The ultraviolet photolysis of acetyl and propionyl radicals studied by infrared emission spectroscopy

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The photodissociation of acetyl and propionyl radicals at 248 and 266 nm has been studied by time-resolved Fourier transform infrared spectroscopy. A vibrationally excited product CO($v \leqslant 8$) was observed in the emission spectra. The vibrational temperatures of the nascent CO products were about 7400 K for the acetyl radical and 6930 K for the propionyl radical. The vibrational energy partitioning of the CO fragments fits a soft impulsive model. © *1997 American Institute of Physics.* [S0021-9606(97)00214-6]

I. INTRODUCTION

Acyl (RCO) radicals are of importance in combustion processes and in atmospheric reactions.[1] The photolysis of the acyl radicals is an intermediate reaction of the degradation of some carbonyl-containing compounds.[2] A number of studies have been carried out dealing with the decomposition of the ground state $X\ ^2A'$ CH_3CO,[3–8]

$$CH_3CO(X\ ^2A') \rightarrow CH_3(X\ ^2A_2'') + CO(X\ ^1\Sigma^+). \tag{1}$$

The reaction is endothermic, $\Delta H = 14.2$ kcal/mol, with a dissociation barrier of 17.8 kcal/mol.[4]

The first excited state $A\ ^2A''$ is a bound state with an energy minimum of 2.6 eV.[7] According to our recent calculation, there is a second excited state $B\ ^2A'$, 4.9 eV vertically above the equilibrium geometry of the ground state.[9] The transition between the $B\ ^2A_1'$ state and the ground state $X\ ^2A'$ promises a moderate optical absorption around 250 nm.

In this paper, we report our study on the dissociation of the second excited state $B\ ^2A'$. The acyl radicals are excited by 248 or 266 nm lasers from their ground state. A technique of time-resolved Fourier transform infrared (TR-FTIR) spectroscopy is used for the detection of the transient infrared emission from the nascent photolytic product CO(v). Analysis of vibrational energy distribution of the product reveals a dynamic process of the photodissociation via the $B\ ^2A'$ state.

II. EXPERIMENT

The time-resolved Fourier transform infrared emission spectrometer has been described in detail elsewhere.[10] A KrF excimer laser beam (Lambda Physik, LPX 305i 248 nm, ~200 mJ/pulse) was slightly focused by a cylinder lens (f =380 mm) and was led to a photolysis chamber. Pure acetyl chloride, acetone, butanone, 3-pentanone, or propionyl chloride flowed into the chamber with a stagnation pressure of 80 Pa. The infrared emission from the photofragments was collected by a pair of gold-coated spherical mirrors to a FTIR spectrometer (Nicolet 800). An InSb IR detector was used to detect the IR emission. The spectral resolution of the instrument was set at 16 cm^{-1}. Interferograms were coadded over 20 scans to improve the signal-to-noise ratio. The data acquisition system provided 20 time-sequenced interferograms with 15 μs spacing from 10 to 295 μs after a laser pulse. About 50 000 laser pulses were used for each experiment.

In a two laser experiment, the KrF laser (248 nm) beam and the fourth harmonics of a Nd:YAG laser beam (266 nm, 20 mJ) were led to the photolysis chamber in opposite directions. The first 248 nm laser beam was not focused and the laser energy was reduced to ~80 mJ/pulse to avoid two-photon absorption. The 266 nm laser pulse was delayed by 100 ns. Pure acetone flowed into the chamber with a stagnation pressure of about 150 Pa.

III. RESULTS AND DISCUSSION

A. The preparation of acyl radicals (RCO)

Because a free radical is very reactive, usually it is not easy to prepare a sufficient amount for further photolysis. For acyl radicals, more difficulty arises from their low dissociation barrier. The rich internal energy would cause the radical to decompose. In addition, in order to obtain an emission spectrum, a weak CO emission background is required. We have overcome the above difficulties by carefully choosing the wavelength and the power of the lasers.

Either acetone or acetyl chloride were used as the precursors of acetyl radical in the photolysis. Similarly, the propionyl radical was prepared via the photolysis of the 3-pentanone or propionyl chloride. The precursor molecule butanone yields both acetyl and propionyl radicals in nearly equal amounts.[11]

The absorption band of alkyl ketones[11] and acetyl chloride[6] centered at ~280 nm corresponds to a $\pi^* \leftarrow n$ ($S_1 \leftarrow S_0$) transition. As a result of the absorption, the above carbonyl compounds dissociate and yield acyl radicals

$$RCOR'(\text{or RCOX}) \rightarrow RCO + R'(\text{or X}). \tag{2}$$

For the case of 248 nm photolysis of acetone, 45% of the available energy distributes to the translational energy of the products.[4] Therefore, vibrational excitation of the acyl frag-

