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The effect of delay time on the CO and CH$_3$ radicals resulting from the photolysis of acetone by 193 nm excimer laser

Y. Badr [a], S. Abd elwanees [b], M.A. Mahmoud [b],*

[a] *National Institute of Laser Enhanced Science, Cairo University, Cairo, Egypt*
[b] *Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt*

Abstract

A time-resolved Fourier transform IR spectrometer is used to measure the emitted spectra of the fragments resulting from the photodissociation of 3S Rydberg state acetone by a 193 nm excimer laser at different delay times between the FTIR and the laser. Two vibrational bands are detected. The first band, a single peak in the range of 3200–2750 cm^{-1}, is assigned to be the CH of the methyl radicals, is unresolved. The second is a resolved double peak band in the range of 2250–1950 cm^{-1} is assigned to be the P and R branches of the CO molecule. The emitted spectra of the CO molecule and the methyl radicals are measured at different delay times from 1 to 50 μs. The integrated intensity of the emitted spectra of CO was found to increase with delay times up to 50 μs, while that of the methyl radicals showed the opposite behaviour. Plotting the relationship between the laser power and the integrated intensity of the CO spectrum yielded a straight line with a gradient ∼1. this may indicate that the process is a single-photon reaction.
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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].

At sufficiently high excitation energies, acetone represents a prototypical three-body dissociation process involving the cleavage of two identical chemical bonds. Of dynamical interest is the extent to which the two bond breaking steps are energetically and temporally coupled. Recent studies on the photodissociation dynamics of acetone showed that the sequence of events leading to the three asymptotically separated fragments is still largely unresolved. The review of Lee and Lewis [2] summarises most of the photochemical research from the pre-laser era.

Baba et al. [3] measured the yield of acetone fragment ions following multi-photon excitation by an ArF excimer laser at 193 nm. The power dependence of the acetyl ion signal ($m/e = 43$) suggested that the ion was produced as

a result of absorption of the laser radiation by a relatively long-lived neutral acetyl fragment. They considered this result as evidence of a sequential bond-rupture mechanism. The initial excitation is to the A adiabatic potential energy surface which is bound along the C–C coordinate. Bond cleavage can occur either by internal conversion or intersystem crossing to the C$'_s\sigma^3\sigma^*$ configuration via out-of-plane motion [4,5]. Consequently; excited-state dissociation can proceed over a small barrier caused by an avoided crossing on the T$_1$ surface. This barrier height has been measured by Zuckermann et al. [6], who observed a pronounced decrease in the fluorescence emission at 305.8 nm. An excimer laser operating at 193 nm is used to photodissociate acetone because the acetone absorption cross section is large (2×10^{-18} cm^2) at this wavelength [3].

Brouard et al. [7] measured the quantum yields for the various dissociation pathways following excitation at 193 nm. For acetone the dominant fragmentation is (CH$_3$)$_2$CO → CH$_3$ + CO + CH$_3$, with a quantum yield of 0.96.

Excitation at 248 nm resulted in the production of CH$_3$ and CH$_3$CO. The nascent acetyl radicals from the primary dissociation contain sufficient energy to undergo spontaneous decomposition [8].

Potzinger et al. [9] photolyzed acetone at 185 nm with a low-pressure mercury arc and determined the quantum yield

* Corresponding author. Tel.: +20-2-55-3052838;
fax: +20-2-55-3052838.
E-mail address: mahmoudchem@yahoo.com (M.A. Mahmoud).

Φ of the final products to be ∼1 for CO and ∼0.95 for C_2H_6. Gandini and Hackett [10] found that the quantum yield for carbon monoxide production in the region 255–280 nm was unaffected by the addition of several 100 Torr of an inert bath gas and concluded that the direct route to carbon monoxide production was most likely. The only temporally resolved studies on the 3S Rydberg state are those by Buzza et al. [11] who used femtosecond laser pulses at 585 nm to induce a three-photon absorption to the 3S Rydberg state, followed by two-photon ionization at the same wavelength to monitor the mass resolved dynamics of the acetyl radical. Zewail and co-workers [12] measured the lifetime of the 4S Rydberg state of acetone using a femtosecond REMPI laser following two-photon excitation at 307 and 280 nm. Kim and Zewail [13] also examined the dissociation of acetyl as the secondary step in several asymmetric ketones. Ultrafast deep-UV mass-resolved photoionisation spectroscopy has been used to investigate the photodissociation dynamics of the 3S Rydberg state of acetone. Single-photon excitation at 193–195 nm is followed by single-photon, at 260 nm and two-photon, at 390 nm, ionization. The signals are measured for both the acetone and acetone photoions [14]. Shibata et al. [15] measured the ion images of the acetyl radical as a function of pump-probe time delay. In the present work, time-resolved FTIR spectroscopy is used to account for the time sequences of the photolysis of acetone by 193 nm excimer laser pulses for different delay times (2, 10, 20, 30, and 50 μs). A suitable delay unit and setup, including the fast-scan facilities of our FTIR system, and a home made electronic system controlled by a PC, are used here, aiming to account for the possibility of the occurrence of a single-photon process rather than a two or a multi-photon processes as previously detected.

