AIP | The Journal of Chemical Physics

Evidence for sequential reactions in the CO2 laser induced multiphoton dissociation of acetic anhydride and acetic acid

A. J. Grimley and J. C. Stephenson

Citation: The Journal of Chemical Physics **74**, 447 (1981); doi: 10.1063/1.440852
View online: http://dx.doi.org/10.1063/1.440852
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/74/1?ver=pdfcov
Published by the AIP Publishing

Evidence for sequential reactions in the CO_2 laser induced multiphoton dissociation of acetic anhydride and acetic acid

A. J. Grimley[a] and J. C. Stephenson

Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234

(Received 3 July 1980; accepted 8 September 1980)

The CO_2 laser induced multiphoton dissociation of acetic acid and acetic anhydride has been investigated. We have observed the prompt formation of $^1CH_2$ and OH by laser excited fluorescence and determined their nascent rotational energy distributions. The rotational energy of each product was the same, regardless of which starting material was photolyzed. This observation leads us to propose a mechanism in which both the $^1CH_2$ and the OH are formed by sequential up-pumping of molecular intermediates. We have also determined the yield versus fluence curves for both the $\tilde{a}$ (0,0,0) and $\tilde{a}$ (0,1,0) levels of $^1CH_2$. The relative yields of these two levels are found to change as a function of intensity.

INTRODUCTION

The CO_2 laser induced multiphoton dissociation (MPD) of acetic anhydride has received considerable attention lately as a source of singlet methylene radicals.[1-3] The possibility of a sequential up-pumping mechanism leading to the observed product has been suggested in Ref. 3.

In this paper we report the product yield and internal energy content of $\tilde{X}$ OH and $\tilde{a}\ ^1CH_2$ radicals formed from acetic anhydride and acetic acid as determined by time resolved laser excited fluorescence (LEF). We interpret these measurements in terms of the thermal dissociation pathway for acetic anhydride:

$$(CH_3CO)_2O \rightarrow CH_2CO + CH_3CO_2H\ ,$$

$$\Delta H = 23.5 \text{ kcal/mol},^{4}\ E_a = 34.5 \text{ kcal/mol},^{5}\ A = 10^{12}\ \text{s}^{-1\,5}. \qquad (1)$$

A sequential up-pumping mechanism starts with the dissociation of the anhydride as above and proceeds by subsequent absorption of more photons by the products to themselves dissociate giving the observed fragments. The dissociation of acetic acid can proceed by either of two paths:

$$CH_3CO_2H \rightarrow CH_2CO + H_2O\ , \qquad (2)$$

$$\Delta H = 31.3 \text{ kcal/mol},^{4}\ E_a = 67.5 \text{ kcal/mol},^{6}\ A = 9\times 10^{12}\ \text{s}^{-1},$$

$$CH_3CO_2H \rightarrow CH_3CO + OH\ ,$$

$$\Delta H = 98.8 \text{ kcal/mol},^{4}\ E_a = 98.8 \text{ kcal/mol},^{7}\ A \approx 10^{16}\ \text{s}^{-1\,7}. \qquad (3)$$

Equation (2) leads to $^1CH_2$ as with acetic anhydride and Eq. (3) gives direct production of OH. For both starting materials it is proposed that the $^1CH_2$ is formed by the subsequent dissociation of ketone:

$$CH_2CO \rightarrow {}^1CH_2 + CO\ ,$$

$$\Delta H \cong 85 \text{ kcal/mol},^{4}\ E_a \cong 85 \text{ kcal/mol}.^{7} \qquad (4)$$

We also report new results bearing directly on the question of branching ratios in MPD. It has been suggested[8,9] that the products and product energies of MPD depend strongly on laser intensity. In the dissociation of acetic anhydride we find that the ratio of $^1CH_2$ formed in the (0, 1, 0) level to that formed in the (0, 0, 0) level increases with increasing energy in the photolysis pulses of constant temporal shape.

EXPERIMENTAL (REF. 10)

The experimental apparatus and procedures are essentially the same as those used to produce and monitor CF_2 following MPD of a variety of fluorocarbons. The details are given in Refs. 11 and 12. A brief summary of the experiment follows: The precursor molecules were photolyzed using the $R(20)$ line (1079 cm^{-1}) of a multimode TEA CO_2 laser (80% of the energy in a 100 ns spike; remainder in a 600 ns tail), focussed with a 30 cm focal length lens (giving fluences up to 37 J/cm^2, 220 MW/cm^2).[13] The $^1CH_2$ or OH was detected by observing its fluorescence excited by pulses (5 ns FWHM) from a N_2 laser pumped tunable dye laser. The fluorescence was observed at right angles to the two collinear laser beams through an $f/1.6$ monochromator with a photomultiplier tube (1P28, C31034, or 4832 all RCA) and gated electronics. By maintaining the radius of the visible or UV probe beam much smaller than that of the IR pump, we observe only a cylindrical region of constant IR fluence. The slits of the monochromator were parallel to the laser beams and were apertured to view an 8 mm length of constant IR beam radius. The precursor gas flowed through the photolysis cell at a rate such that samples were completely changed between pulses. The pressure of 1 to 20 mTorr was monitored by a capacitance manometer.

