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Vibrational energy of the monoalkyl zinc product formed in the photodissociation of dimethyl zinc, diethyl zinc, and dipropyl zinc

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The gas-phase photodissociation of $(CH_3)_2$ Zn, $(C_2H_5)_2$ Zn, and $(n-C_3H_2)_2$ Zn has been examined at 248 nm using laser-induced fluorescence to detect the monoalkyl zinc radical and zinc atom photoproducts. For each compound, the monoalkyl zinc radical is the primary photoproduct and is formed sufficiently hot that it spontaneously dissociates to an alkyl radical and a Zn atom without absorption of a second photon. Photodissociation was examined in the presence of He buffer gas to measure the probability of quenching the secondary spontaneous dissociation of the monoalkyl zinc species. For all three dialkyl zinc compounds, the probability of quenching the secondary dissociation step increases substantially over the He pressure range of 0-400 Torr. The quenching probability vs He pressure was fit using RRKM theory in conjunction with a time-dependent master equation, treating the nascent vibrational energy distribution of the monoalkyl zinc product as an adjustable function. The quenching data for $C_2 H_3 Zn$ and $n-C_3 H_7 Zn$ can be fit only if it is assumed that these species are formed with a hot, narrow vibrational energy distribution, much narrower than that predicted by phase-space theory. A dissociation mechanism involving crossover from an optically prepared singlet state to a repulsive triplet state is proposed to explain this observation. Spontaneous dissociation of CH_3Zn is quenched much more strongly by He than is calculated using any reasonable vibrational energy distribution function for CH_3Zn . This is attributed to the inapplicability of RRKM theory to reactions involving very low-state-density molecules like CH₃Zn.

I. INTRODUCTION

One of the most interesting and technologically important aspects of gas-phase organometallic photochemistry is that absorption of a single uv photon often results in the scission of several metal-ligand bonds. To illustrate this phenomenon, consider the single-photon dissociation of a metal carbonyl such as $Fe(CO)_5$. Because the energy of a uv photon is much greater than the energy required to break the first metal-ligand bond, a large fraction of the initial excitation energy is retained by the metal-containing primary photoproduct, $Fe(CO)_4$.^{1,2} This product will spontaneously dissociate if the energy retained is sufficient to break additional metal-ligand bonds. At very high excitation energies, spontaneous dissociation can continue until all metal-ligand bonds are broken, leaving the bare metal atom.^{3,4} Gas-phase photodissociation of organometallics can thus be exploited to prepare highly unsaturated catalytic species⁵ and to produce metal films under extremely mild conditions.⁶

To understand the multiple-fragmentation process, it is necessary to understand the dynamics of the primary photodissociation step. In particular, we would like to know if energy is partitioned statistically to the photoproducts or is partitioned in a more specific manner. Recent studies have attempted to address this question for the metal carbonyls. For example, Vernon and co-workers have examined the photodissociation of $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in a molecular beam using mass spectrometry to measure the product velocity distributions.^{7,8} Photodissociation of each species was examined at excitation energies where the primary $M(CO)_x$ photoproduct spontaneously dissociates, either partially or completely. When secondary dissociation processes of this kind occur in a molecularbeam experiment, it is not straightforward to define a unique velocity distribution for the products of each dissociation step. Analysis of the mass spectrometric data is further complicated because metal carbonyls fragment readily under the high-energy electron-impact ionization conditions required to detect the photoproducts with an acceptable signal-tonoise ratio. Nevertheless, Vernon and co-workers extracted information on the statistical nature of the primary photodissociation process by fitting the composite velocity distributions determined for each $M(CO)_x^+$ product ion to the distributions predicted by a simple statistical model for each metal-CO dissociation step. They found that the product velocity profiles are consistent with a statistical primary photodissociation process for $Fe(CO)_5$,⁷ but not for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$.⁸

Hepburn and co-workers also performed a series of photodissociation experiments on $Fe(CO)_5$ using vuv laser-induced fluorescence to measure the rovibrational state distribution of the CO product.⁹ The Doppler linewidths of the transitions were used to assign a translational temperature to the CO population. The most complete data were collected at photolysis wavelengths where the $Fe(CO)_4$ primary photoproduct spontaneously dissociates. Under these conditions, it is not possible to determine a unique rovibrational or translational energy distribution for the CO produced in each dissociation step. Information on the photodissociation mechanism was thus obtained by comparing the measured composite CO energy distributions to the distributions expected from a simple statistical model for each dissociation step. The conclusion of Hepburn and co-workers agrees with the conclusion of Vernon and co-workers regarding the statistical nature of the Fe(CO)₅ photodissociation process. Related optical spectroscopic experiments have been performed by Holland and Rosenfeld¹⁰ on W(CO)₆ and by Wight and co-workers on a series of metal nitrosyls.^{11,12}

By combining the information obtained in the Vernon and Hepburn experiments, one would expect to obtain a very complete dynamical picture of the Fe(CO)₅ photodissociation process. Unfortunately, the picture that emerges is less complete than one would like because analysis of the data is complicated by spontaneous dissociation processes. Similar difficulties will often be encountered when molecular-beam or optical spectroscopic experiments of this kind are performed on organometallic molecules. While complications due to spontaneous dissociation can be avoided by employing excitation wavelengths that result in scission of only one metal-ligand bond, one is often interested in an organometallic photodissociation process because of the possibility of spontaneous dissociation processes. Consequently, we have begun to use an indirect technique that exploits spontaneous dissociation of the photoproducts to gain dynamical information about photoprocesses in organometallic molecules. We perform the photodissociation experiment in the presence of a buffer gas in an attempt to quench spontaneous dissociation of the primary photoproduct. Once the probability of quenching as a function of buffer-gas pressure is known, we fit the quenching data using RRKM theory together with a time-dependent master equation that describes the competing processes of reaction and collisional deactivation of the hot primary photoproduct. The fit is extremely sensitive to the choice of initial vibrational energy distribution for the primary photoproduct. While this method will not yield the exact vibrational energy distribution for the photoproduct of interest, it gives the average energy and width of the distribution function. If a functional form is specified for the distribution, e.g., a Gaussian or Boltzmann distribution, a unique vibrational energy distribution can be obtained.

Similar quenching techniques together with RRKM theory were used several years ago to explore the vibrational energy distributions of products formed in the photodissociation of organic molecules.¹³⁻²⁰ The RRKM calculations were performed using the strong-collision approximation to model the collisional vibrational energy transfer process. The conclusions of these earlier papers are subject to question, since it is now generally recognized that the strongcollision approximation provides a very poor picture of collisional energy transfer.²¹ A kinetic master equation offers a much more realistic framework for modeling the pressure dependence of unimolecular rate constants.^{21,22} In addition, collisional vibrational energy transfer in large polyatomic molecules is understood much better than it was a decade ago,²² and solutions to the appropriate kinetic master equations are now available.²³ Hence, we can now apply quenching techniques to problems in photodissociation dynamics with more confidence. These techniques are readily applied to organometallics, since secondary spontaneous dissociation of organometallic photoproducts is extremely common. Indeed, Rayner and co-workers recently used quenching techniques and a simple stepladder form of the master equation to study photodissociation of the Group 6 metal hexacarbonyls.²⁴

In this paper, we use the quenching method combined with a full time-dependent master equation to determine the vibrational energy of the monoalkyl zinc photoproduct formed upon 248 nm photodissociation of three dialkyl zinc compounds: $(CH_3)_2$ Zn, $(C_2H_5)_2$ Zn, and $(n-C_3H_7)_2$ Zn. In an earlier communication on the photodissociation of $(CH_3)_2$ Zn, we showed that the yield of the primary photoproduct, CH₃Zn, increases significantly as the pressure of He increases, with a concomitant decrease in the secondary spontaneous dissociation product, Zn atom.²⁵ This result was attributed to a competition between dissociation and collisional stabilization of the hot CH₃Zn photoproduct, with collisional stabilization becoming more favorable as the He pressure increases. We show here that analogous results are obtained for $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn. Using a numerical solution to the time-dependent master equation that we have described previously,²⁶ we fit the quenching data to obtain the nascent vibrational energy distribution of the monoalkyl zinc photoproduct.