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 and (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 setup gives two signals which are delayed from each other by sub-microseconds. The delayed signal is given to the FTIR (Bruker IFS 66V) 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

3.1. Effect of the delay on the photolysis of acetone

The setup based on the Bruker FTIR spectrometer is used here to measure the emission resulting from the photodissocition of acetone gas by the 193 nm excimer laser. Two vibrational bands are obtained for each time delay between the exciting laser and the monitoring of the fast-scan FTIR spectrometer; the first band is a double peak centred between 1950 and 2250 cm^{-1} which corresponds to a CO stretching vibration; the second band is broad and located 2750–3300 cm^{-1} which corresponds to a CH stretching vibration [18].

The intensities of the two bands are found to be dependent on the time delay between the laser pulse and the fast-scan FTIR. The intensity of the emitted radiation resulting from the bond vibration of the excited CO increases with the increase of the time delay from 2 to 50 μs.

On the other hand, the intensity of the second band resulting from CH emission of the vibrationally hot methyl radical is found to decrease with increasing time delay from 2 to 50 μs.

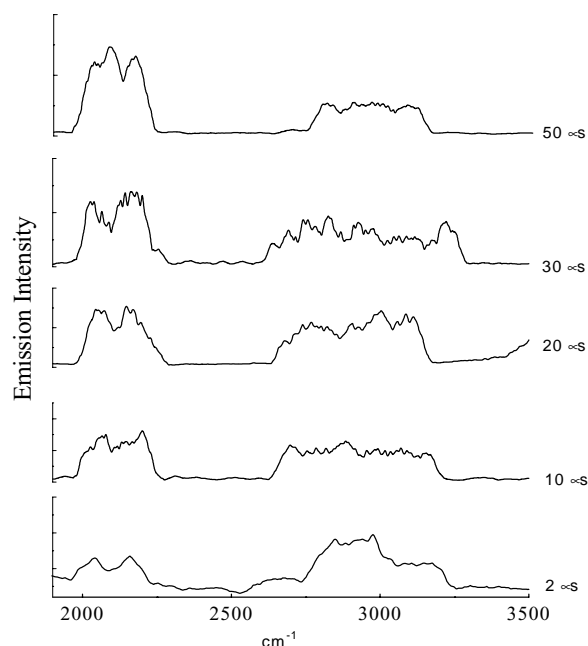Fig. 1 shows the emission spectra resulting from the photolysis of a mixture of 0.1 Torr acetone and 10 Torr He by

Fig. 1. The spectra of CO and CH stretching vibrations with 8 cm^{-1} resolution for the fragment resulting from the photodissociation of a mixture of 0.1 Torr acetone and 10 Torr He by the 193 nm excimer laser with power 4.2 MW cm^{-2}, at different delay times between firing the laser and FTIR measurement started by 2 μs at the bottom to 50 μs at the top.

Table 1
The ratio of the integrated intensities of the CH and CO bond vibration at different delay times normalized to that at 2 μs and the ratio between the integrated intensities of CH and CO at every time delay

Time delay (μs)	I(CH/CO)	I(CH) (n μs/2 μs)	I(CO) (n μs/2 μs)
2	1.05	1	1
10	0.76	0.792	1.19
20	0.67	0.708	1.2
30	0.599	0.67	1.27
50	0.469	0.489	1.19

the 193 nm excimer laser with power 4.2 MW cm^{-2} for time delays 2, 10, 20, 30 and 50 μs.

3.1.1. The ratio of the integrated intensities of CH and CO

The intensity of the emitted spectra of CH or CO stretching vibration at each time delay depends on the life time of the CH$_3$ radical and excited CO molecule. The CH/CO ratio is found to decrease with the increase of the time delay from 2 μs up to 50 μs due to the fast decay rate of the CH$_3$ radical. The integrated intensities of CH or CO bands, as determined by Gaussian fitting of the spectra are shown in Fig. 1.