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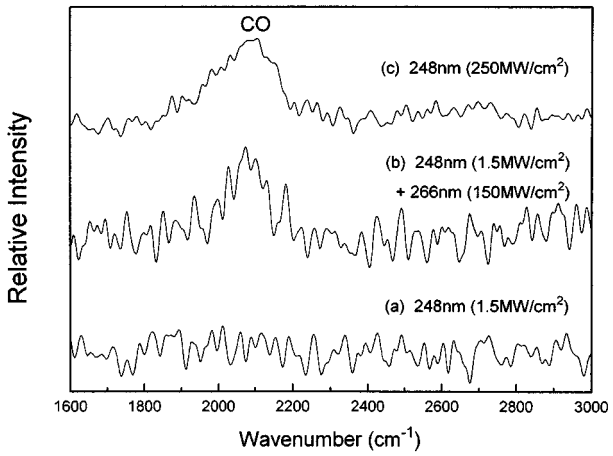

FIG. 1. CO emission spectra from the photolysis of acetone taken at different laser wavelength and fluence: (a) 248 nm laser (1.5 MW/cm^2); (b) 248 nm laser (1.5 MW/cm^2) followed by a 266 nm laser (150 MW/cm^2); (c) 248 nm laser (250 MW/cm^2). All the spectra were obtained at 10 μs after the laser firing. The spectral resolution is set at 16 cm^{-1}.

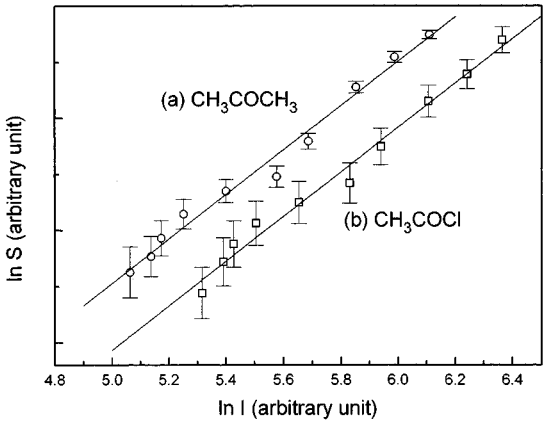

FIG. 2. The laser power dependence of the yield of CO from the photolysis of (a) acetone and (b) acetyl chloride. The laser fluence changed from 125 to 375 MW/cm^2. The slope is 2.0 and 2.1 for (a) and (b), respectively.

ments should not be serious. We have not recorded the IR emission spectra at 1870 cm^{-1}, the wave number of the (C═O) stretching band of the acyl radical.[12]

A part of the acyl radicals spontaneously decompose after 248 nm photolysis.[4–6] Because the available energy of the first photolytic reaction (2) is low, and because the decomposition reaction (1) is endothermic, the product CO must be vibrationally cold, only making a weak IR emission background. Deshmukh *et al.*[6] did not observe the vibrationally excited CO product in the photolysis of acetyl chloride even at a shorter wavelength of 236 nm.

B. The photolysis of acyl radicals at 248 and 266 nm

No CO emission signal was recorded by shining a 266 nm laser (20 mJ, 150 MW/cm^2). Neither was CO emission observed after shining 248 nm laser pulses at a moderate fluence of 1.5 MW/cm^2 [Fig. 1(a)]. However, keeping the fluence of the 248 nm laser pulse unchanged, after 100 ns—leading another 266 nm laser to the chamber collinearly—the CO emission between 1900 and 2200 cm^{-1} appeared [Fig. 1(b)]. Alternatively, the CO emission was also observed by merely increasing the 248 nm laser fluence. The threshold fluence of the CO appearance is about 2 MW/cm^2. Figure 1(c) shows a spectrum obtained at an intense 248 nm laser fluence (250 MW/cm^2). The power dependence of the CO production is measured to be 2.0±0.1 in the range of 125 to 375 MW/cm^2 [Fig. 2(a)]. These observations imply that the CO was produced by a two-photon process via the intermediate species CH_3CO. The precursor carbonyl molecule absorbs the first 248 nm photon and yields an acetyl radical. The acetyl radical absorbs another photon, producing the hot CO fragment. The observed IR emission originated from the vibrationally excited CO(v) fragments

$$CH_3CO(B\ ^2A) \rightarrow CH_3(X\ ^2A_2'') + CO(X\ ^1\Sigma^+, v). \qquad (3)$$

The acetyl radical can also be prepared by the photodissociation of acetyl chloride.[4,6,8,13] In a 248 nm photodissociation experiment of acetyl chloride, an IR spectrum was obtained and is shown in Fig. 3. The emission is very similar to the CO emission from the photolysis of acetone. Again, the power dependence of the emission is 2.1±0.1, also indicating a two-photon process [Fig. 2(b)].