A. Spectroscopy and photochemistry of dialkyl metal compounds

We begin with a brief examination of prior work on the electronic spectroscopy and photochemistry of the dialkyl zincs and the related dialkyls of cadmium and mercury. A more thorough review was published recently.²⁷ The electronic spectra of (CH₃)₂Zn, (C₂H₅)₂Zn, (CH₃)₂Cd, and $(CH_3)_2$ Hg show two partially overlapping broad bands in the deep uv, which were assigned by Chen and Osgood.²⁸ The lower energy band shows little or no discernible structure, while the higher energy band shows diffuse vibrational structure. The spectrum of $(n-C_3H_7)_2$ Zn has not been discussed in the literature, but we found that its spectrum is similar to that of $(C_2H_5)_2$ Zn. Recently, Amirav et al. examined the spectrum of $(CH_3)_2$ Cd in a molecular beam.²⁹ The linewidths of the vibrational structure in the higher energy band narrow to approximately 100 cm⁻¹ at low temperature, consistent with an excited state lifetime of \sim 50 fs. No structure was observed in the lower energy band even at low temperature, but structure in this band could be obscured by a long progression in the low-frequency C-M-C bending mode (~ 140 cm⁻¹ in the ground state³⁰).

It has been known for several decades that uv irradiation of the dialkyl compounds of zinc, cadmium, and mercury in the gas phase yields the corresponding metal atoms,³¹ but the mechanism of the photodissociation process was not known prior to the work of Bersohn and co-workers in 1971.³² They photolyzed (CH₃)₂ Cd in a bulb at low pressure using polarized light from an arc lamp and found that a Cd film formed preferentially on the face of the bulb perpenha

dicular to the electric field vector of the incident light beam. This result shows that the photodissociation process does not involve concerted loss of both methyl groups, since a concerted dissociation process would impart no net momentum to the Cd atom. Strausz and co-workers confirmed the stepwise nature of the photodissociation mechanism by observing the electronic spectrum of CH₃ Zn and CH₃ Cd upon uv irradiation of the respective dimethyl compounds.³³ These spectra have been examined in greater detail recently.³⁴⁻³⁶

From the studies performed to date, we can conclude that uv photodissociation of the dialkyl zinc compounds yields Zn atom by the following mechanism:

$$\mathbf{R}_{2}\mathbf{Zn} \rightarrow \mathbf{R}\mathbf{Zn}^{\dagger} + \mathbf{R}, \tag{1}$$

$$RZn^{\dagger} \rightarrow R + Zn, \tag{2}$$

where R denotes an alkyl group and [†] denotes vibrational excitation. The first and second metal–alkyl bond-dissociation energies for the dialkyl zincs are given in Table I.³⁷ Upon absorption of a 248 nm photon (115 kcal/mol) by the dialkyl zinc compound, the first metal–alkyl bond is broken, leaving 50–60 kcal/mol to be distributed among the product degrees of freedom. The monoalkyl zinc product must retain half of that energy as vibrational excitation for the second metal–alkyl bond to be broken. Photodissociation of the dialkyl zinc compounds at 248 nm does not provide sufficient energy to form any of the products in an electronically excited state.

Additional information on the photodissociation of dialkyl metal compounds comes from ir fluorescence and molecular-beam experiments. Baughcum and Leone³⁸ observed ir fluorescence from the methyl radicals formed in the 248 nm photodissociation of gas-phase $(CH_3)_2$ Hg at low pressure. Fluorescence was observed from the CH₃ umbrella mode (v_2 , 606 cm⁻¹) and the CH antisymmetric stretching mode $(v_3, 3162 \text{ cm}^{-1})$. A line shape analysis of the CH antisymmetric stretch showed that the methyl radical has a rotational temperature of 1200-1500 K. Similar results were obtained by Chu et al. for $(CH_3)_2$ Zn and $(CH_3)_2$ Cd.³⁹ The ir fluorescence experiments do not yield firm conclusions about the primary photodissociation process, however, since methyl radicals are formed via both Eqs. (1) and (2) under the conditions of the experiment. Bersohn and co-workers examined the translational energy distribution of the methyl

TABLE I. Bond dissociation energies for the dialkyl zincs and monoalkyl zincs.

Molecule	DH°RZn-R (kcal/mol)	DH°R-Zn (kcal/mol)
$(CH_3)_2 Zn^a$	63.7 ± 1.5	24.5 ± 4.0
$(C_2H_5)_2Zn^a$	52.4 <u>+</u> 2.0	22.0 ± 4.2
$(n-C_{3}H_{7})_{2}Zn^{b}$	52.4 ± 2.0	22.0 ± 4.2

* Reference 37.

^b Bond dissociation energies in $(n-C_3H_7)_2$ Zn assumed to be equal to those in $(C_2H_5)_2$ Zn. See, S. W. Benson, J. T. Francis, and T. T. Tsokis, J. Phys. Chem. 92, 4515 (1988). radicals formed in the 193 nm photodissociation of $(CH_3)_2 Zn$ and $(CH_3)_2 Cd$ in a molecular beam.⁴⁰ They found that the translational energy distribution was relatively cool. Again, two methyl radicals are formed under the conditions of the experiment, but two separate translational energy distributions were not resolved. Vernon and coworkers performed molecular beam photodissociation experiments on $(C_2H_5)_2 Zn$ at 193 and 248 nm, but because $[(C_2H_5)_2Zn]_n$ clusters were formed extensively in the molecular beam expansion, quantitative product translational energy distributions were not obtained for photodissociation of $(C_2H_5)_2Zn$ monomer.⁴¹

The studies described above provide a good picture of the photodissociation mechanism, but the dynamics of the primary photodissociation process have not been unequivocally established. In the experiments described below, we attempt to understand the dynamics of the primary photodissociation process by determining the vibrational energy distribution of the monoalkyl zinc radical formed as the primary photoproduct in the 248 nm photodissociation of $(CH_3)_2Zn$, $(C_2H_5)_2Zn$, and $(n-C_3H_7)_2Zn$.

II. EXPERIMENT

Dimethyl zinc and diethyl zinc were purchased from Alfa in the highest available purity and were used as received. Dipropyl zinc was prepared by reaction of *n*-propyl iodide with zinc/copper powder (Alfa) followed by vacuum distillation. Analysis by gas chromatography/mass spectrometry showed the product to be 98% pure, with n-propyl iodide as the only detectable impurity. For the photodissociation experiments, the dialkyl zinc compounds were transferred to a Teflon-lined stainless steel bubbler fitted with VCR fittings. To avoid cross contamination when changing the dialkyl zinc compound, the bubbler was emptied by evacuation and then was opened and cleaned with successive rinses of 10% aqueous HCl, deionized water, and isopropanol. The bubbler was then thoroughly vacuum dried prior to use. Caution: the dialkyl zinc compounds flame upon exposure to the atmosphere.

Photodissociation of the dialkyl zinc compounds was performed in a flow cell constructed from a stainless steel cube with 1.33 in. diameter vacuum flanges on each face (see Fig. 1). Two of the opposing side faces of the cube were fitted with 3/4 in. o.d., 2 in. long stainless steel tubes to which quartz windows were attached at Brewster's angle via Viton O rings. A quartz window, which served as the fluorescence viewport, was attached to one of the remaining side faces of the cube, while the face of the cube opposite the fluorescence viewport was blanked off. A valve leading to a vacuum system was attached to the top face of the cube, while the dialkyl zinc bubbler was attached to the bottom face. The cell was evacuated between photolysis runs to a base pressure of 1×10^{-6} Torr using a diffusion pump. During a photolysis run, the cell was continuously pumped with a mechanical pump. Helium carrier gas was used to deliver the dialkyl zinc vapor into the cell, with the flow rate controlled by a mass flow controller. The dialkyl zinc flow was held constant throughout all experiments. Buffer gas was admitted to the



FIG. 1. Experimental apparatus.

cell via ports aimed at each Brewster window (to prevent material deposition on the windows), with the flow rate controlled by a second mass flow controller. The buffer-gas pressure was varied by changing the flow rate of the second flow controller, adjusting the opening of the vacuum valve to maintain a linear relation between buffer-gas flow rate and pressure. The buffer-gas flow rate was always at least 50 times greater than the flow rate of the dialkyl zinc compound.