Table 1 represents the ratio of the integrated intensities of the CH and CO bond vibrations at different delay times. The drop in the CH/CO ratio from 1.14 at 2 μs to 0.76 at 10 μs might be attributed to the decay of the CH$_3$ radical.

Fig. 2 shows the relationship between the ratio of the integrated intensities of the CH/CO bond vibrations at different delay times and the delay time. The CH/CO intensity decreases with increasing delay time, indicating that the ratio of the integrated intensities of CH/CO bond vibrations decreases rapidly with increasing the delay time in the first 10 μs followed by a slow rate after 10 μs, and after 30 μs the rate found to be faster again.

The third column in Table 1, represents the relative integrated intensities of the CH band at each time delay nor-
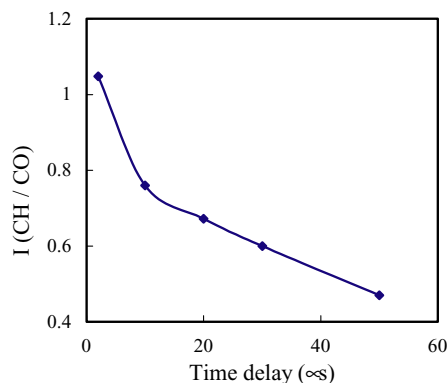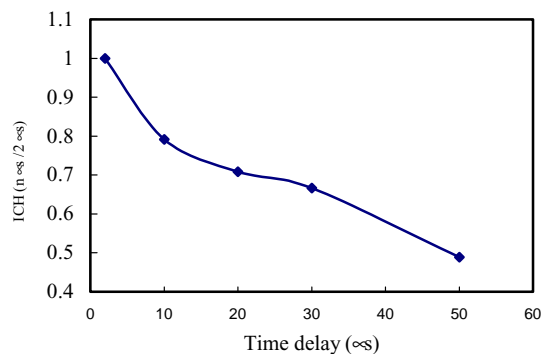

Fig. 3. The normalized integrated vibrational intensities of the CH bond vibration at 10, 20, 30, 50 μs to 2 μs resulting from the photodissociation of 0.1 Torr acetone in 10 Torr He by 193 nm excimer laser with power 4.2 MW cm^{-2}.

malized to the integrated intensity at 2 μs. The fourth column shows the relative integrated intensities of the CO band at each time delay normalized to the integrated intensity at 2 μs. Fig. 3 illustrates the relationship between the normalized vibrational intensities of the CH band and the time delay. Our results show that the normalized integrated intensities of the CH bond vibration decreases with increasing time delay, with a fast rate in the first 10 μs and small rate between (10–30 μs), then decreases after 30 μs with a faster rate.

Fig. 4 shows the relationship between the normalized vibrational intensities of the CO bond and the time delay. The normalized integrated intensities of the CO bond vibration increase with increasing of the time delay, with fast rate in the first 10 μs and small rate after 10 μs, then decreases after 30 μs.

3.2. Effect of the power of the laser on the photolysis of acetone

The experimental results of the laser photolysis of acetone show that in the case of 193 nm (ArF) excimer laser pulses
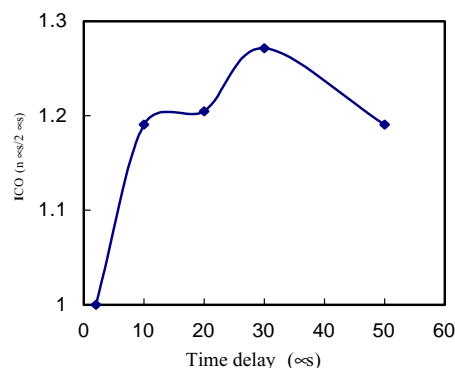

Fig. 2. The ratio of the integrated vibrational intensities of the CH and CO bond vibration at 2, 10, 20, 30, 50 μs resulting from the photodissociation of 0.1 Torr acetone in 10 Torr He by 193 nm excimer laser with power 4.2 MW cm^{-2}.