The acetic acid (glacial) and acetic anhydride were both degassed by extensive pumping at room temperature and used without further purification. Ketene was prepared using the standard method[14] of pyrolysis of acetic anhydride at 500 °C. It was purified by distillation from a trap at 157 K to one at 77 K, degassed by pumping at 77 K, and stored at 77 K. For photolysis it was withdrawn from the liquid at 157 K.

RESULTS

Yield vs fluence

Figure 1 shows a plot of $^1CH_2\ \tilde{a}\,(0,0,0)$ product yield from acetic anhydride and acetic acid and OH ($\tilde{X}\,^2\Pi_{3/2}$, $v = 0$) product yield from acetic anhydride vs CO_2 laser

---

[a] NBS/NRC Postdoctoral Research Associate.

0021-9606/81/010447-06$01.00

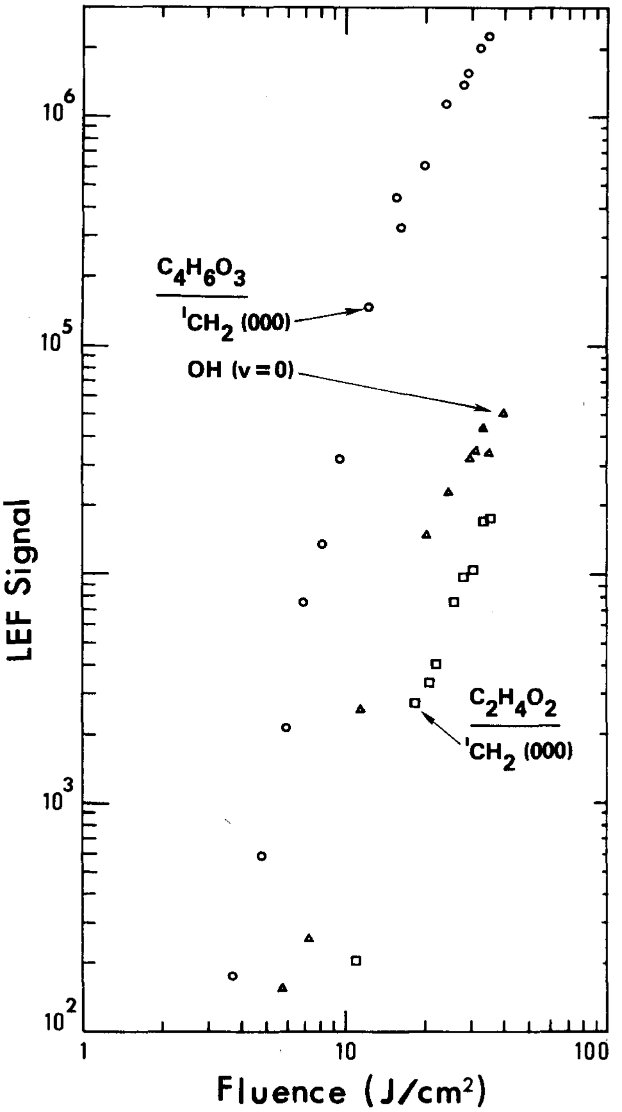

FIG. 1. Yield vs fluence for $^1CH_2$ from acetic anhydride (circles) and acetic acid (squares) and OH from acetic anhydride (triangles). All data using the 1079 cm^{-1} $R(20)$ line of CO_2 laser with 10 mTorr of sample. The OH and CH_2 yields are not on same scale.

fluence for the $R(20)$ (1079 cm^{-1}) line. The yield was determined from the fluorescence signal intensity following probe laser excitation of the Q branch head of the 2_0^{16} transition for CH_2 and excitation of the $Q_1(1)$ line of the (1, 0) transition of OH. The yields were determined at a pressure of 10 mTorr of the starting material of interest, at a time of 200 ns after the start of the CO_2 laser pulse. The CO_2 laser pulses were attenuated outside the laser cavity without changing the temporal or spatial shape of the pulse.