An excimer laser operating on the KrF line at 248 nm was used to dissociate the dialkyl zinc compounds and a Nd:YAG-pumped dye laser was used to detect the products by laser-induced fluorescence (LIF). The lasers were pulsed at 10 Hz. The excimer laser pulsewidth was \sim 20 ns while the dye laser pulse width was ~ 8 ns (FWHM). The excimer and dye laser beams were collinear and counterpropagating. Firing of the excimer and dye lasers was synchronized by controlling the delay between triggering of the excimer laser thyratron and the Nd:YAG laser Q switch. Due to jitter in the firing of the excimer laser, the delay could not be controlled to better than 20 ns. The jitter in the delay, combined with the pulse widths of the excimer and dye laser, translates into a temporal resolution of ~ 40 ns. The intensity of the excimer and dye lasers was measured by directing the reflection from a beamsplitter into calibrated power meters (Scientech). The fluorescence intensities and relative yields are corrected for variations in the intensity of the excimer and dye laser beams during a photolysis run.

Zn atom was monitored by pumping a two-photon transition at 66 037.6 cm⁻¹ from the ground state to the $4s6s^{1}S$ state.42 Fluorescence was observed from the $4s6s^1S \rightarrow 4s4p^1P^0$ transition at 19 292.2 cm⁻¹. CH₃Zn was monitored by pumping the 0_0^0 band of the $\tilde{A} \,^2 E_{1/2} \leftarrow \tilde{X} \,^2 A_1$ transition at 23 956 cm^{-1, 36,38} Fluorescence was observed from several vibronic bands of the same transition. Fluorescence from Zn and CH₃Zn was dispersed using a 0.32 m monochromator with a 1200 groove/mm grating. Zn atom fluorescence was detected using a photomultiplier tube and boxcar integrator, while CH₃Zn fluorescence was detected using a gated diode array (Princeton Instruments). The temporal resolution of the detection system in each case was 6 ns. The Zn atom LIF intensity was determined by scanning the dye laser through the absorption line and integrating the resulting fluorescence peak. The CH_3Zn LIF intensity was determined at a fixed dye laser wavelength by measuring the height of the resulting fluorescence peaks. The relative intensities of the vibronic bands in the CH_3Zn fluorescence spectrum do not depend on pressure when the dye laser is tuned to the 0_0^0 band,³⁴ so we monitored the strongest band in the fluorescence spectrum.

For Zn, the LIF intensity should vary with the square of the dye laser intensity, since we are pumping a two-photon transition. We found, however that the Zn LIF intensity scaled approximately as $I^{1.6}$ under typical dye-laser operating conditions (3-10 mJ/pulse, 5 mm beam diameter, unfocused), reflecting partial saturation of the transition. No Zn LIF signal was detected in the absence of excimer laser radiation or if the dye laser was fired before the excimer laser. For CH₃Zn, the LIF intensity should vary linearly with the dye-laser intensity, but we found that the CH₃ Zn transition is particularly easy to saturate under our typical dye-laser operating conditions. We therefore expanded the dye laser beam $3 \times$ and stopped the beam down to its original size in order to maintain a linear dependence of the fluorescence signal on dye-laser intensity. No CH₃ Zn fluorescence signal was detected if the excimer laser beam was blocked or if the dye laser was fired prior to the excimer laser.

To properly interpret the pressure dependence of the photoproduct LIF signals, we must ensure that the dialkyl zinc partial pressure remains constant as the buffer-gas pressure is varied. We could not directly ensure this by monitoring the product LIF signals at various buffer-gas pressures, since the product yields vary with pressure. We could determine the relationship between the dialkyl zinc partial pressure and buffer-gas flow rate, however, by performing a different experiment: We monitored the intensity of the Zn LIF signal obtained upon photodissociation of $(CH_3)_2$ Zn at constant buffer-gas pressure, but with varying flow rates of buffer gas. If the flow cell is operating as expected, the $(CH_3)_2$ Zn partial pressure, and thus the Zn LIF signal, should vary inversely with buffer-gas flow rate. The Zn LIF intensity indeed depends inversely on buffer-gas flow rate, as shown in Fig. 2 for a He pressure of 250 Torr. Similar results were obtained at all other pressures examined.

III. RESULTS

A. (CH₃)₂Zn

Figure 3 shows the buffer-gas pressure dependence of the LIF signals observed for Zn and CH_3 Zn upon photodissociation of $(CH_3)_2$ Zn. The intensity of the Zn LIF signal decreases while the intensity of the CH_3 Zn LIF signal increases with rising He pressure. The results shown in Fig. 3 may be understood from the two-step mechanism given in Eqs. (1) and (2) for photodissociation of $(CH_3)_2$ Zn. Collisional vibrational energy transfer from the hot CH_3 Zn photoproduct to the buffer gas competes with Eq. (2), reducing the yield of Zn and increasing the yield of CH_3 Zn.

To ensure that fluorescence quenching does not affect our LIF signal intensities, we measured the fluorescence lifetime vs He pressure for both Zn and CH_3Zn . The fluores-



FIG. 2. Plot of the inverse of the Zn LIF intensity obtained upon photodissociation of $(CH_3)_2$ Zn vs the flow rate of He buffer gas. The He pressure was held constant at 250 Torr. The line represents a least squares fit forced through the origin.

cence lifetime for each species was found to be independent of He pressure to 400 Torr, within experimental error. To ensure that pressure broadening does not affect the atomic Zn LIF signal intensity, we scanned the dye laser through the Zn line and integrated over the resulting peak. It is difficult to assess the effect of pressure broadening on the spectrum of CH₃Zn, but we observed no difference in the spectral line shape of the CH₃Zn transition in the vicinity of the dye-laser wavelength as a function of He pressure to 400 Torr. Also, the CH₃Zn transition is several wave numbers wide due to the presence of many overlapping rotational subbands. We therefore do not believe that the LIF signal intensity for CH₃Zn is affected by pressure broadening.

For Zn, the LIF signal rises to full scale at all pressures within the temporal resolution of the experiment, indicating that the reactions in Eqs. (1) and (2) are completed within



FIG. 3. Yield of $CH_3Zn(\blacktriangle)$ and $Zn(\bullet)$ obtained upon photodissociation of $(CH_3)_2Zn$ vs He buffer gas pressure. Data are normalized to an average total yield of 1.0 (O), represented by the dotted line.

40 ns. In contrast, the CH₃ Zn LIF signal rises to about 15% of full scale within 40 ns, followed by a slow rise to full scale with a time constant in the microsecond regime (see Fig. 4). The results for Zn show that this behavior is not due to slow formation of (CH₃)Zn. Instead, the CH₃Zn signal rises slowly because CH₃ Zn is formed with substantial rovibrational excitation. Since we are pumping the 0_0^0 band of CH₃Zn, only molecules in the vibrational ground state will be excited. (Recent high-resolution spectroscopic results suggest that no sequence bands overlap the 0_0^0 band of $CH_3Zn.^{36}$) Thus, as the CH_3Zn population is collisionally cooled, the LIF signal intensity increases. This explanation is consistent with our observation that the rate at which the LIF signal reaches its maximum value increases with increasing buffer gas pressure. The CH₃ Zn fluorescence signal requires ≥ 100 collisions to reach full scale, suggesting that the slow risetime represents predominantly vibrational, rather than rotational, relaxation. To account for the effect of vibrational excitation on the CH₃Zn LIF signal, all of the pressure-dependence measurements were performed with a delay of 10 μ s between firing of the excimer and dye lasers. With this time delay, the LIF signals for both Zn and CH₃ Zn have reached their maximum intensities and are constant. Only when the delay is extended into the millisecond time regime do the LIF signals begin to decay due to transport of the photoproducts out of the region of the cell sampled by the dye-laser beam.

