

coupling of the gas-phase methyl radicals, which are produced mainly by the reaction of CH_4 with active $[\text{Li}^+\text{O}^-]$ centers on MgO . One cannot exclude the additional formation of methyl radicals through branching gas-phase chain reactions. An unusual feature of this reaction system is that both the C_2 selectivity and the CH_4 conversion increase with increasing temperatures up to ca. 700°C . One of the dominant pathways which leads to un-

desirable products of CO and CO_2 is the reaction of $\text{CH}_3\cdot$ with surface O^{2-} ions; therefore, low surface areas favor high C_2 selectivities. The Li/MgO system is a new type of oxidation catalyst which does not contain metal ions having a variable oxidation state.

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Infrared Photochemistry of Tetramethyldioxetane. 2. The Nature of Electronically Excited Products

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Abstract: The decomposition of tetramethyldioxetane (TMD) following either overtone excitation or infrared multiple photon excitation (IRMPE) under low-pressure conditions is discussed and compared to recent results obtained upon UV photoexcitation of acetone vapor. It is shown that the results are consistent with a mechanism by which IR excitation of TMD results in producing electronically excited acetone, which may be considered as a mixed state containing contributions from both the singlet and the triplet states.

The chemiluminescent decomposition of tetramethyldioxetane (TMD) has been studied extensively in liquid solutions¹⁻⁴ and to a somewhat lesser extent in the gas phase. The reaction seems to be well characterized kinetically and in thermal systems an Arrhenius expression of the type $k(T) = A_0 \exp(-E_a/RT)$ fits the unimolecular decay rates reasonably well, with $A_0 = 10^{13} \text{ s}^{-1}$ and E_a in the range of 24-26 kcal/mol. Low-pressure vapor-phase measurements, using overtone excitation (OTE)⁵ and infrared multiphoton excitation (IRMPE),^{6,7} can be interpreted by using a statistical model with $k(E)$, the energy-dependent decomposition rate constant, calculable from the RRKM theory.^{8,9} Since the reaction results in electronically excited products, it has been argued¹⁰ that it does not lead to the statistically most probable products. This fact is not in conflict with applying RRKM theory to the process as rapid energy redistribution in the vibrationally excited parent molecule, prior to the reaction, is the only basic requirement. We have recently proposed^{7,11} that if vibrational energy is indeed rapidly scrambled, the energy distributions of molecules excited by IRMPE can be estimated by comparison with OTE results.

In this paper we discuss another aspect of the reaction, the nature of the electronically excited product. Most early work on

TMD was performed in liquid solutions under conditions where vibrational relaxation is much faster than the reaction rate or the decay of electronically excited states. On the basis of fluorescence sensitization experiments¹² and on chemical titration methods¹³ it has been concluded that the major product is acetone triplet in its vibrationally relaxed state (T_1^{VR}). The quantum yield has been estimated to range between 30 and 50%,⁴ namely almost quantitative. On energetic grounds, only one of the two product acetone molecules can be electronically excited. Some vibrationally relaxed singlet acetone (S_1^{VR}) is also formed. Its yield is low with estimates ranging between 10^{-5} to 10^{-3} .⁴

Low-pressure vapor-phase work, based on rapid excitation by laser sources,⁶ appeared at first to be at variance with these results. Under these conditions, the time evolution of the system can be studied with 10^{-8} s time resolution. The amount of internal energy in the reacting molecules can be controlled by varying the laser's wavelength (in OTE experiments) or fluence (in IRMPE work). Thus, the rate of the reaction can be varied, as well as the internal energy in the product molecules. Furthermore, the resulting kinetics and emission spectra can be studied in real time.

A complicated kinetic pattern is revealed⁵ with the emission decay being distinctly nonexponential. Overtone results could be approximately reproduced by fitting the observed chemiluminescence (CL) signal intensity, I_{CL} , to the following empirical relation

$$I_{\text{CL}}(t) = -A \exp(-kt) + B \exp(-k_2t) + C \exp(-k_3t) \quad (1)$$

The first term relates to the reaction rate and is strongly dependent on the internal energy in the excited TMD molecules. The second and third terms are due to the decay of two kinetically distinct species, termed by Cannon and Crim⁵ (CC) the fast and slow components. The slow component can be identified with T^{VR} , based on its decay time and emission spectrum. The fast one is clearly not the singlet observed in liquid solution or previous

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gas-phase work. Its decay time is strongly pressure dependent with a quenching rate constant of $5.6 \times 10^6 \text{ s}^{-1} \text{ torr}^{-1}$, namely essentially gas kinetic. Measurements close to zero pressure were hampered by unfavorable signals to noise conditions. Thus the collision free lifetime was estimated to be anywhere between 30 and 200 μs . Even the lower limit was orders of magnitude longer than the reported lifetime of S_1^{VR} in solutions (1.7 ns¹⁴) or in the vapor phase (2.4 ns^{14,15}).

In IRMPE experiments, a very similar kinetic scheme was obtained with use of low laser fluence.¹⁶ The nature of the triplet was further confirmed by O_2 quenching experiments.⁶ At high fluence levels, a new feature emerged. In addition to the decay components discussed above (see eq 1), a very short-lived species is observed. As its lifetime is shorter than the duration of the CO_2 laser used in the experiments (typically 100 ns fwhm), its presence is indicated by a fast spike following closely the time evolution of the laser pulse.¹⁷

Earlier work on this component involved single shot experiments and relatively high pressures (70–150 mtorr). We have now repeated them using much lower pressures (10^{-4} – 10^{-3} torr) and extensive signal averaging. In addition, we have initiated a detailed study of the emission characteristics of acetone at low pressures ($\leq 10^{-3}$ torr).¹⁸ In this work we used a tunable UV laser to excite acetone to the $n\pi^*$ state and followed the decay kinetics with 10^{-8} s time resolution. To our knowledge, no previous extensive study of this nature on acetone has been published. Both bulk and supersonic expanded samples were used. In the latter, extensive rotational and vibrational cooling simplifies the interpretation considerably. The results are reported elsewhere in detail. For the purpose of this paper we summarize the pertinent observations.