We observed $^1CH_2$ from the MPD of both acetic acid and ketene in addition to acetic anhydride. The yield of $^1CH_2$ from acetic acid was a factor of approximately 150 smaller than that from acetic anhydride. At this level we cannot preclude the $^1CH_2$ coming from a less than 1% impurity in our acetic acid or from acetic anhydride coming off the cell walls. For ketene this problem is even more apparent since the observed yield is three orders of magnitude less than that for acetic anhydride. Given the possibilities of impurities or wall desorption, the factor 10^{-3} must be viewed as an upper limit to the ratio of $^1CH_2$ formed from ketene to that formed from acetic anhydride.

The data for CH_2 and OH are not on the same scale. We have no estimate of the absolute yield of $^1CH_2$. Based on the method of Ref. 11, we estimate that approximately 1%–10% of the acetic anhydride in the focal volume probed by the UV laser is dissociated to produce OH at our highest fluence of 37 J/cm^2. The direct MPD of acetic acid produces a comparable OH yield.

Several other possible OH donors were investigated as checks on our yield estimate. Pentafluorophenol and methyl alcohol both gave signals approximately 3% that of acetic anhydride under similar conditions (optimum CO_2 laser line, maximum fluence). Hexafluoroisopraponol was about 30% as efficient a source of OH. 1-H, 1-H-pentafluoropropanol was equivalent to the acetic anhydride and pentafluorobenzyl alcohol was about twice as good a donor. While not providing that our value for the absolute yield is correct, this investigation is consistent with our estimate of substantial OH formation.

In order to determine the effect of collisions on product formation we carried out a determination of product yield vs reactant pressure. If collisions are not important, a plot of yield (i.e., LEF signal) vs pressure should be linear. An important parameter in a study of this type is the time of observation with respect to the onset of the CO_2 laser pulse. At very short times even at relatively high pressures, very few molecules will have collisions whereas at long time one has to go to lower pressures to avoid collisions. Due to this dependence on both reactant pressure and delay time, a figure of merit in such a study is the largest range of the pressure–delay time product over which the yield is linear. For CH_2 the upper limit was found to be 2×10^{-2} μs Torr and for OH it is 5×10^{-3} μs Torr. Our studies were carried out at values substantially lower than these in order to minimize the effects of collisions on our results.

Product electronic energy

The CH_2 fragment we detect is in the $\tilde{a}\,^1A_1$ state which lies approximately 10 kcal/mol above the ground $\tilde{X}\,^3B_1$ state. We have no way of observing the ground state population and hence no estimate of the branching ratio between the two states in the dissociation. No visible emission from higher lying states was observed.

In the case of OH the electronic ground state has two components ($^2\Pi_{3/2}$ and $^2\Pi_{1/2}$) separated by 139.7 cm^{-1}.[15] We are able to observe rovibronic transitions from both of these levels. From comparison of several transitions we obtain a population ratio $^2\Pi_{1/2}/^2\Pi_{3/2}=0.34$, consistent with an electronic "temperature" of 185 ± 40 K for the OH produced in the dissociation. Again no higher lying states are observed, so the average electronic energy is ~ 55 cm^{-1}.

Product vibrational energy

A comparison of the relative LEF intensities of several different rotational lines in the 2_0^{14} and 2_1^{14} transitions enabled us to determine the relative populations of $\tilde{a}\,(0,0,0)$ to $\tilde{a}\,(0,1,0)$ ($E_{\mathrm{vib}} = 1353\ \mathrm{cm}^{-1}$) for nascent $^1CH_2$. The 2_0^{14} fluorescence was observed for 2_1^{14} excitation and *vice versa*. The Franck–Condon factors for these transitions are approximately equal. In order to obtain the nascent distribution, the LEF spectra were taken at a pressure of 10 mTorr and a delay time of 100 ns. Under these conditions collisional relaxation of $V_2 = 1$ to $V_2 = 0$ is very unlikely (less than 1% of the molecules undergo a hard sphere collision prior to probing).

The $^1CH_2$ produced from acetic anhydride is found to have $N_1/N_0 = (7.8 \pm 0.8) \times 10^{-2}$ at a CO_2 laser fluence of 37 J/cm^2. While two points do not demonstrate a Boltzmann distribution of vibrational energy, this ratio is consistent with a vibrational temperature of 760 ± 40 K. The ratio N_1/N_0 is found to change both as a function of CO_2 laser fluence and delay time between the pump and probe pulses. When one probes at the end of the intense portion of the CO_2 laser pulse (i.e., a delay time of 100 ns), one finds that N_1/N_0 increases monotonically (see Fig. 2) from $(3.0 \pm 0.9) \times 10^{-2}$ at 16 J/cm^2 to $(7.8 \pm 0.8) \times 10^{-2}$ at 37 J/cm^2. As one goes to longer delay times the difference in these ratios steadily decreases until at a delay of about 2 μs the ratio N_1/N_0 is independent of laser fluence in the range 16–37 J/cm^2. At this delay the ratio corresponds to a vibrational temperature of 600 ± 50 K.