Since we have accounted for the effects of He pressure on the probability of absorbing the dye-laser beam and on the subsequent emission for both Zn and CH_3Zn , the LIF signal intensity may be taken to be proportional to the relative yield of each species. The absolute yields can then be determined by summing the LIF signal intensities for Zn and CH_3Zn to give a total yield of unity. This normalization is reflected in Fig. 3. Normalizing the data in this manner assumes that the primary photodissociation process is not quenched by He. Given the very fast rate of this process, quenching is extremely unlikely.

Figure 3 shows that $\sim 95\%$ of the CH₃ Zn formed at low pressure undergoes secondary spontaneous dissociation to



FIG. 4. Dependence of the CH_3Zn LIF signal on the delay between firing of the excimer laser and the dye laser. Top: 75 Torr Ar. Bottom: 72 Torr He.

Zn, but at He pressures >400 Torr, more than half of the CH₃Zn is stabilized. Fig. 3 differs somewhat from the data presented in our earlier communication,²⁵ since in that paper, we did not properly account for pressure broadening of the Zn atomic absorption line. As a result, the yield of Zn depends slightly less strongly on He pressure than we presented earlier, and the yield of CH₃Zn at low pressure is slightly smaller than we reported earlier (~5% vs ~20%).

We also examined the pressure dependence of the LIF signals for Zn and CH₃ Zn using Ar as a buffer gas. Quantitative data could not be obtained for the dependence of the Zn yield on Ar pressure, since Zn fluorescence is strongly quenched by Ar. In contrast, the CH₃Zn fluorescence lifetime is not affected by Ar at pressures up to 400 Torr. The CH₃Zn yield vs Ar pressure is shown in Fig. 5. To permit direct comparison of the Ar and He data in Fig. 5, we set the CH₃ Zn yield at 20 Torr of Ar equal to the yield at 20 Torr of He. The Ar pressure dependence is somewhat stronger than the He pressure dependence, indicating that Ar stabilizes CH₃ Zn more strongly than He at equivalent pressures. This conclusion is consistent with the noticeably faster risetime observed for the CH₃Zn LIF signal in the presence of Ar vs He (see Fig. 4). $CH_3 Zn/Ar$ collisions occur at a slower rate than CH₃Zn/He collisions at a given pressure, so on a per collision basis, Ar is the more efficient quencher.

The Zn and CH₃Zn LIF signal intensities vs excimer laser fluence are shown in Figs. 6 and 7, respectively. The data for Zn are fit by a straight line through the origin, indicating that Zn is formed predominantly by single-photon dissociation of $(CH_3)_2Zn$. The fluence dependence of the CH₃Zn LIF signal is also linear at low fluence, but then falls off at higher fluences. The falloff is not due to saturation of the $(CH_3)_2Zn$ transition, given the low laser fluence used in our experiments and the small absorption cross section of $(CH_3)_2Zn$ at 248 nm $(1.1 \times 10^{-19} \text{ cm}^2)$. The falloff may be attributed to secondary photodissociation of CH₃Zn, however. Indeed, Strausz³³ and co-workers observed a series of CH₃Zn absorption bands originating at 274 nm that have been assigned to a vibrational progression in the $\tilde{C}^2A_1 \leftarrow \tilde{X}^2A_1$ band.³⁴ The data presented by Strausz and



FIG. 5. Yield of CH₃Zn vs Ar (\bullet) and He (\blacktriangle) pressure.



FIG. 6. LIF intensity obtained for Zn upon photodissociation of $(CH_3)_2 Zn$ vs excimer laser fluence. The He pressure was 100 Torr. The line represents a least-squares fit forced through the origin.

co-workers does not extend to 248 nm, but the fifth peak in the progression would lie at 248 nm.

We can fit the excimer-laser fluence dependence observed for the CH₃Zn LIF signal using the kinetic expressions appropriate for a sequential two-photon dissociation process.⁴³ The only unknown parameter is the photodissociation cross section of CH₃Zn. Adjusting this cross section to fit the data (see Fig. 7) yields a value of 4.1×10^{-17} cm². Figure 7 shows the fluence dependence expected in the absence of CH₃Zn photodissociation. Our pressure-dependence data for Zn and CH₃Zn were taken at an excimer-laser fluence of 5 mJ cm⁻² pulse⁻¹, where secondary photodissociation of CH₃Zn is minimal.

It is important to note that the excimer-laser fluence dependence observed for the Zn LIF signal differs significantly from that observed for the CH_3Zn LIF signal.



FIG. 7. LIF intensity obtained for CH_3Zn vs excimer laser fluence. The He pressure was 100 Torr. The solid line represents a fit to the data for a sequential two-photon dissociation model, where the photodissociation cross section of CH_3Zn is 4.1×10^{-17} cm². The dashed line represents the behavior expected in the absence of secondary photodissociation of CH_3Zn .

 CH_3Zn is the precursor to Zn, so one would expect the LIF signals for both species to show the same dependence on excimer-laser fluence. The difference can be readily understood, however, if secondary photodissociation of CH_3Zn yields predominantly Zn. In that case, Zn is formed via two pathways; the first shows a weaker than linear dependence on excimer laser fluence [Eq. (2)], while the second shows a stronger than linear dependence on excimer laser fluence [Eq. (1) followed by secondary photodissociation of CH_3Zn]. The result is that the yield of Zn depends approximately linearly on excimer-laser fluence.

At the higher excimer-laser fluences, secondary photodissociation of $CH_3 Zn$ makes an important contribution to the overall yield of Zn. The dependence of the Zn yield on buffer-gas pressure may thus be different at high and low excimer-laser fluences, since the quenching probabilities for secondary spontaneous dissociation and secondary photodissociation of $CH_3 Zn$ may be quite different. Figure 8 shows that the yield of Zn depends slightly more weakly on He pressure at an excimer-laser fluence of 15 vs 5 mJ cm⁻² pulse⁻¹, indicating that secondary photodissociation is quenched more weakly than secondary spontaneous dissociation at a given pressure.

Our results for the 248 nm photodissociation of $(CH_3)_2 Zn$ can be summarized as follows. Absorption of a single 248 nm photon by $(CH_3)_2 Zn$ yields vibrationally hot $CH_3 Zn$; ~95% of the $CH_3 Zn$ population is formed sufficiently hot that it spontaneously dissociates to Zn in <40 ns. In the presence of a buffer gas, collisional vibrational energy transfer stabilizes some fraction of the $CH_3 Zn$ population. The probability of stabilization increases with increasing buffer-gas pressure. At He pressures >400 Torr, $CH_3 Zn$ more efficiently than He at a given pressure. Secondary photodissociation of $CH_3 Zn$ yields predominantly Zn and becomes a significant reaction pathway at higher excimer laser fluences.



FIG. 8. Yield of Zn obtained upon photodissociation of $(CH_3)_2Zn$ at an excimer laser fluence of 5 (\bullet) and 15 (\blacktriangle) mJ cm⁻² pulse⁻¹. The He pressure was 100 Torr.

B. $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn

Buffer-gas quenching experiments identical to those performed for $(CH_1)_2$ Zn were also performed for $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn. The effect of He pressure on the relative yield of Zn obtained from $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn, shown in Fig. 9, is qualitatively the same as that shown in Fig. 3 for $(CH_3)_2$ Zn. Unfortunately, data on the relative yield of C_2 H₂Zn and n-C₃ H₇Zn as a function of buffer-gas pressure were not obtained, since the fluorescence spectrum for these two monoalkyl zinc compounds was not observed. We carefully scanned the dye laser over the spectral region from 23 470-25 480 cm⁻¹ in search of fluorescence from these two monoalkyl zinc species following photodissociation of their respective dialkyl zinc precursors. For CH₃Zn, several vibrational bands of the $\tilde{A}^2 E_{1/2} \leftarrow \tilde{X}^2 A_1$ and $\tilde{A}^2 E_{3/2} \leftarrow \tilde{X}^2 A_1$ transitions are observed in this spectral region.^{34,36} It is possible that all vibrational bands of the $\tilde{A} \leftarrow \tilde{X}$ transition for C₂H₅Zn and *n*-C₃H₇Zn lie outside this spectral region, but this is highly unlikely, given the minimal perturbation of the molecular orbitals involved in this transition upon changing the alkyl group from methyl to ethyl or propyl.³⁴ It is also possible that the photodissociation mech-



