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The ro-vibrational spectra of CO molecule resulting from the photolysis of acetone

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Abstract

A time-resolved Fourier-transform emission spectroscopy was used to detect the IR emission of the fragments resulting from the photolysis of acetone by 193 nm excimer laser; a double peak vibrational spectrum in the range of 1950–2250 cm^{-1} corresponding to the P and R branches of the CO stretching vibration. At 0.3 cm^{-1} resolution; the ro-vibrational lines appeared for the first three vibrational transitions. The experimental spectra match greatly the simulated one. Using the fitting methods, the populations were found for the first four vibrational levels. The vibrational spectrum and populations of the CO resulting from the photolysis of acetone in helium differ from acetone alone due to the relaxation effect of helium.

Keywords: Rotational spectra; Vibrational population; Simulation

1. Introduction

As the simplest ketone, acetone has long been used for studying the photophysics and photochemistry of this important class of carbonyl compounds. Photolysis proceeding via α-bond cleavage (Norrish I) is the most studied of the photochemical processes [1], much of the photochemical research from the pre-laser era was summarized in the review of Lee and Lewis [2], these early experiments indicated that the primary photochemical events is the cleavage of one or both C–C bonds, producing one or two methyl radicals in coincidence with acetyl radical or CO, respectively.

Lightfoot et al. [3] have found from the time-resolved absorption measurements and product analysis; the quantum yield for $CO + 2CH_3$ to be 0.95 at 193 nm. The initial excitation is to the adiabatic potential energy surface which is bound along the C–C coordinate, bond cleavage can occur by either internal conversion or intersystem crossing to the $C'_s\sigma^3\sigma^*$ configuration via out-of-plane motion [4,5].

An excimer laser operating on 193 nm is used to photo-dissociate acetone because its absorption cross-section at 193 nm is large ($2 \times 10^{-18}\,\text{cm}^2$) [6] a Rydberg state which is initially excited on a (n, 3S) transition [7]. Brouard et al. [8] have measured the quantum yields for the various dissociation pathways following 193 nm excitation for acetone the dominant fragmentation is CO and $2CH_3$ with a quantum yield of 0.96. Donaldson and Leone [9], have been detected the CO and two CH_3 fragments resulting from the photolysis of acetone at 193 nm. Vibrational excitation is detected in both products immediately following the dissociating laser pulse by observing the resulting infrared emission.

Vacuum-ultraviolet laser induced fluorescence was used to probe the CO fragment following 193 nm dissociation of acetone ($\nu = 0, 1$) [10].

Potzinger et al. [11] photolyzed acetone at 185 nm with a low-pressure mercury arc and determined quantum yield Φ of the final products to be ∼1 for CO and ∼0.95 for C_2H_6, generated by the mechanism. Gandini and Hackett [12] found that the quantum yield for carbon monoxide production in the region 255–280 nm was unaffected.

The available evidence that suggests that the photolysis of acetone at around 200 nm using a high-intensity pulsed light source such as an exciplex laser at 193.3 nm. The extinction coefficient (ε) of acetone at 193.3 nm is around $700\,\text{M}^{-1}\,\text{cm}^{-1}$ over a factor of six greater than the maximum of the first absorption band [13].

Woodbridge et al. [14] have studied the photophysics and photochemistry of acetone excited to its lowest $^1(\text{n},^*\pi)$ excited state at wavelengths longer than 200 nm, the primary photoproducts of acetone in this special region are CH_3 and CH_3CO, with a strong dependence on pressure,

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temperature and excitation wavelength; at low-pressures, dissociation primary occurs from vibrationally excited levels of the strongly mixed ^{1}(n,*π) and ^{3}(n,*π) states, at higher pressures, there is a temperature dependent dissociation of both the vibrationally relaxed triplet and the acetyl radical to yield a second methyl radical and CO. Hall et al. [15] have measured the vibrational population of the CO molecule resulting from the 193 nm photolysis of acetone and diethyl ketone.