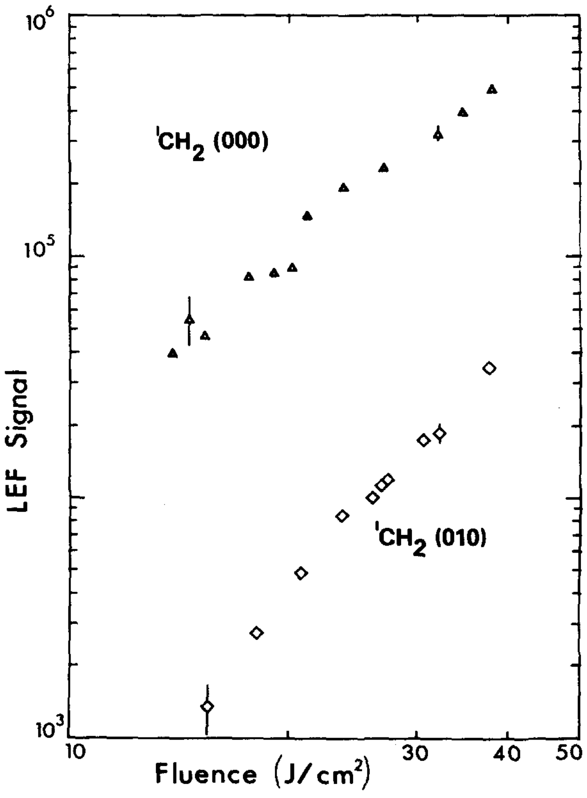

FIG. 2. Yield vs fluence for $V_2 = 0$ (triangles) and $V_2 = 1$ (diamonds). Both are for acetic anhydride at 10 mTorr using the 1079 cm^{-1} $R(20)$ line of CO_2 laser.

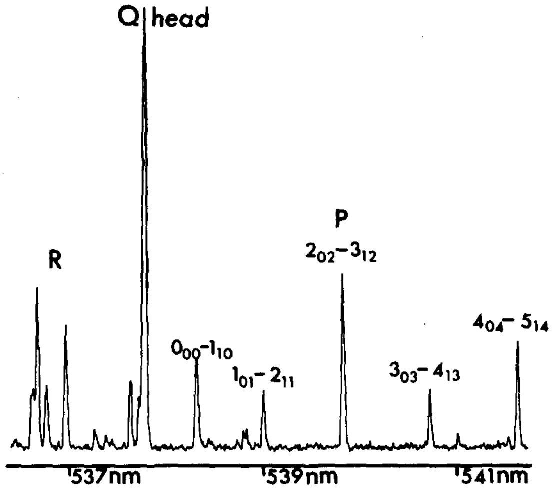

FIG. 3. LEF spectrum of $\tilde{b}(0,16,0) \leftarrow \tilde{a}(0,0,0)$ of $^1CH_2$.

We were unable (under conditions where collisions were unimportant) to obtain a signal from OH ($\tilde{X}$, $v = 1$). This allows us to put an upper limit on the vibrational temperature of OH (assuming a Boltzmann distribution) of 700 K.

Product rotational energy

Figure 3 shows a typical $^1CH_2$ LEF spectrum obtained from the MPD of 5 mTorr of acetic anhydride at a delay time of 200 ns. The transition probed is the $\tilde{b}\,(0,16,0) \leftarrow \tilde{a}\,(0,0,0)$ Σ band of $^1CH_2$. It is evident from this figure that rotational quantum numbers can be assigned to the original levels of a fair number of rovibronic transitions. In order to determine the rotational energy content of the nascent $^1CH_2$ we have used the intensity of the P branch lines of this transition for $J = 1-7$. The rotational energies of these states are given by Ref. 16. Using $S_{JK_aK_c}$ that we have calculated (see below) along with our excitation spectra and the nuclear degeneracy factor ($g_J = 3$ for J odd and $g_J = 1$ for J even), we can determine relative populations for several rotational levels. A plot of $\log P(J)$ vs E_J gives a straight line indicative of a Boltzmann distribution in the rotational degree of freedom of the nascent $^1CH_2$. In order to assure ourselves that we are in fact looking at the nascent distribution, we determined rotational populations for $^1CH_2$ under conditions where collisions are unimportant, within 100 ns of its formation at a pressure of 1 to 5 mTorr.