FIG. 9. Yield (\textcircledlambda) of Zn obtained upon photodissociation of $(C_2H_5)_2$ Zn (top) and $(n-C_3H_7)_2$ Zn (bottom) vs He pressure. The data are normalized to an extrapolated (Stern-Volmer) yield of unity at zero pressure. The solid line represents the best fit obtained from master equation calculations (see the text). The dotted line represents the fit obtained assuming that the vibrational energy distribution is a Gaussian function with a width (FWHM) of 3000 cm⁻¹. The dashed line represents the fit obtained assuming that the vibrational energy distribution is given by phase-space theory.

anism changes so radically upon going from $(CH_3)_2$ Zn to $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn that the monoalkyl zinc is not formed. This is also highly unlikely, given the qualitatively similar effect of He pressure on the yield of Zn formed via photodissociation of all three compounds. Our report on the formation of ZnH via sequential two-photon dissociation of $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn provides additional evidence that the monoalkyl zinc is the primary photodissociation product for both molecules.44

The absence of fluorescence from C₂H₅Zn and n- $C_3H_7Z_n$ can be attributed to an increased rate of internal conversion relative to CH₃Zn. The rate of internal conversion is proportional to the square of matrix elements of the nuclear kinetic energy operator connecting the upper and lower states.⁴⁵ For CH₃Zn excited to the ground vibrational level of the A state, it can be readily shown that many of these matrix elements vanish for reasons of symmetry. Internal conversion therefore occurs slowly, giving the excited state time to fluoresce. For C_2H_5Zn and $n-C_3H_7Zn$, symmetry places few restrictions on these matrix elements. In addition, the density of accepting vibrational states in the internal conversion process is much higher for $C_2 H_5 Zn$ and $n-C_3 H_7 Zn$ than for CH₃Zn. Internal conversion of electronically excited C₂H₃Zn and n-C₃H₇Zn may therefore occur quickly, resulting in a much lower fluorescence quantum yield. We note that related behavior is observed in the fluorescence of the $n\pi^*$ states of aldehydes.⁴⁶ Internal conversion is much slower, and thus the quantum yield for fluorescence is much higher, for the small, symmetric molecule formaldehyde than for the larger asymmetric aldehydes, such as acetaldehyde and propanal.

For $(CH_3)_2$ Zn, we obtained the absolute yields of Zn and CH₃Zn vs buffer-gas pressure by normalizing to a total yield of unity. The same normalization cannot be performed for $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn, since LIF data are not available for the monoalkyl zinc photoproduct. The normalization shown in Fig. 9 reflects a fit of the Zn data to a Stern-Volmer model, with the yield of Zn chosen to be 100% at zero pressure. This fit is reasonable, given that the yield of Zn obtained from $(CH_3)_2$ Zn is ~95% at zero pressure and that more energy is released to products upon photodissociation of $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn than upon photodissociation of $(CH_3)_2$ Zn (see Table I). Hence, we expect that C_2H_5Zn and $n-C_3H_7Zn$ are formed hotter than CH_3Zn , resulting in a higher yield of Zn from $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn than from $(CH_3)_2$ Zn at zero pressure. The data in Fig. 9 thus accurately represent the relative yield of Zn vs He pressure, but only an estimate to the absolute yield, limited by the accuracy of our assumption that the yield of Zn is 100% at zero pressure.

We found that the Zn LIF signal rises to full scale within the temporal resolution of the experiment at all pressures. We also found that the Zn LIF signal depends linearly on excimer-laser fluence, indicating that coherent two-photon dissociation of $(C_2 H_5)_2$ Zn and $(n-C_3 H_7)_2$ Zn does not contribute significantly to the yield of Zn. These results are identical to those found for Zn formed from $(CH_3)_2$ Zn. As we noted above for $(CH_3)_2$ Zn, however, the linear dependence of the Zn LIF signal on excimer-laser fluence does not rule out secondary photodissociation of the monoalkyl zinc photoproduct. Indirect evidence that $C_2 H_5 Zn$ and $n-C_3 H_7 Zn$ undergo secondary photodissociation comes from a comparison of the relative yield of Zn vs He pressure at high and low excimer-laser fluence. The pressure dependence of the Zn yield is weaker at an excimer-laser fluence of 15 $mJ cm^{-2} pulse^{-1}$ than at 5 $mJ cm^{-2} pulse^{-1}$ for $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn, just as it is for $(CH_3)_2$ Zn. From this, we conclude that secondary photodissociation of $C_2 H_5 Zn$ and $n-C_3 H_7 Zn$ does take place, but that secondary photodissociation is no more important for these species than for CH₃Zn. Additional evidence for the secondary photo dissociation of $C_2 H_5 Zn$ and $n-C_3 H_7 Zn$ may be found in Ref. 44.

Our results for $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn are less complete than those for $(CH_3)_2$ Zn, but in cases where the same experiment could be performed on all three compounds, the results are qualitatively identical. From this, we conclude that the photodissociation process for $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn is analogous to that for $(CH_3)_2$ Zn. Photodissociation of all three dialkyl zinc compounds at increasing buffer-gas pressure results in a decreasing yield of Zn, which we attribute to collisional stabilization of the monoalkyl zinc primary photoproduct.

IV. MODELING OF MONOALKYL ZINC SPONTANEOUS DISSOCIATION

A. RRKM calculations

RRKM calculations on the monoalkyl zincs were based on the standard RRKM equation⁴⁷

$$k(E,J) = \frac{W^{\dagger}(E,J)}{h\rho(E,J)'},$$
(3)

where W^{\dagger} is the internal sum of states for the transition state and ρ is the internal density of states for the reactant. Vibrational contributions to the internal state sums and state densities were computed within the harmonic oscillator approxusing imation the Beyer-Swinehart state-counting algorithm.⁴⁸ The vibrational frequencies for the monoalkyl zincs are largely unknown, but they are readily derived from those of the corresponding alkyl bromide.49,50 The derived frequencies should be quite accurate, since few significant variations are observed among the vibrational frequencies of a given family of substituted hydrocarbons, RX (e.g., C_2H_5F , C_2H_5Cl , C_2H_5Br , and C_2H_5I), except for modes involving substantial deformation of the C-X bond.^{49,50} These deformations will have a lower frequency in the monoalkyl zincs than in the alkyl bromides, since the C-Zn bond strength37 is significantly weaker than the C-Br bond strength.⁵¹ Table II summarizes the vibrational frequencies and rotational constants used in the calculations.

We determined the transition state vibrational frequencies using a procedure that worked well in RRKM calculations on $(CH_3)_2Zn$, $(C_2H_5)_2Zn$, $(CH_3)_2Cd$, and $(CH_3)_2$ Hg.³⁷ In those calculations we found that the highpressure A factor, as well as the temperature- and pressure dependence of the pyrolysis rate constants, could be reproduced by taking the vibrational frequencies of the transition

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TABLE II. Vibrational frequencies and rotational constants for the monoalkyl zincs used in the RRKM calculations.

CH ₃ Zn	C_2H_5Zn	$n-C_3H_7Zn$				
Vibrational frequencies (cm ⁻¹)						
2900 (3)	2900 (5)	2900 (7)				
1400 (2)	1450 (3)	1450 (4)				
1060 (1)	1380 (1)	1350 (2)				
500 (2)*	1100 (2) [*]	1300 (1)				
445 (1)°	950 (3)	1100 (3)*				
	650 (1)	1000 (2)				
	445 (1)°	800 (1)				
	250 (1)	750 (2)				
	200 (1) ^b	445 (1)°				
		300 (1)				
		200 (2) ^b				
		120(1)				
R	otational constants (cm ⁻	¹) ^d				
A,B = 5.239 (5.239)	$A,B = 0.9370 \ (0.8556)$	A,B = 0.8465 (0.759)				
C = 0.2591 (.04383)	C = 0.1046 (0.03480)	C = 0.04877 (0.0258)				

^a Mode involving twist of the carbon atom adjacent to the Zn atom; frequency lowered to 150 cm⁻¹ in the transition state (only one frequency of the group lowered in $C_2 H_5 Zn$ and $n-C_3 H_7 Zn$).

