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Two photon dissociation of acetone, acetaldehyde, and acetic acid at 243 nm: translational energy releases in the H atom channel

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Abstract

The hydrogen atom channels from photodissociation of acetone, acetaldehyde, and acetic acid at 243 nm have been investigated by detecting H atoms using two photon absorption at 243.2 nm and induced fluorescence at 121.6 nm. Translational energies of the H atoms were measured by Doppler broadened H atom spectra. By absorption of two photons at 243 nm, the H atoms were produced from acetyl radicals. The possible dissociation mechanisms are discussed from the measured translational energy releases. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photodissociation; Translational energy; Acetone

1. Introduction

Studies on photodissociation of carbonyl compounds such as acetone in UV have been extensively reported [1–4]. Absorption centered at around 280 nm is assigned as n $\rightarrow$ π^* which produce methyl and acetyl radicals as major products with the quantum yield of near unity. On the other hand, at shorter wavelengths, the n $\rightarrow$ 3s Rydberg transition breaks two C–C bonds in acetone producing two methyl radicals and CO as fragments. Previous studies on the dissociation of these compounds were concentrated on mechanisms whether this three body dissociation takes place via concerted or step-wise manner. The very recent study on acetone by the femtosecond pump-probe technique demonstrated that dissociation occurs in a step-wise manner when the photon energy is large enough to break both C–C bonds [5]. The measured lifetime of the acetyl radical is around 500 fs and the dissociation dynamics of the acetyl radical is successfully modeled by the RRKM theory.

The dynamics of photodissociation depends upon the excited state and potential energy surfaces along the reaction coordinates. Thus, by studying the photodissociation dynamics, one can explore the electronic structure and the potential energy surfaces of the molecules in the excited electronic states. The coupling between the excited states and the dissociation coordinate leads to specific dissociation channels. In order to figure out the complete potential energy surfaces, all the dissociation channels should be investigated. None of the earlier studies on the above carbonyl compounds paid attention to the H atom channels, which are minor.

In the present study, the H atom channels from photodissociation of acetone, acetaldehyde, and acetic acid at 243 nm have been investigated. At 243 nm, one photon energy is not enough to break both the C–C and C–H bonds and thus the mechanisms of the two photon dissociation of the above compounds have been studied by measuring the translational energies of the H atoms produced from the reaction. The H atoms are produced from the acetyl radicals and possible mechanisms are discussed.

2. Experiments

The experiments were performed in a flow cell whose pressure was maintained at around 1×10^{-3} Torr without the sample. The gaseous samples were slowly flowed through the cell at pressures of about 100 mTorr controlled with needle valves. The photolysis and probe light was introduced to the cell through quartz windows and the resulting fluorescence was detected through a LiF window at a right angle to the light beam. The liquid samples with stated purity higher than 99.9% were purchased from Aldrich and used without further purification.

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The photolysis and probe light, that is, 243.2 nm light was a frequency-doubled output of a dye laser (Lumonics HD-500) pumped by the third harmonic of an Nd:YAG laser (Lumonics YM-800). The sample molecules were photodissociated at 243.2 nm and the fragment H atoms absorbed two photons of the same light within the pulse and reached the 2s state. The H atoms were then quenched to the 2p state followed by relaxation to the ground state resulting in Lyman-α fluorescence at 121.6 nm. The resulting fluorescence was detected by a solar blind photomultiplier tube (Hamamatsu R1259). In order to increase the S/N ratio in the spectra, a Lyman-α filter was placed and dry nitrogen was flowed between the viewing window and the PMT. The detected signal was fed to the boxcars and signal processors and stored in a PC.

Since the present experiment needed at least three photons to detect the fragment H atoms, the light was focused with a lens. In order to avoid saturation in the observed H atom spectra, the lenses of various focal lengths were tested and power dependence was studied. The linewidth of the laser beam was 0.07 cm^{-1} in the visible measured from the rotationally resolved gaseous I$_2$ spectra at ambient temperature. This linewidth was deconvoluted from the measured Doppler line profiles to measure the width of the spectra.