Similar to the acetyl radical, propionyl C_2H_5CO was generated by the 248 nm photolysis of 3-pentanone or propionyl chloride. A further photodissociation of the propionyl by the 248 nm photon was also performed at the same condition. CO(v) emission was recorded (Fig. 3). Finally, the photolysis of butanone was also performed. The primary photodissociation produced a mixture of acetyl and propionyl radicals. Both were further photolyzed by 248 nm photons, leading to a similar CO emission IR spectrum shown in Fig. 3.

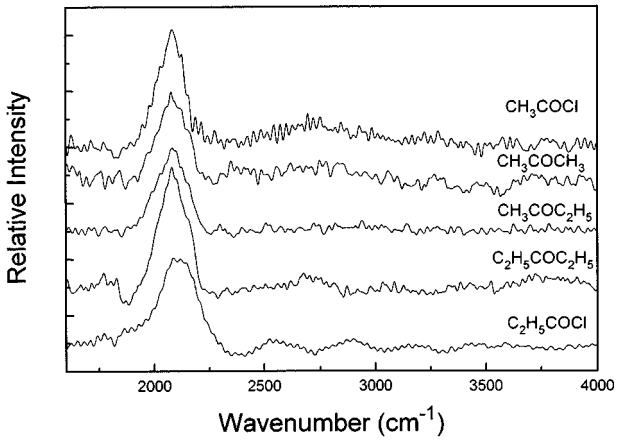

FIG. 3. CO emission from the photolysis of acetyl chloride, acetone, butanone, 3-pentanone, and propionyl chloride between 1600 and 4000 cm^{-1}. The spectra were taken at 10 μs after the laser firing with a spectra resolution of 16 cm^{-1}.

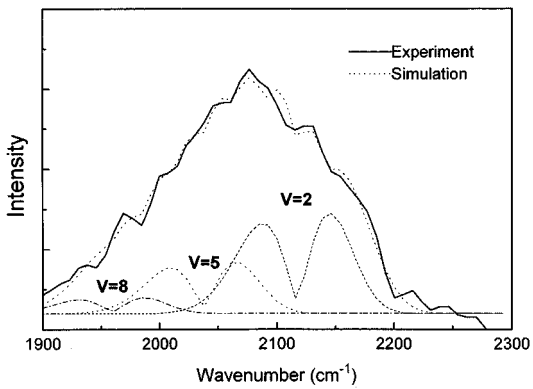

FIG. 4. The simulation of the CO emission spectrum. The solid line is the spectrum taken from the photolysis of CH_3COCH_3. The dashed and the dotted lines are the simulated results.

C. The vibrational population of the CO fragment

In order to evaluate the vibrational population of the nascent CO species, the observed spectrum taken at 10 μs was simulated with a rotational temperature of 350 K (Fig. 4). The quantum numbers up to $v=7$ for 266 nm and $v=8$ for 248 nm were observed. The different excitation reflects the difference of photon energy between two wavelengths. The logarithms of the vibrational populations of CO(v) versus the vibrational level v for acetone, butanone, and 3-pentanone are shown in Fig. 5. The data are nearly in straight lines indicating a Boltzmann distribution. The vibrational temperatures of 7440, 7160, and 6930 K for CH_3COCH_3, $CH_3COC_2H_5$, and $C_2H_5COC_2H_5$ are evaluated from the respective slopes.

No significant vibrational relaxation was found in the delay time of 40 μs after photolysis. Only about 240 collisions occur in 40 μs, which does not seriously change the vibrational population from the nascent one.

The nascent vibrational population of CO($v=0$) cannot be directly obtained from the IR emission spectrum. However, assuming that the rotational population is completely thermalized and does not change too much in 10 μs, the population of CO($v=0$) can be extrapolated from Fig. 5. The

TABLE I. Vibrational temperature and energy of CO in the 248 nm photodissociation of CH_3CO and C_2H_5CO.

Photolytic radical	CH_3CO	$CH_3CO+C_2H_5CO$	C_2H_5CO
Precursor molecule	CH_3COCH_3	$C_2H_5COCH_3$	$C_2H_5COC_2H_5$
Vibrational temperature (K)	7400±300	7200±500	6900±300
Vibrational energy (kcal/mol)			
Experimental	10.5±1.2	10.0±1.6	9.1±0.9
Statistical model	6.0	···	2.1
Impulsive model	12.1	12.1	12.2

average vibrational energy $\langle E_v \rangle$ is obtained by $\langle E_v \rangle = \Sigma N_v E_v / \Sigma N_v$ and is shown in Table I, where N_v is the vibrational population of CO(v) and E_v is the vibrational energy at vibrational level v.