At room temperature and an acetone pressure of up to 10^{-3} torr, the emission decay is nonexponential for all excitation wavelengths. A very short-lived (≤ 20 ns) component appears, followed by another with an approximate decay time of a few microseconds. We refer to these components as I and II, respectively. The decay time of the second component τ_{II} is strongly pressure dependent. Quenching rate constants by several collision partners were found to be close or exceeding the gas kinetic rate constant. It follows that upon increasing the pressure, component II merges with component I so that when the pressure exceeds ~ 1 torr a 10^{-8} s decay time is obtained. We find that other decay components appear concurrently having a much smaller amplitude and longer decay times. At high pressures (in the torr range), the dominant species can be identified with T_1^{VR} , based on its lifetime. At intermediate pressures, the decay time is significantly shorter—on the order of 20–40 μs . We term this collision induced component as component III.

Preliminary results on jet cooled acetone indicate a somewhat different behavior. Near the origin, the excitation spectrum consists of well separated vibronic bands.¹⁹ Excitation of these bands, up to an excess energy of about 1000 cm^{-1} (i.e., between 320 and 330 nm), leads to a decay pattern that is nearly exponential.²⁰ The fast decay (component I) is absent or, if present, has a very small amplitude. The decay time is between 1 and 2 μs , depending on excitation energy. At wavelength shorter than 320 nm the excitation spectrum becomes very congested, even in the cold beam. The decay shows an initial spike similar to component I observed at room temperature but with smaller relative amplitude.

In this paper we correlate the low-pressure results pertaining to electronic excitation of acetone by optical and chemical means. The apparent inconsistencies between liquid-phase results and low-pressure work are resolved, and the appearance of a very short

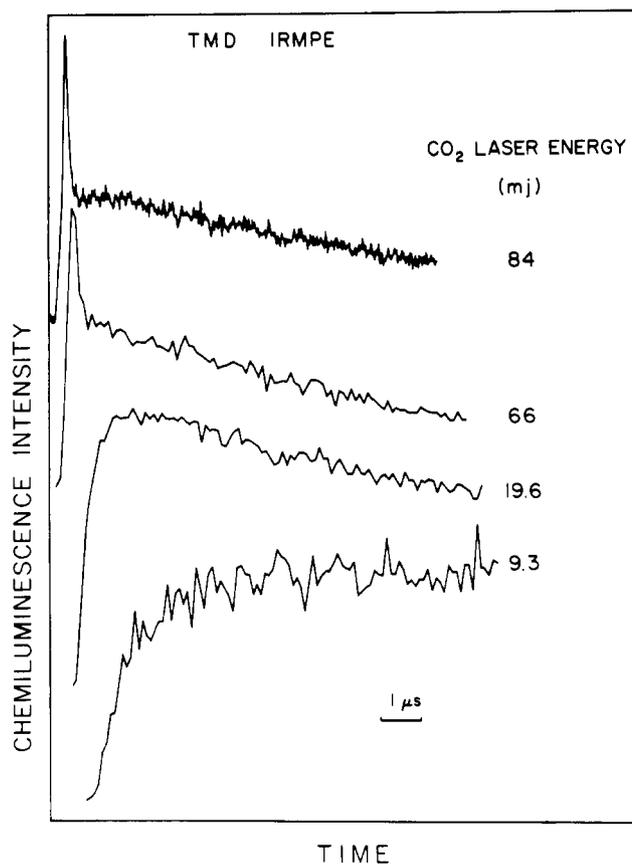


Figure 1. TMD time-resolved chemiluminescence obtained upon IRMPE at various CO_2 laser pulse energies—the first 10 microseconds.

lived emitting species upon increasing the fluence in the IRMPE experiments is accounted for.

We propose that under collision-free conditions, dissociation of TMD leads to a statistical energy disposal into all possible states of electronically excited acetone. A spin selection rule, such as is obtained in optical excitation, does not seem to hold for chemical excitation. The results are consistent with liquid solution work in the high-pressure limit. It is thus probably not necessary to assume the existence of a dark intermediate,⁵ or an excimer state,¹⁷ in order to account for the data.

Results

The experimental setup was described in previous publications.^{7,16} Briefly, the laser-induced decomposition of TMD vapor was studied by irradiating it with a TEA CO_2 laser pulse of about 100 ns fwhm without a "tail". The total chemiluminescence (CL) was imaged on a slit in front of a photomultiplier tube and the resulting signal was digitized with 10 ns per point time resolution and averaged until a satisfactory signal to noise was obtained. A similar procedure was followed for the overtone experiments, except that the source laser was a dye laser pumped by a Nd:YAG laser, with Raman shifting when necessary. The CL time evolution following IRMPE showed a marked dependence on the laser pulse energy. Figure 1 shows representative results obtained at 3 mtorr. Since a fixed geometry was used in all experiments, increasing the laser energy is equivalent to increasing the fluence (energy incident on unit area). At low fluence levels, the signal rise is slow compared to the laser width, and the overall kinetics may be approximately described by the triexponential expression (1). On the time scale used in Figure 1, the slowest decay component is barely observable (see Figure 3). As the fluence is increased, k_1 becomes larger and eventually the signal rise is inseparable from the laser risetime. At still higher fluences one observes a qualitative new feature—the CL displays an intense "spike" that follows closely the temporal profile of the exciting CO_2 laser pulse.