We have determined the rotational temperature of $^1CH_2$ molecules in both the (0, 0, 0) and (0, 1, 0) vibrational levels for both precursor molecules and find that the rotational energy is independent of vibrational state. The rotational temperatures thus determined are $T_{\mathrm{rot}} = 354 \pm 34$ and $T_{\mathrm{rot}} = 352 \pm 28$ K, respectively, for the acetic anhydride and acetic acid starting materials. These are averages of several measurements on both the $V_2 = 0$ and $V_2 = 1$ states of $^1CH_2$.

The rotational line strength factors $S_{JK_aK_c}$ that we used in determining the rotational temperature of $^1CH_2$ are given in Table I. These values were calculated using an NBS program specifically written to calculate intensities of rotational transitions in asymmetric top molecules. This program diagonalizes an energy matrix obtained from Watson's Hamiltonian[17] and uses the eigenvectors to calculate the rotational transition strengths. The program input is the set of rotational constants for both upper and lower states of the molecules which, in our case, were those of Herzberg and Johns.[16]

The $S_{JK_aK_c}$ given in Table I are valid for both the 2_0^{16} and 2_1^{16} transitions (separate calculations for each transition show differences of less than 2%). We have calculated these constants for the 2_0^{14} and 2_1^{14} transitions as well but a comparison with our spectra indicate that perturbations on the $\tilde{b}\,(0, 14, 0)$ state render the results meaningless.

As a check of our $S_{JK_aK_c}$ we measured relative rotational populations under conditions in which the average $^1CH_2$ would have undergone approximately 100 collisions (4 Torr Argon at 4 μs delay time) to achieve rotational equilibration. Under these conditions we found the plot of $\log P(J)$ vs E_J to be linear, as expected if our calculated $S_{JK_aK_c}$ did correspond to the actual values. Marked nonlinearity in such a plot under these conditions would only be due to a perturbation making our calculation of $S_{JK_aK_c}$ invalid. Such a perturbation was found for the 2_0^{14} and 2_1^{14} transitions.

The rotational energy content of the OH fragment was determined for dissociation of both acetic acid and acetic anhydride. The plot of relative population (corrected for line strength factors, etc.) vs rotational energy of OH ($V = 0$) is given in Fig. 4. At low pressures and short delay times ($p\tau < 3\times10^{-3}$ μs Torr) the rotational temperature for OH from both starting materials was found to be 175 ± 30 K. At this T_{rot} only the low lying rotational levels are populated. At longer delay times and higher pressures ($p\tau \gtrsim 3\times10^{-3}$ μs Torr) we found that the higher lying rotational levels were also populated and had a distribution corresponding to a rotational temperature of 650 ± 100 K.

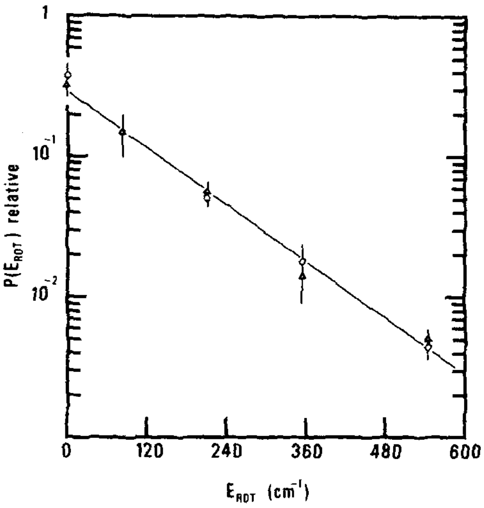

FIG. 4. The fraction $P(E_{rot})$ of OH ($\tilde{X}\,^2\Pi_{3/2}$) fragments initially formed with rotational energy E_{rot} from acetic anhydride (circles) and acetic acid (triangles). (CO$_2$ laser at 1079 cm^{-1}, 37 J/cm^2.) The least squares fit gives $T_{rot} = 175 \pm 30$ K.

Translational energy of the $^1CH_2$ fragment

The translational energy of the $^1CH_2$ fragment has been measured using the technique of Ref. 11. This method yields only an average velocity for $^1CH_2$ moieties in the particular vibrational and rotational state probed but does not determine a velocity distribution function. These measurements have been carried out at pressures of 2 to 4 mTorr and typically extend over a measurement period of 2 μs. Under these conditions we are observing collision free expansion of the $^1CH_2$ fragments out of the beam.