^b Mode involving a skeletal deformation that is lost in the products; frequency lowered to 90 cm⁻¹ in the transition state.

^cC–Zn stretching mode; treated as the reaction coordinate.

^dValues in parentheses are for the transition state. $C_2 H_5 Zn$ and $n-C_3 H_7 Zn$ are taken to be prolate symmetric tops.

state to be the same as those of the reactant, except for the five vibrations that become rotations in the products. Two of these five incipient rotations are derived from C-M-C bends, to which we assigned a frequency of 90 cm⁻¹ in the transition state. The three remaining incipient rotations are derived from higher frequency C-Zn deformations, to which we assigned a frequency of 150 cm^{-1} in the transition state. Note that for the monoalkyl zincs, only two vibrations become rotations in the products, since one of the products is an atom.

The geometry of the monoalkyl zinc was taken to be equivalent to that of the corresponding dialkyl zinc,⁵² except that the C–Zn bond was lengthened to reflect the lower bond dissociation energy of the monoalkyl zinc. Using the bondenergy/bond method,⁵³ we derived a C–Zn bond length of 2.2 Å for the monoalkyl zincs. The molecular geometry was assumed to be unchanged on going from reactant to transition state, except for the length of the breaking C–Zn bond.

The internal rotors of C_2H_5Zn and $n-C_3H_7Zn$ were included as active degrees of freedom in the state-density and state-sum calculations. Internal rotors are typically treated as classical free rotors in RRKM calculations,⁴⁷ but this can lead to significant errors in the rate constants at energies close to the activation energy.⁴⁸ We treated the internal rotors as harmonic oscillators, since this is more accurate at the relatively low energies of interest in the monoalkyl zinc calculations.⁴⁸

For a symmetric top, the rotational degree of freedom associated with the top axis is an active degree of freedom, since it exchanges energy with the degenerate vibrational modes via coriolis coupling.⁴⁷ CH₃ Zn is a prolate symmetric top, while C_2H_5Zn ($\kappa = -0.980$) and $n-C_3H_7Zn$

 $(\kappa = -0.996)$ are near-prolate tops. Consequently, we treated the rotation associated with the top or near-top axis as an active degree of freedom for all three molecules. The two remaining rotations are inactive, but these rotations affect k(E,J) by altering the centrifugal barrier.⁴⁷ This effect was included via the *J*-averaging method of Smith and Gilbert.⁵⁴ The transition state was located by canonical variation.⁵⁴

The uncertainty in the vibrational frequencies and molecular geometries of the monoalkyl zincs lends some uncertainty to the RRKM calculations, but we note that the highpressure A factors computed at 295 K for dissociation of CH_3Zn (log A = 14.7), C_2H_5Zn (log A = 14.4), and n- C_3H_7Zn (log A = 14.2) are quite reasonable. They compare favorably with estimates by O'Neal and Benson of the high-pressure A factors for dissociation of related alkyl and aryl bromides.⁵⁵ Troe and co-workers have previously shown that if the vibrational frequencies chosen for an RRKM calculation reproduce the high-pressure A factor for the reaction, the exact choice of frequencies is not critical.⁵⁶ We thus expect that our RRKM rate constants are accurate to within a factor of 2.

B. Time-dependent master equation

To model the quenching process in the monoalkyl zincs, the RRKM rate constants must be combined with a timedependent master equation to describe the competition between spontaneous secondary dissociation and collisional energy transfer. We have previously described the time-dependent master equation and its solution in photochemical quenching problems.²⁶ Denoting the monoalkyl zinc species as A, the time-dependent master equation appropriate to the problem at hand is

$$\frac{dA(E,t)}{dt} = A(E,0)\phi(E)dE + \omega \int_0^\infty P(E,E')A(E',t)dE' - \omega A(E,t) - k(E)A(E,t).$$
(4)

The first term on the rhs of Eq. (4) defines the concentration and vibrational energy distribution of A created by photodissociation at t = 0, the second and third terms define the rate of inelastic collisions between the monoalkyl zinc and a buffer gas, and the fourth term defines the rate of spontaneous dissociation of the monoalkyl zinc. The meaning of the variables and their values are given below.

 $\phi(E)dE$ is the probability that photodissociation of X yields A with internal energy between E and E + dE. This function is the differential form of the vibrational energy distribution for the monoalkyl zinc, and is thus treated as an adjustable function. $\phi(E)dE$ is normalized to the overall quantum yield of the reaction, which we take to be unity.

 ω is the collision rate between A and the buffer gas. We employed Lennard-Jones collision rates calculated using the parameters defined in Table III. For the collision diameters and Lennard-Jones interaction parameters of the monoalkyl zinc, we used the values for the corresponding alkyl bromides.⁵⁷ The Lennard-Jones collision rates differ little from hard-sphere collision rates, so errors in the interaction parameters will not have a significant effect on the master equation calculations.

 TABLE III. Parameters used to calculate the Lennard-Jones collision rates for the monoalkyl zincs.

Molecule	Diameter (Å)	Interaction parameter (K)	
CH ₃ Zn	4.31	416	
C ₂ H ₃ Zn	4.86	455	
n-C, H, Zn	5.32	485	
He	2.55	10	

k(E) is the J-averaged RRKM rate constant for dissociation of A. The energy grain size was 100 cm⁻¹.

P(E',E) is the normalized probability that a single collision transforms A(E) into A(E').²³ Theories of collisional vibrational energy transfer are not yet sufficiently well developed for polyatomic molecules to yield a general functional form for P(E',E), so a suitable mathematical model for P(E',E) must be specified. A common model, and the one we use in this paper, is the exponential-down model.²³

$$P(E',E) = \frac{1}{N(E)} \exp\left(-\frac{E-E'}{\alpha(E)}\right), \quad E \ge E', \qquad (5)$$

where N(E) is a normalization factor and $\alpha(E)$ is a parameter with units of energy that determines the average quantity of vibrational energy transferred per collision. The value of $\alpha(E)$ can be determined from direct measurements, as have been performed on several polyatomic molecules,²² but data of this kind are not available for the monoalkyl zincs. Semiquantitative data on the rate of thermalization of CH₃Zn are available, however, from Fig. 4. These data do not give $\alpha(E)$ directly, since the initial energy distribution of CH₃Zn is not known nor are the Franck-Condon factors required to translate the LIF signal intensity into a vibrational temperature. We thus calculated $\alpha(E)$ for each choice of $\phi(E)$ such that the time required to reach thermal equilibrium is reproduced. Data similar to that in Fig. 4 are not available for $C_2 H_5 Zn$ and $n-C_3 H_7 Zn$, but recent studies indicate that the quantity of vibrational energy removed per collision by a given buffer gas does not vary greatly from one molecule to the next.⁵⁸ Hence we used Fig. 4 to determine $\alpha(E)$ for all the monoalkyl zincs.

Figure 4 provides only a semi-quantitative measure of $\alpha(E)$, since we do not know how the quantity of energy transferred per collision varies with energy. Direct measurements indicate that for large molecules like azulene,⁵⁸ this quantity is linearly proportional to E, while for small molecules like CS₂,⁵⁹ it is proportional to E^2 . For intermediate size molecules like CF₃I,⁶⁰ it depends approximately on $E^{1.5}$. We calculated $\alpha(E)$ assuming a dependence of $E^{1.5}$ for the monoalkyl zincs.

C. Fits to the quenching data for CH_3Zn , C_2H_5Zn , and *n*- C_3H_7Zn

The results obtained from the RRKM calculations and the time-dependent master equation were used to fit the quenching data of Figs. 3 and 9. The fits were performed by choosing a distribution function $\phi(E)$ and then deriving $\alpha(E)$ as described above. The time-dependent master equation was then solved²⁶ to obtain the yield of monoalkyl zinc at several pressures from 0-400 Torr. This procedure was repeated until the calculated quenching curve reproduced the data.