This spike is not observed upon single photon overtone excitation in the wavelength range 660–1200 nm.⁵ Figure 2 shows some

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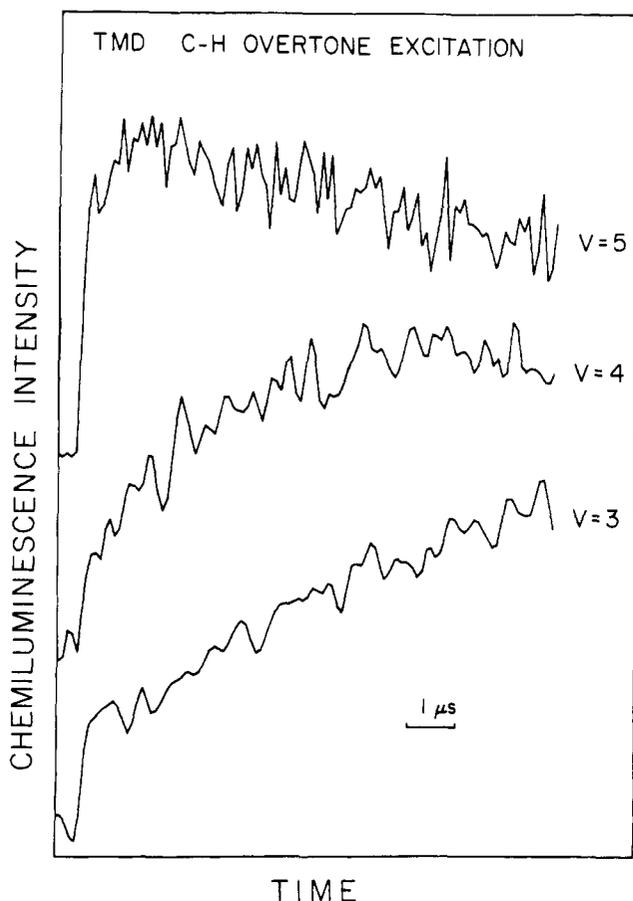


Figure 2. TMD time-resolved chemiluminescence obtained upon OTE to $v = 3, 4,$ and 5 of the CH stretch. The pressure is 3 mtorr.

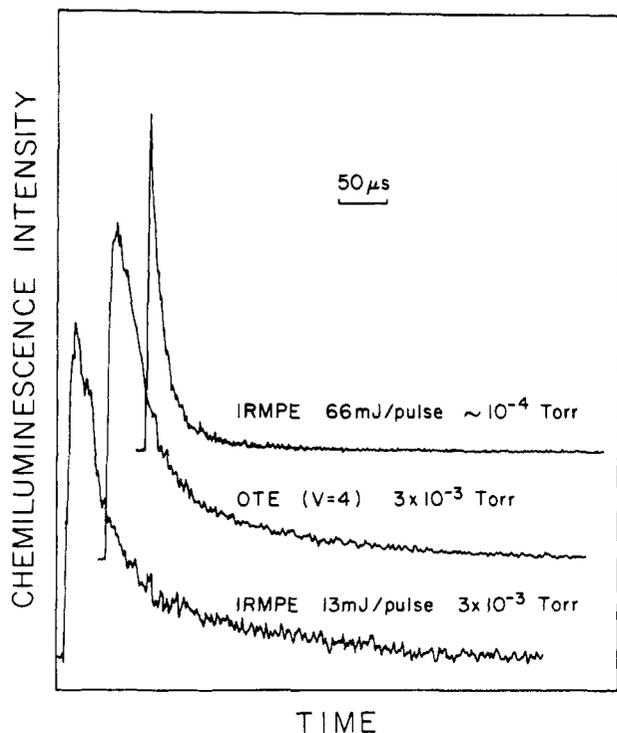


Figure 3. The CL of TMD excited by OTE or IRMPE—full decay history.

typical examples obtained by OTE at 3 mtorr. It is seen that the behavior is very similar to that observed in the low fluence IRMPE experiments.

As clearly shown in both Figures 1 and 2, the CL persists for much longer times than $10 \mu\text{s}$. A second exponentially decaying

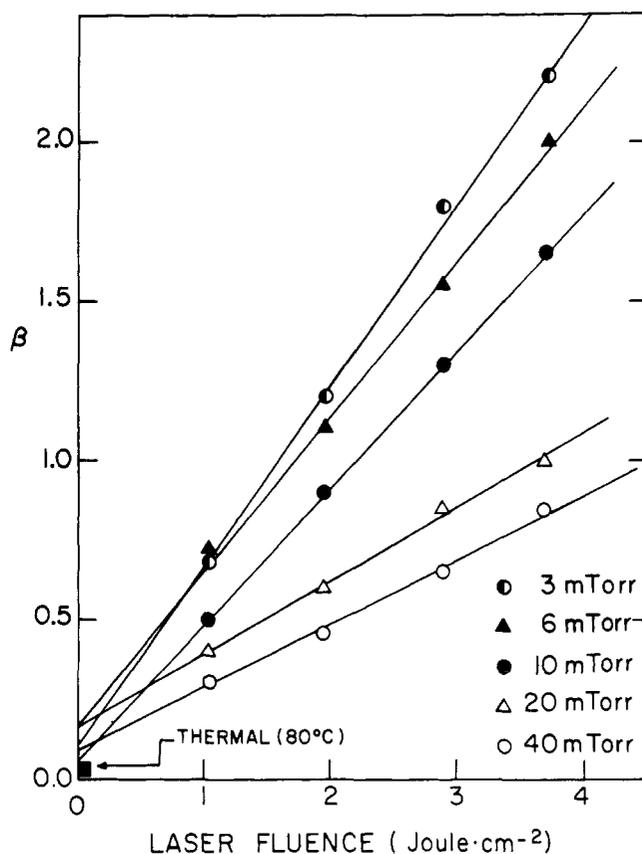


Figure 4. The ratio of the intensity of the long and short components as a function of pressure and laser energy. β is calculated as the ratio between the yield of the fast and slow components obtained by integrating the areas under the respective decay curves.