TABLE I. Rotational line strength factors[a] for $^1CH_2$ $\tilde{b}(0,16,0) \leftarrow \tilde{a}(0,0,0)$.

J'	K_a'	K_c'	J''	K_a''	K_c''	$S_{JK_aK_c}$
0	0	0	1	1	0	1.0
1	0	1	2	1	1	1.5
2	0	2	3	1	2	1.98
3	0	3	4	1	3	2.37
4	0	4	5	1	4	2.58
5	0	5	6	1	5	2.56
6	0	6	7	1	6	2.39
7	0	7	8	1	7	2.19

[a] The intensity of an individual rotational line is defined by $S = [S_{JK_aK_c}/(2J''+1)]\,|\mu_c|^2$, where μ_c is the dipole component responsible for the transition.

These measurements have been performed for the $^1CH_2$ in both $V_2 = 0$ and $V_2 = 1$ from acetic anhydride and for $V_2 = 0$ from acetic acid, using photolysis pulses of 37 J/cm^2. The laboratory velocity is found, like the rotational energy, not to depend on the vibrational energy level. The kinetic energy was also found to be independent of rotational level for several different levels with rotational energies up to 210 cm^{-1}. If one assumes a thermal velocity distribution, a characteristic translational temperature can be assigned. It is found that T_{lab} is 280 ± 25 K for acetic acid and 320 ± 50 K for acetic anhydride.

Radiative lifetime and quenching of CH$_2$ $\tilde{b}(^1B_1)$ (0,16,0)

Using a Tektronix 7912 transient digitizer and a microcomputer, we have measured the quenching of $^1CH_2$ $\tilde{b}\,(0, 16, 0)$ as a function of argon and acetic anhydride pressure. The decay time is given by $\tau^{-1} = k_x\,[X] + \tau_r^{-1}$ so the slope of a plot of τ^{-1} vs $[X]$ gives k_x, the quenching rate of $^1CH_2$ $\tilde{b}\,(0, 16, 0)$ by X, and the intercept gives τ_r^{-1}, where τ_r is the radiative lifetime of the $V_2'' = 16$ level of $\tilde{b}$ $^1CH_2$.

Using this method we obtain $k_{AcAn} = (3.98 \pm 0.99)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} and $\tau_r = 1.3 \pm 0.3$ μs. Quenching of $\tilde{b}\,(0, 16, 0)$ by argon is found to occur with a rate constant of $(6.8 \pm 0.9)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}.

The measured radiative lifetime and quenching rates were found to be independent of rotational level. We performed themeasurements at three different rotational levels 0_{00}, 2_{02}, and 6_{06} ($E_{rot} = 0$, 47, and 333 cm^{-1}, respectively as well as a measurement using the Q

branch which excites four different rotational levels within the bandwidth of our excitation laser.

DISCUSSION

Dissociation mechanism

The internal energy distributions determined in this work provide strong support for a sequential up-pumping mechanism in two different ways. Consider Reactions (1)–(4) proceeding from acetic anhydride to both observed products through molecular intermediates that absorb in the region of interest. For both products we have given the lowest energy, spin-allowed dissociation pathways. The channel leading to OH, while being higher in energy than that leading to ketene (and hence CH_2), would be expected to be competitive due to its much larger A factor.

The first experimental observation that leads us to the sequential up-pumping mechanism is the fact that the rotational energy in the OH and $^1CH_2$ is independent of starting material. This observation is very suggestive of a mechanism in which the actual parent is, in fact, the same regardless of initial molecule. The energy distributions of product fragments arising from the MPD of several small molecules have been determined. The CF_2 fragment from the MPD of CF_2HCl,[11,18] CF_2Cl_2,[12] CF_2Br_2,[12] CF_2CFCl,[19] and $C_3F_4H_2$[20] (1, 1, 2, 2-tetrafluocyclopropane) has been found to have an energy distribution that depends strongly on the identity of the parent molecule. This has also been true in the CH fragment resulting from MPD of CH_3OH[21] or CH_3CN.[22] We feel it would be very unlikely for $^1CH_2$ formed directly from the two different reactants to have the same distribution of rotational energy.

A consideration of the relatively small amount of energy found in the $^1CH_2$ product leads one to believe that it is the result of a reaction which does not have a significant barrier in the reverse direction. Pyrolysis studies on ketene[23,24] suggest that there is in fact little or no barrier to the reverse reaction. No significant barrier is expected for unimolecular reactions involving simple bond fission.[7] The lowest energy single step eliminations of $^1CH_2$ from either acetic acid or acetic anhydride involve simultaneous making and breaking of bonds. In such cases one would expect the activation energy to significantly exceed the enthalpy for the reaction,[25] in which case the $^1CH_2$ formed from the elimination would have more internal or translational energy than we find in the $^1CH_2$ ($E_{CH_2} \approx 2$ kcal/mol).