Fig. 4. The normalized integrated vibrational intensities of the CO bond vibration at 10, 20, 30, 50 μs to 2 μs resulting from the photodissociation of 0.1 Torr acetone in 10 Torr He by a 193 nm excimer laser with power 4.2 MW cm^{-2}.
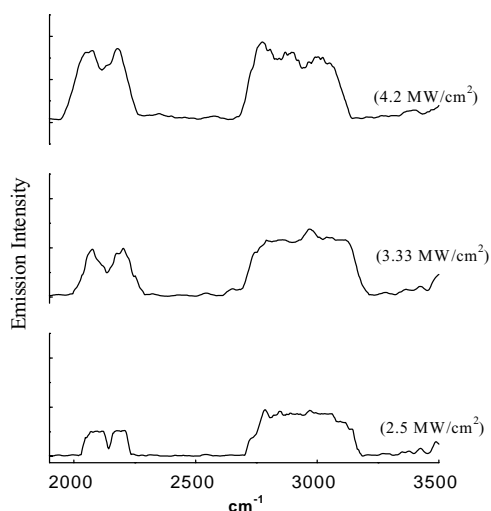
Fig. 5. The spectra of CO and CH stretching vibration with resolution 8 cm^{-1} for the fragment resulting from the photodissociation of a mixture 0.1 Torr acetone in 10 Torr He by 193 nm excimer laser with powers 2.5, 3.33, 4.2 MW cm^{-2} and the time delay between the laser and FTIR is 1 μs.

of duration 6 ns the minimum power required for photodissociation of acetone is 2 MW cm^{-2}. Moreover, the yield of the resulting a fragments CO molecule and CH$_3$ radicals, is found to depend essentially on the power of the laser. For example, a mixture of 0.1 Torr of acetone in 10 Torr of He bombarded by a pulsed 193 nm excimer laser at powers of 2.5, 3.33, or 4.2 MW cm^{-2}, with a delay time of 1 μs, resulted in an increasing yield of CO molecule and CH$_3$ radicals as the laser power increased. Fig. 5 shows the emitted spectra of the CO and CH stretching bands of methyl radicals resulting from the photodissociation of 0.1 Torr acetone in 10 Torr He by excimer laser with powers 2.5, 3.33, or 4.2 MW cm^{-2} at time delay 1 μs. The intensities of the spectra of both the CO molecule and CH$_3$ radicals increase with increasing laser power.
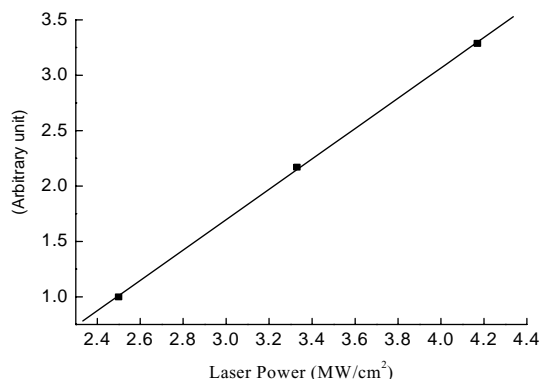

Fig. 6. The relationship between the yield of CO resulting from the photodissociation of 0.1 Torr acetone in 10 Torr He and the time delay between the laser and FTIR is 1 μs. The laser power changed from 2.5, to 3.33, to 4.2 MW cm^{-2}, the resulting straight line has a gradient of 1.3.
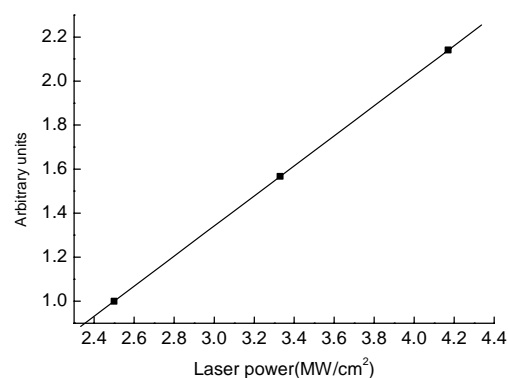

Fig. 7. The relationship between the yield of CH resulting from the photodissociation of 0.1 Torr acetone in 10 Torr He and the time delay between the laser and FTIR is 1 μs. The laser power changed from 2.5, to 3.33, to 4.2 MW cm^{-2}. The resulting straight line has a gradient of 0.7.

A Gaussian fitting of the CO and CH stretching modes in Fig. 5 shows that the integrated intensities increase with increasing power of the laser due to the increasing yield of the fragments. Fig. 6 gives the relationship between the normalized integrated intensities of the CO stretching vibration for each laser power to intensity of the CO band at 2.5 MW cm^{-2} at a time delay of 1 μs.

Plotting the relationship between the normalized integrated intensities of the CO starching vibration, "which might represents the CO yield", and the power of the laser gives a straight line with gradient of 1.3 (Fig. 6). This might indicate that a single-photon process is occurring and no evidence for a multi-photon process which might lead to a slope more than one or equal to two, as in the case of a multi-photon absorption process, more than several photons are required to produce a CO molecule. Similarly, a linear relationship is obtained for CH$_3$ radicals (see Fig. 7) confirming the single-photon absorption hypothesis.

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