component, with a lifetime of about $150\text{--}200 \mu\text{s}$, is observed under all excitation conditions. Figure 3 shows some results obtained with IRMPE and OTE excitation. In terms of eq 1, k_2 and k_3 are sufficiently distinct, so as to cause a pronounced break in the decay curve. It has been argued that k_3 relates to the decay of the vibrationally relaxed triplet, T_1^{VR} , whereas k_2 reflects the decay of a yet unassigned excited state, temporarily referred to as X. The relative amplitudes of X and T_1^{VR} , given by B and C (eq 1), respectively, vary with excitation conditions—at low fluence levels (and low overtone bands for OTE) B/C is smaller than for high fluence (high overtone bands). We ran experiments to below 10^{-4} torr (exact determination being impossible with our 1 torr full-scale capacitance manometer). The appearance of two clearly distinct decay components persisted even at the lowest pressure. Upon increasing the pressure beyond 10^{-3} torr, a marked increase in k_2 indicates effective quenching of the emission of X. The overall intensity of the X and T_1^{VR} components may be estimated by integrating the area under the respective decay curves. Figure 4 shows the resulting ratio at different pressures and CO_2 laser pulse energies. It is evident that as the pressure increases, the triplet component becomes dominant.

Recent work on acetone optical excitation conducted in this laboratory bears on the issue at hand. The room-temperature work was reported elsewhere¹⁸ and summarized in the introduction. In addition, we observed the kinetics of the decay of electronically excited acetone cooled by supersonic expansion.¹⁹ The results are discussed in more detail elsewhere²⁰ and only an outline will be given here. Figure 5 shows the decay pattern near the origin, where separate vibronic bands are clearly resolved.¹⁹ The decay time is about 10^{-6} s, but being non-exponential, no definite value can be given to the rate constant. At energies 700 cm^{-1} above the origin, the excitation spectrum becomes congested, even for jet cooled acetone. In this range we observe a similar decay time,

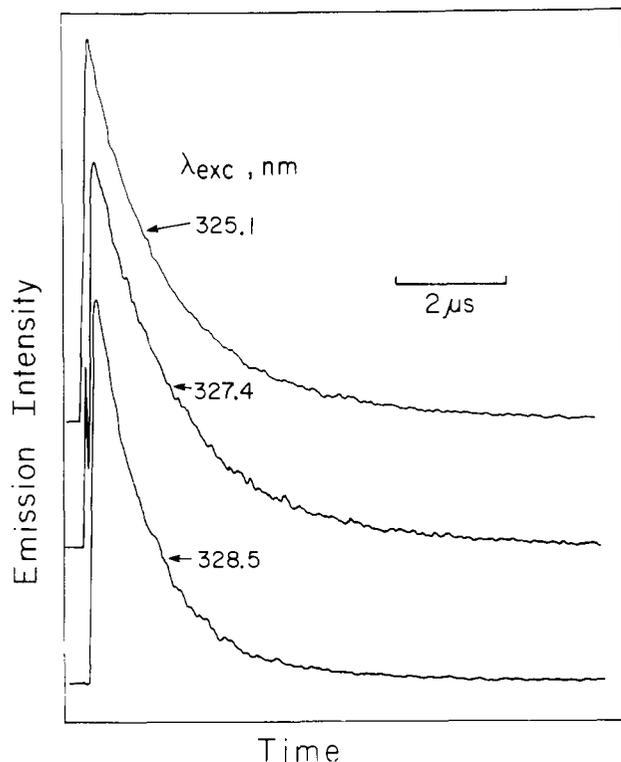


Figure 5. Decay curves for jet cooled acetone, excited to selected energy levels. The assignment of the levels is as follows: 328.5 nm, 0-0 band; 327.4, a single quantum of CH_3 torsion excited; 325.1 nm, two quanta of CH_3 torsion excited. These assignments are from ref 19.

but in addition, a very short-lived component appears, similar to that observed at room temperature.

Discussion

We propose to interpret the low-pressure chemiluminescence kinetics of TMD in terms of the energy level diagram shown in Figure 6. The salient features of the model are the following:

(1) The dissociation of TMD leads to the production of a pair of acetone molecules, one of which is electronically excited.

(2) The available energy is distributed between the two acetone molecules in a statistical manner; namely, most energy is funneled into vibrational degrees of freedom.

(3) A corollary of the previous point: in the electronically excited states, some of the molecules are formed with energy below the origin of the S_1 singlet state—they have mostly a triplet character.

(4) Above the origin of the singlet, a mixed state is formed. There is no preferential formation of S_1 (relative to T_1) in contrast with optical electronic excitation.

(5) As the excitation energy is increased, the relative contribution of the mixed state becomes more important.

(6) The "spike" observed at very high fluence levels in the IRMPE experiments is due to emission from highly excited acetone singlet, whose lifetime is very short compared to the CO_2 laser pulse width.

(7) Collisions cause vibrational relaxation and intersystem crossing so that at high pressure and in liquid solution, the dominant product is the thermalized triplet.

Optical Excitation of Acetone. Intersystem crossing (ISC) in carbonyl compounds is known to be quite efficient.²¹ In the case of acetone it is reported that upon excitation of the $n\pi^*$ band, an almost quantitative conversion to the triplet takes place.²² These results were obtained in condensed phases, or in the vapor phase when the collision frequency was high.