This same argument can be made for the OH as well. That OH is produced from acetic acid with little internal energy is not surprising since we again have a simple bond fission with no significant barrier in excess of the enthalpy to overcome. However, to get OH in a concerted way from acetic anhydride would require a four-center transition state[25] in which one bond is formed and three are broken (either three single bonds or one single and one double bond). It is unlikely that there is no excess energy requirement for this process to take place. This is also a situation in which a significant amount of energy would be expected in OH vibration based on geometric arguments. Given the low upper limit on the OH vibrational energy (no level other than $v = 0$ could be observed) and the very low rotational energy, we feel that the OH is produced by a simple bond fission.

Our inability to unambiguously detect $^1CH_2$ from the MPD of ketene appears, at first glance, to contradict our proposed mechanism. A closer examination of the system can show that this result is not surprising. At the CO_2 laser line of interest we are pumping the weak $\nu_5 + \nu_6$ combination band of ketene. Low resolution absorption spectra show that acetic anhydride has approximately a 20 times larger integrated absorption in the 1025 to 1200 cm^{-1} spectral region. By comparison, fluorocarbon molecules such as CF_2HCl, which can be dissociated with 10%–100% efficiency at these laser fluences, have integrated absorptions 40 times larger than ketene.

Another factor expected to lead to inefficient excitation of room temperature is its low density of states. In this small dihydride, there may not be a series of rotation–vibration states resonant with the fixed laser frequency, a condition which is necessary for efficient excitation. Such resonant states are assured if the density of vibrational states $N(E)$ at the pumped level is at least ω_R^{-1} (the inverse of the Rabi frequency). For ketene, this condition is satisfied with $N(E) \geq 10/cm^{-1}$; however, this density of states is not reached until the molecule has vibrational energy $E = 21$ kcal. Therefore, it is not surprising that room temperature ketene ($E \approx 1$ kcal) is difficult to dissociate. For acetic anhydride, on the other hand, the condition $N(E) \geq \omega_R^{-1}$ requires that $N(E) \geq 2.5/cm^{-1}$ which is already satisfied at room temperature for this larger molecule. For acetic acid this condition is satisfied at $N(E) \geq 5/cm^{-1}$, which is satisfied once the first CO_2 laser photon is absorbed.

The ketene resulting from the dissociation of acetic anhydride would not however be expected to have a room temperature vibrational energy content. Lee and coworkers[26] have observed that dissociation occurs when the dissociation rate and the up-pumping rate are comparable. For the laser pulses employed in this work[13] this should occur for a dissociation rate of 10^8 s^{-1}. Acetic anhydride will have this dissociation rate at an energy content of about 55 kcal/mol above the dissociation limit. This 55 kcal plus the 11 kcal barrier height in excess of the enthalpy for dissociation provides 66 kcal to be distributed to the products. A statistical distribution would provide approximately 25 kcal to the ketene putting it in the energy region where efficient up-pumping would be expected. This same argument also holds for ketene formed from acetic acid where the total energy available to both products is about 75 kcal/mol.

Internal energy distribution measurements

Our direct observation that the vibrational energy content of one of the dissociation products depends on laser pulse energy is an unambiguous demonstration of the competition between the rate of laser excitation of the highly excited reactant and its rate of dissociation. The shorter RRKM lifetimes of more highly excited molecules require that the energy be put in faster in order to reach these levels. As the intensity increases, this condition is satisfied; the reactants on the average dissociate from higher levels, more energy is therefore available in the products, and hence we observe a larger fraction of more excited fragments at shorter delay times. This same reasoning explains why the ratio of $^1CH_2(010)$ to (000) was observed to decrease at longer times following the intense portion of the laser pulse.

Radiative lifetime and collisional removal of $^1CH_2$ $\tilde{b}$ (0,16,0)

There have been two other reports of radiative lifetimes for the $\tilde{b}\,^1B_1$ state of CH_2. Welge and co-workers[27] report a τ of 4.2 μs for the (0, 14, 0) level and Mohlmann and DeHeer[28] report a lifetime of (1.90± 0.15) μs for a broad range of emission wavelengths. Our value of 1.3 ± 0.3 μs for three different rotational levels of the $\tilde{b}$(0,16,0) state compares favorably with both these values.