A variety of vibrational energy distribution functions was used in the fitting procedure, including Boltzmann, Gaussian, and Poisson functions. For C_2H_3Zn and $n-C_3H_7Zn$, we found that our quenching data could be reproduced only by assuming a very narrow vibrational energy distribution. The exact shape of the function is not critical. For C_2H_5Zn , a good fit to the data is obtained by representing $\phi(E)$ as a Gaussian function with a full-width at halfmaximum (FWHM) of 500 cm⁻¹ centered at 7600 cm⁻¹, while for $n-C_3H_7Zn$, a good fit is obtained for a Gaussian function with a FWHM of 1250 cm⁻¹ centered at 9200 cm⁻¹ (see Fig. 9). For comparison, a fit is also shown in Fig. 9 for C_2H_5Zn and $n-C_3H_7Zn$ using a broader Gaussian distribution (FWHM = 3000 cm⁻¹). The fit is clearly poorer.

The narrow vibrational energy distribution functions we used to fit the quenching data for $C_2 H_5 Zn$ and n- $C_3 H_7 Zn$ may be compared with distribution functions derived from phase-space theory (PST)⁶¹ and separate statistical ensemble theory (SSE),⁶² both of which have been used successfully to compute product rovibrational and translational energy distributions in photodissociation processes. The input to the calculations is summarized in Tables II and IV. The vibrational energy distributions obtained from PST and SSE are very broad and are nearly Gaussian in shape, with energy maxima and widths given in Table V. Figure 9 shows that the PST and SSE distributions provide a very poor fit to the data.

TABLE IV. Vibrational frequencies for the alkyl radicals and rotational constants for the dialkyl zincs and alkyl radicals used in the PST and SSE calculations.

$R = CH_3$	$R = C_2 H_5$	$R = n - C_3 H_7$
-	Vibrational frequencies (cm ⁻¹)*	
3162 (2)	3112 (1)	2950 (7)
3044 (1)	3033 (1)	1450 (4)
1396 (2)	2987 (1)	1350 (2)
617 (1)	2920 (1)	1300 (1)
	2842 (1)	1100 (2)
	1462 (1)	1000 (1)
	1440 (1)	900 (1)
	1427 (1)	700 (2)
	1366 (1)	530(1)
	1138 (1)	300 (1)
	948 (2)	200 (2)
	713 (1)	
	540 (1)	
	193 (1)	
	Rotational constants (cm ⁻¹) ^b	
RZn: 0.706	RZn: 0.221	RZn: 0.126
R.737	R 1 21	R: 0.428

^aFrequencies for CH₃ from A. Snelson, J. Phys. Chem. **74**, 537 (1970), for C_2H_5 from J. Pacansky and B. Schrader, J. Chem. Phys. **78**, 1033 (1983). Frequencies for *n*-C₃H₇ extrapolated from those for C_2H_5 , C_2H_5 Br (Ref. 50), and *n*-C₃H₇Br (Ref. 49). ^bGeometric mean (ABC)^{1/3}.

TABLE V. Energy maximum and width (FWHM) of the vibrational energy distributions computed via PST and SSE theory.

Molecule	PST		SSE	
	Maximum (cm ⁻¹)	Width (cm ⁻¹)	Maximum (cm ⁻¹)	Width (cm ⁻¹)
CH ₃ Zn	7 800	8200	9 200	7500
C_2H_5Zn	10 800	7600	11 200	7800
$n-C_3H_7Zn$	11 100	7000	9 000	7600

Quenching curves were also calculated for CH_3Zn , but we were not able to reproduce the data using any reasonable distribution function, including very narrow Gaussian distributions and the distributions obtained from PST and SSE theory. The effect of buffer-gas pressure on the spontaneous dissociation of the CH_3Zn photoproduct is much stronger than that predicted by our calculations.

V. DISCUSSION

The master equation fits to the monoalkyl zinc quenching data yield two surprising results: (1) The quenching curves for $C_2 H_5 Zn$ and $n-C_3 H_7 Zn$ can be reproduced only if the nascent vibrational energy distribution of the monoalkyl zinc photoproduct is hot and is much narrower than that predicted by statistical theories of energy partitioning; (2) The quenching data for CH₃Zn cannot be fit using any vibrational energy distribution, narrow or otherwise. We begin by focusing on the results for $C_2 H_5 Zn$ and $n-C_3 H_7 Zn$ and then on the results for CH₃Zn.

A. Quenching of C₂H₅Zn and *n*-C₃H₇Zn

Before we can conclude that the nascent vibrational energy distributions of the C₂H₅Zn and n-C₃H₇Zn photoproducts are indeed narrow, we must be certain that the master equation results are reasonable. In fact, it would be possible to fit the quenching data for C₂H₅Zn and n-C₃H₇Zn using a much broader nascent vibrational energy distribution if we have grossly underestimated the quantity of energy transferred per collision from the monoalkyl zinc to the buffer gas. For the vibrational distributions used to obtain the best fits in Fig. 9, \sim 90 cm⁻¹ is transferred per collision at $E = 20\ 000\ \text{cm}^{-1}$, while \sim 30 cm⁻¹ is transferred per collision at $E = 10\,000$ cm⁻¹. These values compare very favorably with values measured at similar energies for many molecules.^{22,58} To fit our quenching data using the statistical vibrational energy distribution functions obtained from PST or SSE would require the energy transferred per collision to be > 35 times higher for $n-C_3 H_7 Zn$ and > 100 times higher for $C_2 H_5 Zn$.

It would also be possible to fit the quenching data for C_2H_5Zn and n- C_3H_7Zn using the PST or SSE vibrational energy distributions if we have overestimated the values of k(E) for Eq. (2) by a factor of ~ 30 for n- C_3H_7Zn and a factor of ~ 100 for C_2H_5Zn . We do not believe that our RRKM calculations could be in error by such a large factor, given that the k(E) values yield proper high-pressure A factors. Large errors in k(E) can arise, however, if the funda-

mental statistical assumption of RRKM theory, i.e., that internal vibrational relaxation (IVR) occurs at a rate much faster than the rate of reaction, does not apply to C_2H_5Zn and $n-C_3$ H₇Zn. While this explanation cannot be unequivocally dismissed, we note that $n-C_3H_7Zn$ is a relatively large molecule with several low-frequency vibrational modes and correspondingly high vibrational state a density $(1.1 \times 10^{5}/\text{cm}^{-1})$ at the activation energy for dissociation). IVR in n-C₃H₇Zn would be expected to occur in the picosecond or faster time regime,⁶³ while the k(E) values for dissociation of n-C₃H₇Zn are $\leq 10^9$ s⁻¹. IVR is more likely to might compete with dissociation in $C_2 H_5 Zn$, since the k(E)values for $C_2 H_5 Zn$ are higher by a factor of 5 to 8 than those for n-C₃H₇Zn and IVR in molecules with comparable vibrational state densities $(1.0 \times 10^3/\text{cm}^{-1})$ at the activation energy for dissociation) requires on the order of 10–100 ps.⁶³ We were equally successful in fitting the quenching data for C_2H_5Zn and *n*- C_3H_7Zn , however, and a narrow vibrational energy distribution was required to fit the data in each case. Given the qualitatively similar conclusions of our



FIG. 10. Cross section taken along the breaking C-Zn bond of the potential energy surfaces involved in photodissociation of the dialkyl zincs.

RRKM/master equation fits for both C_2H_5Zn and $n-C_3H_7Zn$, we do not believe that RRKM theory provides inaccurate rate constants for either species.

In fitting the quenching data for $(C_2H_5)_2Z_n$ and $(n-C_3H_7)_2Z_n$, we assumed that the yield of Zn is unity at zero pressure. This is a reasonable assumption, given that the yield of Zn formed from $(CH_3)_2Z_n$ is ~95%, but relaxing this assumption does not alter our conclusions. If we assume that the yield of Zn at zero pressure is 75%, rather than 100%, the best fit to the quenching data requires a vibrational energy distribution that is somewhat broader (~3×) and shifted to lower energies (by~300 cm⁻¹) than the distribution function used to obtain the best fit in Fig. 9. Even these functions are much narrower than those predicted by PST or SSE, however.