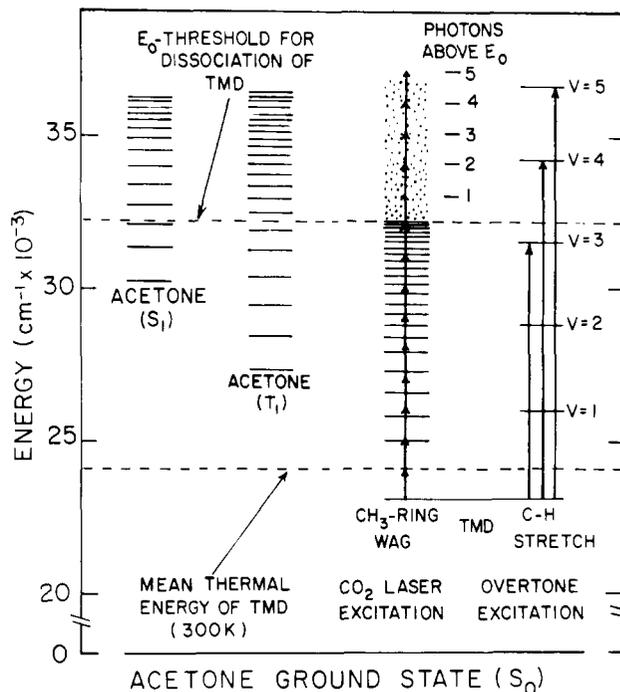


Figure 6. A schematic energy level diagram for the TMD-acetone system.

Our low-pressure results show that, near the origin of the S_1 state, the decay time is of the order of 10^{-6} s. At higher energies, a much faster decay component appears (component I) which may be identified with the nanosecond decay time reported previously.^{14,15} Acetone may be treated as an intermediate-case molecule in terms of the radiationless transition theory at energies sufficiently high above the origin. Thus, the radiative decay of an isolated molecule in this region is expected to be quasi-biexponential,²³ with a prompt decay component having a rate of $k_s + k_{nr}$ and a slow component with a rate of $k_s/N + k_T$, where k_s is the radiative rate constant of pure singlet states, k_{nr} the radiationless transition rate constant, N the number of triplet states interacting with a singlet state, and k_T the radiative rate constant of T_1 . It has been recently pointed out that rotations strongly affect the coupling between different vibrational states via the Coriolis interaction.^{24,25} It is thus expected that for any given vibrational band a complicated decay pattern will be exhibited.

The photophysics of acetone have as yet not been studied with sufficient detail, to allow quantitative determination of factors affecting radiationless transitions. Yet, in view of our recent results obtained with isolated, jet cooled molecules, a qualitative account can be given.

Near the origin of S_1 and under isolated molecule conditions, the dominant decay channel is fluorescence. The observed lifetime is close to that calculated from the integrated absorption spectrum. Thus, intersystem crossing is not a major route. As the excitation energy is increased, a very fast decay channel is activated. We tentatively assign it to vibrationally or rotationally excited state of S_1 that are efficiently coupled to T_1 . Room temperature data are not conclusive, as even with a monochromatic source, a large distribution of excited states is formed due to the thermal population of many excited rovibrational states in S_0 . Even in the jet, with this cause of uncertainty removed, the spectrum is very congested, indicating the population of many different states. We thus assume that intersystem crossing (or other radiationless processes, if present) is promoted by rotational or vibrational excitation of S_1 . It follows that a fraction of molecules, excited

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by light absorption to one of those promoting modes, exhibits a faster decay rate than the others. This leads to the spike observed in the decay curve.

As the excitation energy is further increased, one must consider also another decay channel, dissociation of acetone into $\text{CH}_3\text{CO} + \text{CH}_3$. Energetically this process is possible at the S_1 origin, but there appears to be a barrier. The height of that barrier is not yet well known. In a recent attempt to account for the temperature dependence of acetone photodissociation,²⁶ it was suggested that the Arrhenius activation energies are 15 kcal/mol for S_1 and 5.7 kcal/mol for T_1 .

Qualitatively, upon excitation to sufficiently high levels, dissociation will follow. In that case we expect to observe no long-lived emission. The short-lived component still observable is due to molecules emitting radiation before being decomposed. Similar observations were recently reported for O_3 and CH_3I excited to dissociative absorption bands.²⁷

In the presence of collisions, a different situation prevails. Collision-induced intersystem crossing can be very efficient. One should distinguish at least two types of vibrational states belonging to T_1 —those lying above the S_1 origin and those with lower energy. The former set can be populated from the nascent, optically prepared state by very weak collisions, since energy mismatch is minimal. Stronger collisions may lead to triplet states lying below the origin of S_1 .

As is well known, the radiative $T_1 \rightarrow S_0$ transition (phosphorescence) is not strictly forbidden. This is due to coupling between T_1 and S_1 , leading to a finite radiative probability. The extent of the spin-orbit coupling interaction depends, among other factors, on the vibrational excitation of S_1 . For the purposes of this discussion we propose to divide T_1 states into two categories— T_1^{VR} , lying mostly below the S_1 origin, and vibrationally excited triplet states. The vibrationally relaxed states are well known from previous studies. In the gas phase the phosphorescence decay time turns out to be 200 μs .

Above the S_1 origin, one should actually refer to a mixed state having a partial singlet, partial triplet character. Due to the higher density of states in the triplet component, this state is still predominantly of triplet character. Optical excitation selectively populates the singlet component. Being nonstationary it may evolve into the triplet state, provided the coupling coefficient is large enough. For states very near to the S_1 origin, the coupling may be weak as the densities of states are small, and therefore, chance coincidences between the Born Oppenheimer (BO) states originally belonging to S_1 and T_1 and may be rare. At higher energies, it may be more appropriate to treat the system as being in a mixed state, partly singlet, but with a predominantly triplet character. This state will be termed for now T_1^{M} .

The emission decay following optical excitation of acetone can now be interpreted as follows. Initially, S_1 states are populated. Near the origin, they are weakly coupled to T_1 states leading to an almost exponential decay. The weak coupling manifests itself by the fact that the decay is actually nonexponential (see Figure 5). At higher excitation energies, some states are much more strongly coupled to the triplet, giving rise to the fast ($<10^{-8}$ s) decay component.

