably (by more than a factor of five) when H is replaced by D. Thus, $k_{\text{DISS}}/k_{\text{LC}}$ decreases with deuteration.

V. SUMMARY

This paper has been devoted to the spectroscopy of predissociating cadmium dimethyl. The earlier experiments and theory of Chen and Osgood are confirmed and extended. The structured absorption in the region 230–200 nm is a result of particular vibrations on the upper surface. Between the vibrational bands an underlying continuum is seen which is due to an absorption to a directly dissociating state. Electronic predissociation to a lower state which directly dissociates to a cadmium atom and two methyl radicals is the dominant process. From the widths of the 0–0 bands it is inferred that the molecules dissociate in a time of the order of 53 fs for $\text{Cd}(\text{CH}_3)_2$ and 265 fs for $\text{Cd}(\text{CD}_3)_2$. A minor but very helpful alternate process is vibrational predissociation to give a fluorescent cadmium monomethyl radical.

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- ¹C. Jonah, P. Chandra, and R. Bersohn, *J. Chem. Phys.* **55**, 1903 (1971).
- ²M. Tamir, U. Halavee, and R. D. Levine, *Chem. Phys. Lett.* **25**, 38 (1974).
- ³M. E. Kellman, P. Pechukas, and R. Bersohn, *Chem. Phys. Lett.* **83**, 304 (1981).
- ⁴M. D. Pattengill, *Chem. Phys.* **75**, 59 (1983).
- ⁵S. I. Baughcum and S. R. Leone, *Chem. Phys. Lett.* **89**, 183 (1982).
- ⁶J. O. Chu, G. W. Flynn, C. J. Chen, and R. M. Osgood, *Chem. Phys. Lett.* **119**, 206 (1985).
- ⁷C.-F. Yu, F. Youngs, K. Tsukiyama, R. Bersohn, and J. Preses, *J. Chem. Phys.* **85**, 1382 (1986).
- ⁸C. J. Chen and R. M. Osgood, *J. Chem. Phys.* **81**, 318, 327 (1984).
- ⁹M. Suto, C. Ye, and L. C. Lee, *J. Chem. Phys.* **89**, 160 (1988).
- ¹⁰K. S. Rao, B. P. Stoicheff, and R. Turner, *Can. J. Phys.* **38**, 1516 (1960).
- ¹¹A. Amirav, C. Horwitz, and J. Jortner, *J. Chem. Phys.* **88**, 3092 (1988).
- ¹²A. Amirav, *J. Phys. Chem.* **92**, 3725 (1988); *Chem. Phys.* **126**, 327, 347, 365 (1988).
- ¹³M. Sonnenschein, A. Amirav, and J. Jortner, *J. Phys. Chem.* **88**, 4214 (1984).
- ¹⁴A. Amirav (unpublished).
- ¹⁵J. Chenault and F. Tatibouet, *C. R. Acad. Sci. Paris* **267**, 1492 (1968).
- ¹⁶J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.* **7**, 149 (1969).
- ¹⁷I. S. Butler and M. L. Newbury, *Spectrochim. Acta Part A* **33**, 669 (1977).