D. Statistical model

The prior distribution of vibrational energy in CO fragment has been used as the vibrational distribution of CO in a statistical model.[14,15] The available energy after photodissociation is 97.8 kcal/mol for the CH_3CO radical and 98.4 kcal/mol for the C_2H_5CO radical. The statistical information-theoretic prior predicts an average CO vibrational energy of 6.0 kcal/mol for acetyl, and only 2.1 kcal/mol for propionyl. It is seen from Table I that the vibrational energy predicted by this statistical model is much lower than that of the experimental results, especially for the photolysis of propionyl radical.

Figure 6 shows the surprisal plots for both acetyl and propionyl radicals. The plots are basically linear. The surprisal parameter is only about -6.0 for the acetyl radical, but more than -18.9 for the propionyl radical. Increasing the number of degrees of freedom in the alkyl fragments could make a substantial difference in the vibrational energy, whereas the experimental values were only modestly reduced. Such deviation reveals that the available energy in the photodissociation has not been statistically distributed.

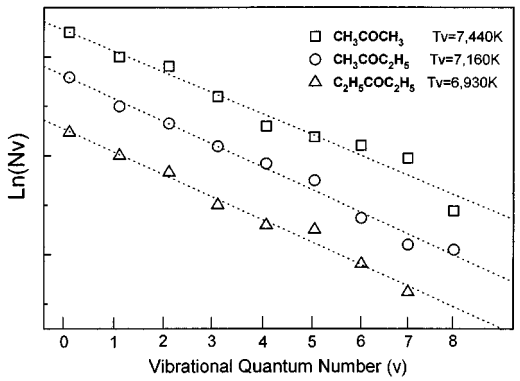

FIG. 5. The vibrational distributions of the CO(v) product from the photolysis of acyl radicals at 10 μs after laser firing. Vibrational temperatures of 7440, 7160, and 6930 K are evaluated from the slope for acetone, butanone, and 3-pentanone, respectively.

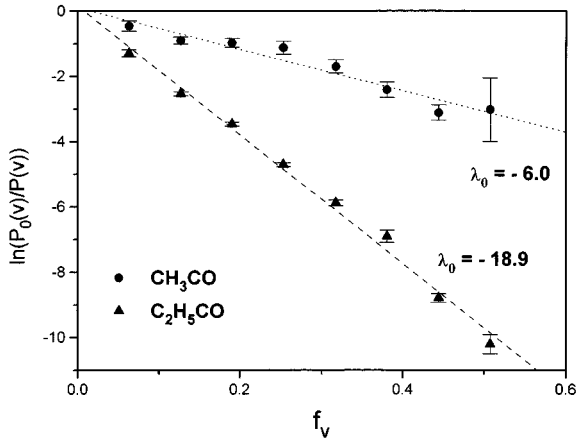

FIG. 6. Surprisal plots for the fraction of the available energy in CO vibration from the photolysis of acetyl and propionyl radicals.

E. Impulsive model

The impulsive model of photodissociation is based on the assumption that the bond in a molecule suddenly breaks due to vibrational motion, without redistribution of internal energy.[16] Supposing the bond angle χ of C–C═O is 130° for both CH_3CO and C_2H_5CO radicals, about 28.6% ($\cos^2 \chi$) of the available energy will be distributed to CO vibration. The average vibrational energy is about 12 kcal/mol, which is slightly higher than that of the observed one.

It is seen in Table I that the prediction from the impulsive model is much closer to the experimental result. Therefore, the photodissociation process of acyl radicals should take place in a very short time and the available energy should not be sufficiently distributed to the alkyl group.

IV. CONCLUDING REMARKS

(1) Time-resolved FTIR emission spectroscopy has been applied to study the photolysis of acetyl and propionyl radicals at 248 and 266 nm. The acyl radicals are produced by the 248 nm photodissociation of acetone, acetyl chloride, butanone, 3-pentanone, and propionyl chloride.

(2) Vibrationally excited CO emission was obtained at an intense 248 nm laser fluence (250 MW/cm^2) or at moderate 248 nm laser fluence (1.5 MW/cm^2) followed by a 266 nm laser beam (150 MW/cm^2). The process is a photodissociation of the $B\ ^2A'$ state of acetyl radical.

(3) The laser power dependence of the CO production was determined to be 2.0, indicating a two-photon process.

(4) The CO vibrational distribution is thermalized and fits a temperature of ~7000 K.

(5) The dissociation of the acyl radical fits the impulsive model of photodissociation.

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