Collisions are very effective in populating T_1^{M} as a result of the very small energy mismatch. This state has an energy-dependent lifetime on the order of 30–50 μs . It appears as component III in the optical excitation experiments.¹⁸ Finally, collisional deactivation leads to T_1^{VR} , which is observed at high pressures and in condensed phases.

We now proceed to discuss TMD chemiluminescence in view of this scheme. Electronically excited acetone molecules, formed with a small excess of vibrational energy, decay primarily by luminescence. Triplet states are formed either directly or by collisions. These states may be roughly divided into two categories: states with energy above the S_1 origin and states below it. The

former set is strongly coupled to the singlet manifold, and the resulting decay rate, "diluted" by the dark triplet states, is given approximately by $\tau^{-1} = k_s/N$ and is found experimentally to be about 20–30 μs . Soft collisions suffice to populate this set as the triplet states may be isoenergetic with the singlet ones.

The second set is populated by stronger collisions and may practically be identified with T_1^{VR} . Emission from these states would have been strictly forbidden, except for the fact that they are also interacting with S_1 . Spin-orbit coupling is strong enough to lead to readily observed phosphorescence, with a longer decay time of about 200 μs , which is probably determined by nonradiative coupling to S_0 . The separation into two distinct sets is admittedly an oversimplification, but it may be a good approximation for all states that are not too near to the S_1 origin.

As the excitation energy is increased, one must consider another decay channel, dissociation of acetone into $\text{CH}_3\text{CO} + \text{CH}_3$. Thermodynamically, the reaction threshold is at about 80 kcal/mol. The actual barrier is not known.

TMD Dissociation at Low Pressures. a. Excitation Near Threshold. This section relates to OTE experiments and to IRMPE at low laser fluence. It also corresponds to thermal excitation although no real-time low-pressure data are yet available.

The threshold energy for TMD dissociation is about 9000 cm^{-1} .¹ At this energy, production of S_1 acetone is energetically possible with up to 1000 cm^{-1} of internal energy (see Figure 6). However, the triplet is statistically more likely to be formed. The density of states of S_1 and T_1 was calculated by using the Whitten Rabinovitch²⁸ approximation. This calculation assumes complete separation between S_1 and T_1 as in the BO approximation and shows that the density of T_1 states is ~ 100 times that of S_1 . In the absence of dynamic bias, the T_1/S_1 initial population ratio is given by their respective densities at any given energy. Recalling that, on the average, the other acetone molecule, formed in the ground state, takes up half of the available energy, we find that near the threshold T_1^{VR} is expected to be the dominant product.

The experimental results (Figures 1–3) show that in the low fluence IRMPE and $\nu = 3$ –5 OTE experiments, only two rather long-lived excited species are formed. Comparing with direct acetone optical excitation, there is no evidence for decay components I and II. We rationalize this result by assuming that unlike optical excitation, chemiexcitation of TMD does not preferentially populate the singlet states of acetone. Thus, X may be identified with states above the S_1 origin. The longer lived component is due to the vibrationally relaxed triplet. It thus corresponds to the third component appearing in acetone fluorescence upon collisional quenching of component II.

According to this interpretation of the results, any energetically accessible, vibrationally excited state of acetone above the triplet origin can be populated by the reaction. The average strength of the interaction between singlet and triplet states increases upon increasing the vibrational energy since the average separation between zero-order states decreases. This reasoning leads to a *gradual* (rather than abrupt) increase of the singlet character. The experimental appearance of two clearly distinct decaying components appears to be at variance with this conclusion. It is suggested that, to the accuracy of the present work, and of ref 5, the decay times bunch together around the two different values discussed in the previous section. The region immediately near the S_1 origin is expected to be characterized by the sharp dependence of the lifetime on energy. The statistical nature of the chemical dissociation process normally does not lead to the preferential preparation of products with a narrow, well-defined energy content. We thus assume that these transition ranges are difficult to observe experimentally. Furthermore, the two decay rates which have been experimentally observed are in fact statistical averages.

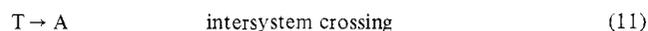
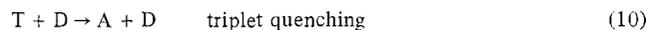
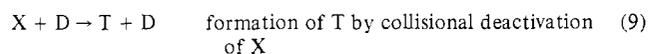
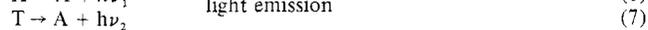
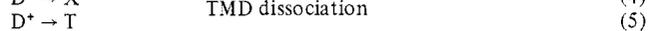
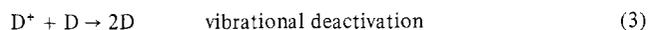
The foregoing arguments are supported by a simple kinetic analysis¹⁶ assuming that in the reaction only two kinetically distinct species are obtained. For brevity, we shall term them X and T.

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Equations 2–11 can be used to faithfully reproduce the kinetic



behavior at low fluence levels. Here D is thermally relaxed TMD, D^+ , vibrationally excited TMD; and A, acetone in the electronic ground state.

The rate constants measured by Cannon and Crim⁵ allow the reconstruction of the rise and decay curves.