2. Experiment

The time-resolved Fourier-transform IR has been described in detail previously [16]. Some modifications have been made for these experiments: (1) the IR source is replaced by the emission from the fragments resulting from the photodissociation by the laser; (2) the function generator in the (TR-SS) is replaced by the delay generator, which consists of a function generator (Stanford research system, Model DS 345, 30 MHz) connected to a delay unit (Stanford research system, Model DG 535). This set-up gives two signals, which are delayed from each other by sub-microseconds. The delayed signal is given to the FTIR (Bruker IFS 66 V) spectrometer, while the original one is given to the external trigger of the 193 nm ArF excimer laser (Lambda Physics) via a light-emitting diode. The photolysis mixture, consisting of either acetone or acetone and helium are introduced to the photolysis chamber [17]. The ArF excimer laser pulses pass through the chamber and photolyze acetone. Time-resolved IR vibrational emissions from vibrationally excited photofragments produced by the dissociation are detected through the TR-FTIR.

3. Results

The time-resolved emission FTIR is a high-resolution medium because it allows us to resolve the emitted spectra of the molecules over a broad wavelengths range in a relatively short period of time. Such a high-resolution spectra can be analyzed directly to obtain the ro-vibrational state populations.

3.1. Experimental spectrum of CO

When a mixture of acetone 0.2 Torr in 30 Torr He or acetone 0.2 Torr gases bombarded by 193 nm excimer laser pulsed of power 4.2 MW cm^{-2} it undergoes photodissociation producing vibrationally-excited CO and CH$_3$ radicals. The presence of He buffer gas serves as a rotationally relax the CO and CH$_3$ photoproducts on a short time scale. At least three vibrational levels are populated in the CO molecule at time delay 10 μs between the laser and the measurement of FTIR spectrometer, mainly, ν= 1, 2, and 3 (see Figs. 1 and 2) the resolution of our FTIR is 0.3 cm^{-1}.

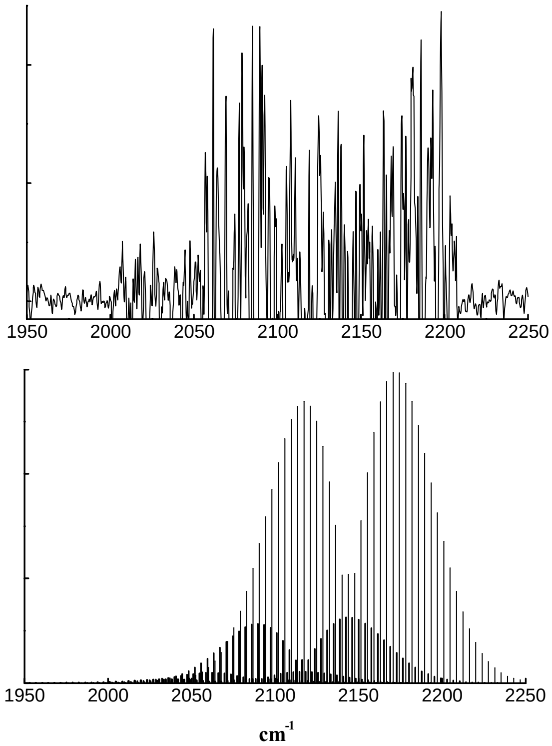

Fig. 1. A comparison of the observed and simulated spectra (upper spectra) the experimental spectrum of the CO emission obtained from the photodissociation of 0.2 Torr acetone in 30 Torr He by the 193 nm excimer laser at time delay 10 μs, (lower spectrum) the simulated spectrum of the CO at rotation temperature 300 K.