The removal rates of $\tilde{b}$ (0, 16, 0) by both argon and acetic anhydride are both slightly slower than the removal rate reported by Danon *et al.*[27] for the (0, 14, 0) level by ketene. The argon rate is an order of magnitude faster than that determined by Ashfold *et al.*[2] for the collisional removal of $\tilde{a}\,^1A_1$ CH_2 by argon. Whether the removal of the $\tilde{b}$ (0, 16, 0) is by vibrational, electronic, or collision induced intersystem crossing cannot be deduced from our experiments. In the case of acetic anhydride there is also the possibility of reaction to be considered.

CONCLUSION

Two important effects in CO_2 laser induced multiphoton dissociation are reported in this paper. First, evidence is provided for a sequential up-pumping mechanism in the MPD of acetic anhydride leading to both $^1CH_2$ through a ketene intermediate and OH by way of acetic acid formed in the same step as the ketene. This is shown by the insensitivity of product internal energy to the identity of the material photolyzed. In general, the product energy is found to depend strongly on the identity of the parent so we conclude that the same parent must be dissociated in the final step regardless of starting material. The second observation is the dependence of product vibrational energy (in the $^1CH_2$) on laser intensity. Our results correspond to what would be expected based on a microscopic model in which more energetic molecules have shorter lifetimes.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Arthur Maki and Dr. Jon T. Hougen for their help in calculating the $S_{JK_aK_c}$.

[1] D. Feldman, K. Meier, R. Schmiedl, and K. H. Welge, Chem. Phys. Lett. 60, 130 (1978).
[2] M. N. R. Ashfold, G. Hancock, G. W. Ketley, and J. P. Minshull-Beech, J. Photochem. 12, 75 (1980).
[3] S. V. Filseth, J. Danon, D. Feldmann, J. D. Campbell, and K. H. Welge, Chem. Phys. Lett. 66, 329 (1979).
[4] D. R. Stull and H. Prophet, JANAF Thermochemical Tables, Natl. Bur. Stand. Publ. 37 (1971).
[5] C. H. Bamford and M. J. S. Dewar, J. Chem. Soc. 1949, 2877.
[6] J. Murawski and M. Szwarc, Tran. Faraday Soc. 47, 269 (1951).
[7] S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," Natl. Bur. Stand. Publ. 21 (1970).
[8] C. Reiser, F. M. Lussier, C. C. Jensen, and J. I. Steinfeld, J. Am. Chem. Soc. 101, 350 (1979).
[9] E. Thiele, M. F. Goodman, and J. Stone, "Can lasers be used to break chemical bonds selectively," Opt. Eng. 19, 10 (1980) and works cited therein.
[10] Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
[11] J. C. Stephenson and D. S. King, J. Chem. Phys. 69, 1485 (1978).
[12] D. S. King and J. C. Stephenson, Chem. Phys. Lett. 51, 58 (1977).
[13] E. Thiele, J. Stone, M. Goodman, J. C. Stephenson, and D. S. King, J. Chem. Phys. 73, 2259 (1980).
[14] R. L. Nutall, A. H. Laufer, and M. V. Kilday, J. Chem. Thermodyn. 4, 167 (1971).
[15] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950), 2nd edition.
[16] G. Herzberg and J. W. C. Johns, Proc. R. Soc. (London) Ser. A 265, 107 (1966).
[17] J. K. G. Watson, J. Chem. Phys. 46, 1935 (1967).
[18] D. S. King, M. F. Goodman, and J. Stone, J. Chem. Phys. 70, 4496 (1979).
[19] J. C. Stephenson, S. E. Bialkowski, and D. S. King, J. Chem. Phys. 72, 1161 (1980).
[20] D. S. King and J. C. Stephenson (unpublished results).
[21] S. E. Bialkowski and W. A. Guillory, J. Chem. Phys. 68, 3339 (1978).
[22] M. L. Lesiecki and W. A. Guillory, J. Chem. Phys. 69, 4572 (1978).
[23] Von H. Gg. Wagner and F. Zable, Ber. Bunsenges. Phys. Chem. 75, 114 (1971).
[24] M. Tsuda and K. Kuratani, Bull Chem. Soc. Jpn. 41, 53 (1968).
[25] P. J. Robinson and K. A. Holbrook, *Uni-Molecular Reactions* (Wiley, New York, 1972).
[26] A. S. Sudbø, P. A. Schulz, E. R. Grand, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. 70, 912 (1979).
[27] J. Danon, S. V. Filseth, D. Feldmann, H. Zacharias, C. H. Dugan, and K. H. Welge, Chem. Phys. 29, 345 (1978).
[28] G. R. Mohlmann and F. J. DeHeer, Chem. Phys. Lett. 43, 236 (1976).