A point not addressed directly by Cannon and Crim is the importance of process 9—the collisional induced population of T from X. According to the presently proposed mechanism, this process should be observable at sufficiently high pressures. A related issue is the collision-free branching ratio to product X and T, namely the k_4/k_5 ratio. The proposed scheme allows the determination of the relative amplitudes of the emission components due to X and T as a function of pressure. We have carried out a careful measurement of these amplitudes in the 3–40 mtorr range for the case of the $\nu = 4$ overtone excitation. The peak intensity of the X component is given by

$$X(t) = \frac{k_4[D^+]_0}{k_u - k_X} \{ \exp(-k_X t) - \exp(-k_u t) \} \quad (12)$$

where $k_X = k_6 - (k_8 + k_9)[D]$ and $k_u = k_4 + k_5 + k_3[D]$ and $[D^+]_0$ is the initial concentration of TMD molecules excited beyond the dissociation limit. Figure 7 shows that this equation, with independently measured parameters, leads to an excellent agreement with the experimental results.

The amplitude of the longer lived component was measured 100 μ s after the excitation pulse, allowing sufficient time for the decay of the faster component (except perhaps at 3 mtorr). Figure 8 shows two calculations: one assuming that T is formed only directly by the reaction ($k_9 = 0$) and the other that all of T is formed by collisional deactivation of X. In the former case

$$T(t) = \frac{k_5[D^+]_0}{k_T - k_u} \{ \exp(-k_u t) - \exp(-k_T t) \} \quad (13)$$

where $k_T = k_7 + k_{11} + k_{10}[D]$. In the latter

$$T(t) = \frac{[X]_0 k_9 [D]}{k_T - k_X} \{ \exp(-k_X t) - \exp(-k_T t) \} \quad (14)$$

where $[X]_0 = k_4[D^+]_0/k_u$, and where it is assumed that X is formed instantaneously. The figure indicates that, in fact, an intermediate case prevails—the experimental data are consistent with the preparation of T, partially by direct reaction and partly by collisional deactivation. A more exact estimate of the relative contribution of the two species is not feasible, as we have no simple way to convert emission intensities to populations.

This conclusion is consistent with the data presented in Figure 3 and the very low pressure IRMPE results. The long-lived component identified with T is seen to be formed under collision free conditions (pressure less than 10^{-4} torr).

b. IRMPE at High Fluence Levels. We have demonstrated that IRMPE results are compatible with OTE at low fluence levels. As the fluence is increased, a feature not found in any OTE experiment appears in the CL decay curve. The fast “spike” is obtained only upon strong multiphoton pumping (see Figure 1). According to our model, there are at least two possible ways to account for the spike.

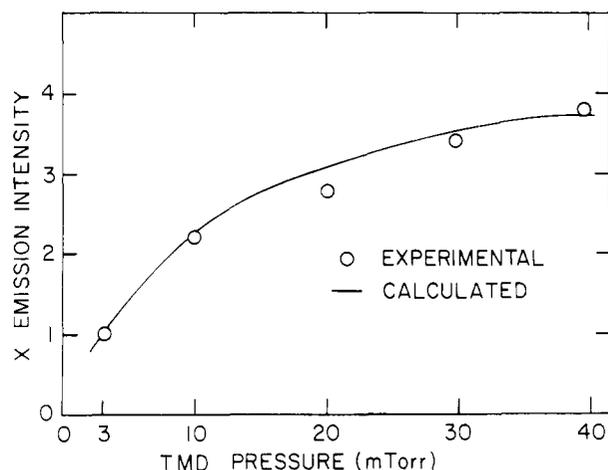


Figure 7. The observed and calculated (eq 12) peak intensity of the X component in an OTE experiment. Excitation is to $\nu = 4$.

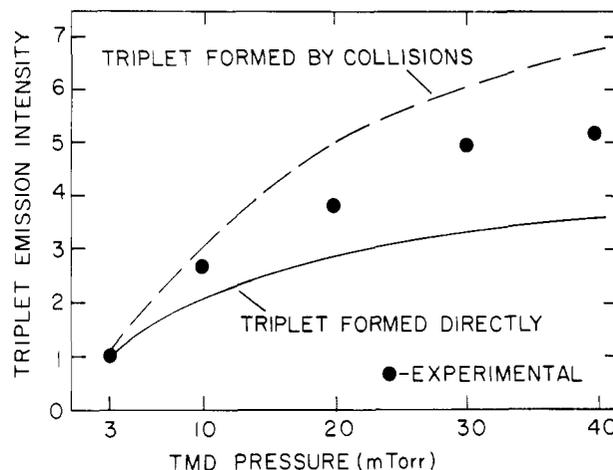


Figure 8. The observed and calculated intensity of the long-lived (triplet) component in an OTE experiment, upon excitation to $\nu = 4$. The top calculated line assumes that the triplet is formed solely by deactivation of X (see eq 14). The lower line assumes that the triplet is formed only by direct dissociation of TMD (cf. eq 13). The experimental intensities were measured 100 μ s after the laser pulse.

In the IRMPE process, up-pumping competes with dissociation for levels above the dissociation limit. It is reasonable to assume that vibrationally excited TMD molecules continue to absorb CO_2 laser photons. On the basis of the up-pumping rates needed to reconstruct CL rise and decay curves for low fluence IRMPE experiments,⁷ we estimate that under our experimental conditions, the up-pumping rate at a laser energy of 30 mJ is 10^8 s^{-1} . The dissociation rate, calculated from RRKM theory, reaches a comparable value only for excess energies of 10000 cm^{-1} or more. At such energies it is likely that the internal energy of some of the electronically excited acetone molecules exceeds the dissociation threshold significantly. Under these conditions, a significant fraction of the products dissociate in a shorter time interval compared to the CO_2 laser pulse. The observed “spike” is due to emission from this fraction.

An alternative possibility is that electronically excited acetone molecules, created by the first part of the CO_2 laser pulse, absorb further infrared photons from the tailing part of the same pulse. IRMPE of electronically excited molecules was observed for the excited states of NO_2 ²⁹ and biacetyl.³⁰ In the presence of the strong IR field, some of the $n\pi^*$ molecules are dissociated and only the short-lived ones can be observed. After the termination

(29) Tsao, J. Y.; Simpson, T. B.; Bloembergen, N.; Burak, I. *J. Chem. Phys.* **1982**, *77*, 1274.