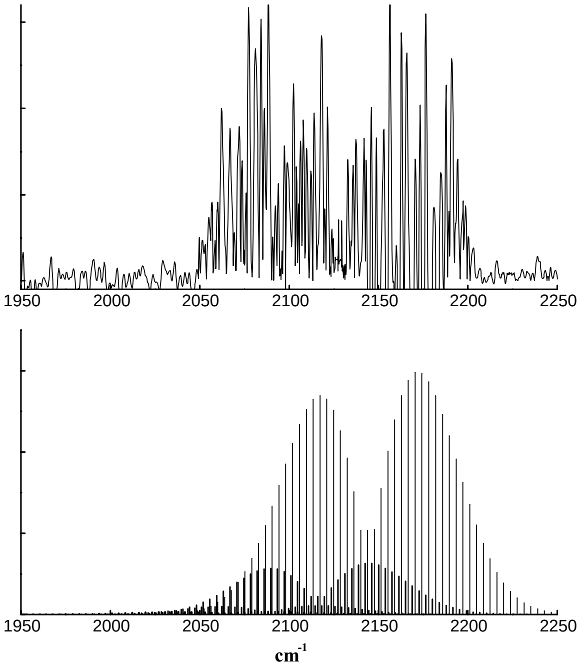

Fig. 2. A comparison of the observed and simulated spectra (upper spectra) the experimental spectrum of the CO emission obtained from the photodissociation of 0.2 Torr acetone by the 193 nm excimer laser at time delay 10 μs (lower spectrum) the simulated spectrum of the CO at rotation temperature 300 K.

The time-dependent emission spectra in the 1950–2250 cm^{-1} region revels the rotational and vibrational distributions of the CO molecule produced from the photodissociation and subsequent relaxation in the presence of the helium gas. The CO emission spectrum has two branches P and R, each branch has the different rotational lines. It is essential to know the rotational distribution in order to extract the vibrational population of CO molecule.

An experiment is performed with excess of He buffer gas to relax the rotation of levels without affecting the CO vibrational distribution at all. We could maintain the rotational temperature at 300 K, since the collision with the He gas is obviously hinders its rotation; but will retain its nascent vibrational distribution.

The row spectra obtained are a convolution of the actual emission intensity with the response function of the detector, the transmission/reflection functions of all the optics, and the black body background. To correct the spectra a very high signal to noise ratio spectrum is taken at 300 K ambient radiation without pulsing the laser. This black body spectrum is then divided by a calculated 300 K black body spectrum to give an approximate instrumental response function. The raw spectra are then divided by this instrumental response function to obtain a spectrum that reflects the true emission.

3.2. *Simulation the rotation vibration spectra of CO*

The coupling between P and R branches of the vibration–rotation spectra takes place in the experimental spectra of the CO; so to resolve this spectra we should "simulate" it this simulation and fitting procedure has been developed to match the computer generated CO spectra from different vibration-rotation levels to the observed emission. This simulation is used determining the appropriate creation processes for the vibrationally excited CO.

The first step in such interpretation involves the determination of vibrational population distributions. The basis functions "$\zeta_V(V)$" were generated which are representative of the spectrum arising from all possible rotational transitions taking place with the vibration transition (V→V − 1).

Combining these basic functions in the manner to best match the observed radiations signatures yielded weighting factors proportional to the desired vibrational populations. The details of the generation of the synthetic spectra and fitting technique are provided as following.

3.2.1. *Generation of the simulated spectra*

The computer generated CO spectra obtained as the summation of the contributions of the radiation per unit population in each vibration level.

The integrated intensity of a given rotational transitions in the vibrational band may be specified by

$$I^{(V\to V-1)}_{(J\to J-I)}(\nu_T) = \frac{hc\nu_T^4 S_J^{P,R} A_{(J\to J-1)} N_{(V,J)}}{(2J+1)\nu^3_{(V\to V-1)}} \tag{1}$$

where $A_{(V\to V-1)}$ is the Einstein coefficient for the spontaneous emission is calculated as in reference [18], h is the Planck's constant, c is the speed of light, $S_J^{P,R}$ is the Honl–London factor; $S_J^P = (J-1)$, $S_J^R = (J+2)$; $\nu_{(V\to V-1)}$ is the frequency of the band origin in cm^{-1}; $\nu_{(V\to V-1)} = E_{(V)} - E_{(V-1)}$ where $E_{(V)}$ and $E_{(V-1)}$ are the vibration energies of (V) and (V − 1) states.