We now turn to a discussion of the photodissociation pathways available in the dialkyl zincs to rationalize the hot, narrow vibrational energy distribution of the monoalkyl zinc photoproducts. Figure 10 shows a one-dimensional cross section, taken along the breaking C-Zn bond, of the potential-energy surfaces involved in photodissociation of the dialkyl zincs. The diagram is constructed from the valence electron model of Chen and Osgood,²⁸ noting that the symmetries of $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn are much lower than the symmetry of the quasitriatomic molecule they considered. Interaction of the ground state monoalkyl zinc with a ground state alkyl radical creates two states: the bound singlet ground state of the dialkyl zinc and a repulsive triplet state. Within the highest symmetry maintained along the reaction coordinate (C_s) , both states are totally symmetric (A'). Interaction of the excited monoalkyl zinc with a ground state alkyl radical creates two quasibound (metastable) singlet states, which give rise to the two transitions observed in the uv spectrum of the dialkyl zincs.²⁸ The symmetry of the lower energy excited state is A' while the symmetry of the higher energy excited state is A". Neither excited state can dissociate directly to ground state products. Hence, dissociation must involve internal conversion to the ground state or intersystem crossing to the repulsive triplet state.

Numerous examples are known of photoprocesses that involve reaction of a hot ground state formed via internal conversion. The reaction rates can be very adequately modeled by RRKM theory^{64,65} or variational transition-state theory,⁶⁶ where one assumes that the initially prepared distribution of vibronic states evolves into a statistical distribution before the molecule fragments. For small molecules that dissociate via this pathway, such as ketene^{64,67} and NCNO,⁶² measurements of the product rovibrational state distributions can be very adequately modeled by PST or SSE. Consequently, we conclude that photodissociation of the dialkyl zincs does not proceed via the internal conversion mechanism, but rather via intersystem crossing onto the repulsive triplet potential surface.

To understand the intersystem crossing process, the simple picture of Fig. 10 is inadequate. Both the excited singlet state and the repulsive triplet state are complicated polydimensional potential surfaces that are functions of all nuclear coordinates. Because of the proximity of the two states, accidental degeneracies (zero-order level of approximation) are likely at a number of positions of the nuclear coordinates. Strong spin-orbit interaction between these states is to be expected in the regions of accidental degeneracy because both states belong to the same symmetry species and because Zn is a relatively heavy element. Accidental degeneracies that lie within the Franck-Condon region sampled by optical excitation from the ground state thus provide a doorway for crossover from the excited singlet state to the repulsive triplet state. Actually, the continuous nature of the absorption band suggests that the crossover occurs in less than one vibrational period, so it is more precise to represent the optically prepared state as an admixture of the zero-order excited singlet and repulsive triplet states, with the excited singlet state carrying the oscillator strength of the transition from the ground state.

As the fragments separate from one another on the repulsive triplet hypersurface, vibrational excitation will be derived predominantly from the large geometry changes that occur during the transition from reactant to product: The C–Zn bond in the monoalkyl zinc fragment lengthens considerably (~0.3 Å), while the geometry about the α carbon in the alkyl radical fragment changes from tetrahedral to trigonal. Other less dramatic geometry changes also occur. In addition, part of the translational energy of recoil will be converted into internal energy of the products, since the recoil force is not exerted on all atoms equally.

Based on this picture of the dissociation process, we propose the following model to account for the hot, narrow vibrational excitation of the monoalkyl zinc product. Because optical excitation prepares an excited state that is an admixture of a quasibound (metastable) singlet state and a repulsive triplet state, the reactant is placed on the repulsive hypersurface within a very specific region of phase space, defined by the wavelength of the photon source and the overlap of two sets of matrix elements: the Franck-Condon matrix elements connecting the ground state with the excited singlet state and the spin-orbit matrix elements connecting the excited singlet state and the repulsive triplet state. The products thus begin to separate with a well-defined recoil velocity from a well-defined initial geometry similar to the geometry of each product within the ground state dialkyl zinc reactant. This produces a hot monoalkyl zinc fragment with a narrow vibrational energy distribution, much narrower than expected from a statistical dissociation process, where all regions of phase space are equally accessible.

B. Quenching of CH₃Zn

For CH₃Zn, we must explain why the observed quenching probability is much higher than that calculated for any CH₃Zn vibrational energy distribution. The calculated quenching probability could be increased by increasing $\alpha(E)$ or decreasing k(E), but as we indicated in our discussion of $(C_2H_5)_2Zn$ and $(n-C_3H_7)_2Zn$, it is doubtful that our $\alpha(E)$ values are in serious error. That shifts the focus onto the k(E) values calculated by RRKM theory as a possible source of the problem.

As we pointed out earlier, RRKM theory assumes that the rate of IVR is faster than the rate of reaction. The success of RRKM theory attests to the validity of that assumption in most cases. Very few experiments that demonstrate the breakdown of this assumption have withstood close scrutiny, but probably the best examples come from the work of Bauer and co-workers.⁶⁸ In studying isomerization reactions of relatively small molecules over very low activation barriers, they found that RRKM theory could not be used successfully to model the pressure dependence of the rate constant. They argued that RRKM theory fails due to the very low state density of the reactant, $\sim 10/\text{cm}^{-1}$ in the vicinity of the activation barrier. At such low state densities, the rate of IVR will not be fast, but the calculated RRKM rate constant may be very fast, since k(E) depends inversely on the vibrational state density of the reactant [see Eq. (3)]. We note that the vibrational state density of CH₃Zn is also ~ 10 per cm⁻¹ at the activation barrier. We thus attribute our lack of success in fitting the quenching data for CH₃Zn to the inadequacy of RRKM theory in modeling the rate constants for dissociation of CH₃Zn.

Since we cannot model the quenching data for CH_3Zn , we do not have quantitative information on its nascent vibrational energy distribution. We can be certain, however, that PST does not provide a completely adequate picture, since it predicts a Zn yield of 76% upon photodissociation of $(CH_3)_2Zn$ in the absence of collisions. This number does not depend on the accuracy of a calculated k(E) value, but merely reflects the fraction of the CH_3Zn population with energy in excess of the CH_3 -Zn bond dissociation energy. The measured yield of Zn at low pressure is ~95%. This higher yield is consistent with a relatively narrow, hot vibrational distribution for CH_3Zn . We thus conclude that the nascent vibrational distribution for CH_3Zn may be similar to that found for C_2H_5Zn and n- C_3H_7Zn .

VI. CONCLUSION

Photodissociation of $(CH_3)_2 Zn$, $(C_2H_5)_2 Zn$, and $(n-C_3H_7)_2$ Zn was examined at 248 nm in the presence of He buffer gas. For each molecule, the yield of Zn is substantially reduced by increasing the He pressure from 0-400 Torr. This result was attributed to collisional cooling of the hot monoalkyl zinc photoproduct, thereby reducing the probability that this species will spontaneously dissociate to Zn atom and an alkyl radical. Using RRKM theory in conjunction with a time-dependent master equation to model the competition between collisional stabilization and spontaneous dissociation of the monoalkyl zinc photoproduct, we fit the quenching data for each molecule treating the nascent vibrational energy distribution of the monoalkyl zinc as an adjustable function. For $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn, we found that the quenching data could be fit only if the vibrational energy distribution is taken to be hot and relatively narrow, much narrower than predicted by phase-space theory. To account for this result, we proposed that $(C_2H_5)_2$ Zn and $(n-C_3H_7)_2$ Zn photodissociate via excitation to a state this is best described as an admixture of a metastable excited singlet state and a repulsive triplet state. Optical excitation places the reactant on the repulsive hypersurface within a very specific region of phase space, with a geometry similar to that of the ground state. Because the monoalkyl zinc and

alkyl radical products separate from a well-defined initial geometry very different from their equilibrium geometries, the products are formed with a hot, narrow vibrational energy distribution. Although we were able to fit the quenching data for $(C_2 H_5)_2 Zn$ and $(n-C_3 H_7)_2 Zn$, we could not fit the quenching data for $(CH_3)_2 Zn$. This result was attributed to the inability of RRKM theory to model the rate constant for dissociation of $CH_3 Zn$, which has a very low vibrational state density and thus does not undergo rapid intramolecular vibrational energy redistribution.

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