(30) Tsao, J. Y.; Black, J. G.; Yablonovitch, E.; Burak, I. *J. Chem. Phys.* **1980**, *73*, 2076.

of the pulse, the remaining molecules decay in the usual fashion according to their internal energy. In the MPI field a similar process by which excitation switches from one molecular species to another was termed "ladder switching"³¹ and used to account for extensive fragmentation.

Overtone excitation, particularly to the $v = 5$ state, results by statistical arguments with considerable vibrational excitation of the product. We expect that some of them will be formed at energies exceeding 700 cm^{-1} above the S_1 origin and thus have a fast decay component. The fact that this component is not observed can be understood in terms of the kinetic analysis presented above and in ref 16.

Assume that X, formed in process 4, is actually two species, X_f , which decays in 10^{-8} s (the fast component) and X_s , that decays at a slower rate ($k_6 = 10^4\text{--}10^6\text{ s}^{-1}$). Equation 12 can be written for each component as follows:

$$X_f(t) = \frac{k_4^f[D^+]_0}{k_u - k_x^f} \{ \exp(-k_x^f t) - \exp(-k_u t) \} \quad (12a)$$

for the fast component, and for the slow one

$$X_s(t) = \frac{k_4^s[D^+]_0}{k_u - k_x^s} \{ \exp(-k_x^s t) - \exp(-k_u t) \} \quad (12b)$$

k_4^f and k_4^s denote the unimolecular dissociation rate constants of TMD to form X_f and X_s , respectively. They are not necessarily different. Inspection of eq 12a and 12b shows that since per assumption $k_x^f \gg k_u$, the contribution of $X_f(t)$ to the observed signal intensity is much smaller than that of $X_s(t)$. This is evident from the fact that the denominator of eq 12a is much larger (by 2 or 3 orders of magnitude) than that of eq 12b as $|k_u - k_x^f| \gg |k_u - k_x^s|$.

In order that the fast component be observed, the energy states giving rise to it should be formed preferentially by the reaction.

(31) For possible examples of ladder switching, see: Catanzarite, J. H.; Haas, Y.; Reisler, H.; Wittig, C. *J. Chem. Phys.* **1983**, *78*, 5606. Boesl, U.; Neusser, H. G.; Schlay, E. W. *J. Chem. Phys.* **1980**, *72*, 4327; Bernstein, R. B. *J. Phys. Chem.* **1982**, *86*, 1178.

As the optical studies show, this is not the case for energies at least up to 2000 cm^{-1} above the origin. We thus conclude that in the overtone experiments (up to $v = 5$) the dominant contribution to the chemiluminescence signal is due to the slowly decaying product molecules.

In the high-intensity IRMPE experiments, excitation may well exceed 2000 cm^{-1} above the acetone S_1 origin, leading to preferential population of short-lived X states. Thus, a third possibility for the observation of the spike in the high-power IRMPE experiments is provided.

Summary

Comparison of the decay kinetics of acetone excited by pulsed ultraviolet radiation with those obtained upon fast ground-state dissociation of TMD using IRMPE or OTE shows that the primary products of TMD dissociation may be assigned as vibrationally excited acetone in the $n\pi^*$ state. In the absence of collisions, distinction between singlet and triplet components is not as clear-cut as in condensed phases. Still, it appears that the triplet contribution is dominant and in agreement with statistical expectations. Vibrational relaxation leads to preparation of T_1^{VR} , the thermal triplet, which is the major product in condensed phases.

The rapid decay component observed upon IRMPE at high fluence levels is assigned to one (or all) of the following possibilities: decomposition of electronically excited acetone molecules formed in the reaction, made possible by the fact that TMD is pumped by the IR laser to energies far beyond the dissociation threshold of acetone; dissociation of electronically excited acetone molecules that absorb CO_2 laser photons during the laser pulse (ladder switching) or preparation of a large fraction of high energy, short-lived S_1 acetone molecules. These short-lived states are observed upon optical excitation of acetone, both in the bulk and in supersonic nozzle beam expanded molecular beams.

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Multiphoton Infrared Laser Activation of Organometallic Species: A Novel Probe of the Potential Energy Surfaces for Reactions of Cobalt Ions with C_5H_{10} Isomers

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Abstract: Multiphoton infrared activation has been used to probe the potential energy surfaces for the reactions of cobalt ions with C_5H_{10} isomers. Infrared activation of stable $\text{Co}(\text{C}_5\text{H}_{10})^+$ adducts, formed by ligand-exchange processes, is highly selective, with dissociation occurring only by the lowest energy pathway. For example, infrared multiphoton activation of $\text{Co}(\text{1-pentene})^+$ and $\text{Co}(\text{2-pentene})^+$ adducts leads to the exclusive loss of C_2H_4 and CH_4 , respectively, in processes which can be interpreted as resulting from the facile insertion of the metal ion into an allylic carbon-carbon bond. This can be compared to the bimolecular association reactions of cobalt ions with these molecules, which result in the formation of a highly energetic species having sufficient energy to decompose by competitive elimination of H_2 , CH_4 , C_2H_4 , and C_3H_6 . On the basis of the observed photoproducts, 1-pentene and cyclopentane are readily distinguished from each other and from 2-pentene and the methylbutenes. Photodissociation rates are determined for all the cobalt pentene isomers. Dissociation yields are independent of IR excitation wavelength in the region accessible to the CO_2 laser. This contrasts with the single photon absorption spectra of the neutral pentenes which are highly structured in this wavelength region.

Preparation of an active transition-metal catalyst often involves the creation of a coordinately unsaturated species. The ability

of the metal to shuttle between a stable, saturated electron configuration and one capable of undergoing oxidative addition is