$$E_V = \omega_e\left(\nu+\frac{1}{2}\right) - \omega_e\chi\left(\nu+\frac{1}{2}\right)^2 + \omega_e y_e\left(\nu+\frac{1}{2}\right)^3 \tag{2}$$

where $\omega_e = 2171.1\,\text{cm}^{-1}$, $\omega_e\chi_e = 13.8\,\text{cm}^{-1}$ and $\omega_e\sigma_e = 0.01059\,\text{cm}^{-1}$ are the anharmonic constants, so; $\nu_{(1\to 0)} = 2143.9\,\text{cm}^{-1}$, $\nu_{(2\to 1)} = 2116.1\,\text{cm}^{-1}$, $\nu_{(3\to 2)} = 2088.9\,\text{cm}^{-1}$, and $\nu_{(4\to 3)} = 2061.3\,\text{cm}^{-1}$. ν_T is the frequency of the individual transition in cm^{-1} ($\nu_T = E(_{V,J}) - E(_{V-1,J})$ where $E(_{V,J})$ and $E(_{V-1,J})$ are the vibration-rotation energies of the states.

$$E_{V,J} = \omega_e\left(\nu+\frac{1}{2}\right) - \omega_e\chi_e\left(\nu+\frac{1}{2}\right)^2 + \omega_e y_e\left(\nu+\frac{1}{2}\right)^3 + B_V J(J+1) - D_e J^2(J+1)^2 \tag{3}$$

where B_V and D_e are the rotational term values, therefore, the frequency of the rotational transitions in the R and P branches are:

$$\upsilon^P_{(V\to V-1)} = \upsilon_{(V\to V-1)} - 2B_V(J+1) + D_e(J+1)^3 \quad \textit{and}$$
$$\upsilon^R_{(V\to V-1)} = \upsilon_{(V\to V-1)} + 2B_V(J+1) + D_e(J+1)^3 \tag{4}$$

where $B_V = B_e + \alpha_e\left(\upsilon+\frac{1}{2}\right)$

For the CO, $\alpha_e = 0.017459\,\text{cm}^{-1}$, $B_e = 1.93127\,\text{cm}^{-1}$, and $D_e = 5.628 \times 10^{-5}\,\text{cm}^{-1}$, therefore, $B_1 = 1.905$, $B_2 = 1.8876$, $B_3 = 1.87$, and $B_4 = 1.8527\,\text{cm}^{-1}$ spectroscopic constants were obtained from the Huber and Herzerg [19].

$N_{V,J}$ is the population of the radiating state. According to the Boltzmann distribution $N_{V,J}$ can given by

$$N_{V,J} = N_V\left(\frac{hcB_V}{KT}\right)(2J+1) \times \exp\left(\frac{-hc(B_V J(J+1) - D_e J^2(J+1)^2)}{KT}\right) \tag{5}$$

From Eqs. (1) and (5)

$$\frac{I^{(V\to V-1)}_{(J\to J-I)}(\nu_T)}{N} = \frac{h^2c^2\nu_T^4 S_J^{P,R} A_{(V\to V-1)} B_V}{KT\nu^3_{(V\to V-1)}} \times \exp\left(\frac{-hc(B_V J(J+1) - D_e J^2(J+1)^2)}{KT}\right) \tag{6}$$

From Eq. (6), the intensity of a given (vibration-rotation) molecular transitions per vibrationally excited molecule $[I^{(V\to V-1)}_{(J\to J-I)}(\nu_T)/N]$ can be determined by Green et al. [20].

Table 1
The vibrational population distributions for the CO molecule obtained from the photodissociation of 0.2 Torr acetone in 30 Torr He Experiment (I) and 0.2 Torr acetone Experiment (II) by the 193 nm excimer laser 4.2 MW cm^{-2} at time delay 10 μs

Vibration population	Experiment (I)	Experiment (II)	Reference [10]	Reference [14]	Reference [9]	Reference [15]
$P(f_0)$	–	–	0.73	–	–	–
$P(f_1)$	0.79 ± 0.03	0.78 ± 0.03	0.2	0.73 ± 0.04	0.75 ± 0.05	0.79 ± 0.02
$P(f_2)$	0.18 ± 0.03	0.17 ± 0.03	0.07	0.23 ± 0.02	0.16 ± 0.05	0.17 ± 0.02
$P(f_3)$	0.021 ± 0.03	0.04 ± 0.03	≤0.03	0.04 ± 0.01	0.09 ± 0.5	0.03 ± 0.02
$P(f_4)$	0.009 ± 0.03	0.01 ± 0.03	–	–	–	0.01 ± 0.02

The simulated spectra result from plotting the intensity per vibrationally excited molecule versus the frequency of the individual transition (ν_T). The resultant spectra per vibrational-excited molecular (basis function) for each of the vibrational levels is used in generating the synthetic spectrum (see Figs. 1 and 2).

3.3. *Effect of He on the vibrational population of CO*

The presence of helium gas with acetone affects the vibrational population of the energy levels of CO molecule. To account for this effect; we used two mixtures one of acetone alone and the other is acetone in He using the same power of the dissociating laser. All the experiments were done at the same time delay between the laser and FTIR measurement. This idea was summarized in Figs. 1 and 2. The higher spectrum is the experimental rotational vibrational spectrum of CO molecule resulting from the photodissociation of 0.2 Torr acetone in 30 Torr He and 0.2 Torr acetone at time delay 10 μs after the 193 nm excimer laser of power 4.2 MW cm^{-2} pulse. The lower spectrum represents the rotation vibration simulated spectrum of CO. The vibrational population of the first four vibrational levels of CO molecule can be calculated from both the experimentally obtained fully resolved rotational lines and the simulated ones. To determine the relative vibrational populations; we simply measured the areas of the peaks divided by the appropriate Einstein spontaneous emission coefficient, and sum over the vibrational states, only the lines that are fully resolved in all the three levels are used for such analysis.

3.3.1. *Fitting of the data and determination of N_V population*

The best fit to our experimental data is obtained by a routine that minimizes the squares χ^2 of the differences between the data and the sum of the weighted vibrational basis function [15].

$$\chi^2 = \left[I_n(\nu) - I^{(V\rightarrow V-1)}_{J\rightarrow J-1)}(\nu_T) \right]^2$$

where $I_n(\nu)$ is the intensity of experimental spectra, $I^{(V\rightarrow V-1)}_{(J\rightarrow J-I)}(\nu_T)/N = \zeta_V(\nu)$ is the basis function so; when the square of the differences is minimized $I_n(\nu) \approx \sum N_V \zeta_V(\nu)$. Since the ζ_v(v) is linearly proportional to the Einstein coefficients $A_{(V\rightarrow V-1)}$ the quantities actually determined by the least squares fit are the product $N_V\ A_{\ (V\rightarrow V-1)}$; so the quantities of N_V can be calculated. A rotational temperature of 300 K was taken to generate the simulated spectra. The normalized populations of the vibrational energy levels to the population of the first vibrational level for the two experiments are given in Table 1.

A comparison of the vibrational population distributions for the CO molecule resulting from the photolysis of acetone in argon by 193 nm excimer laser is given in Table 1, including the FTIR measurements [9,14,15] and the laser-induced fluorescence measurements of Trentelman et al. [10].

In the presence of helium relaxing-gas; the first two vibrational energy levels of the CO resulting from the photolysis of acetone is highly populated at the expense of the third and fourth vibrational levels, but; the opposite behavior in case of acetone alone.

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