3. Results

Fig. 1 displays the spectra of H and D produced from the 1:1 mixture of acetone and acetone-d$_6$. To ensure that the observed H atom spectra should not be from any impurities in the system but from acetone, D from acetone-d$_6$ was also measured. Since the experiment has been performed by so-called one color, that is, pump-probe by the same light and the light from the dye laser output is horizontally polarized, the polarization direction of the dissociating light, ε_d is consequently perpendicular to the probe direction, k_p. Judging from the Gaussian profiles observed in the spectra, we assumed no polarization dependence of the H atom
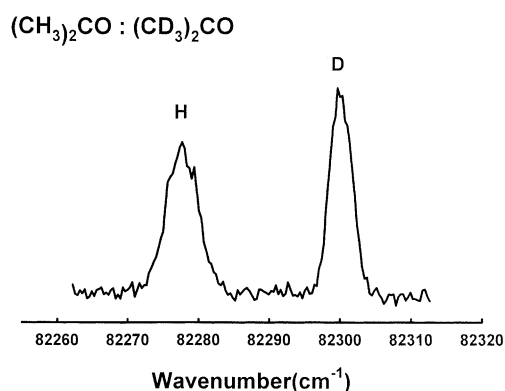
Table 1
Translational energy releases in the H atom channel from photodissociation of acetone, acetic acid, and acetaldehyde at 243 nm

	(CH$_3$)$_2$CO:(CD$_3$)$_2$CO		CH$_3$COOD		CD$_3$CHO	
	H	D	H	D	H	D
$\langle E_T \rangle$ (kJ/mol)	85.9	80.9	66.5	87.0	73.0	78.3

production channels although we could not attempt a different experimental geometry such as $\varepsilon_d \| k_p$. In addition, as will be mentioned in the discussion, the H atoms are not produced from the direct photodissociation but produced from the unimolecular dissociation from the acetyl radicals, it is believed that there is no initial polarization dependence and thus isotropic distribution of the H atoms can be assumed. In this case, the relations, $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$ and thus $\langle E_H \rangle = 1/2 m_H (\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle) = 3/2 m_H \langle v_z^2 \rangle$ hold. Then, from the observed one dimensional Doppler broadened spectra, translational energies of the H (D) atoms were measured from the second moment of the spectra using the equation

$$\langle E_H \rangle = \tfrac{3}{2} m_H \langle v_z^2 \rangle = 3 m_H \langle (v - v_0)^2 \rangle \tfrac{1}{2} (c/v_0)^2$$

where v_0 is the center frequency of the spectrum, v_z the velocity along the probe direction, and c the speed of light. The center-of-mass translational energy releases were calculated and are listed in Table 1. The spectra of H and D from acetic acid-d (CH$_3$COOD) and acetaldehyde-d$_3$ (CD$_3$CHO) are shown in Fig. 2(a) and (b), respectively.
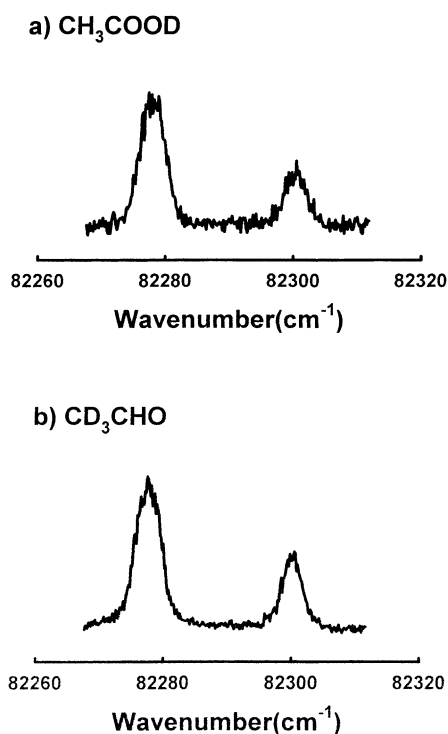
a) CH$_3$COOD

b) CD$_3$CHO

Fig. 2. H (D) atom spectra from photodissociation of (a) CH$_3$COOD and (b) CD$_3$CHO at 243 nm.

(CH$_3$)$_2$CO : (CD$_3$)$_2$CO

Fig. 1. H (D) atom spectra from photodissociation of 1:1 mixture of (CH$_3$)$_2$CO and (CD$_3$)$_2$CO at 243 nm.

From the spectra, the translational energy releases in the systems were measured and are listed in the table. Since the spectra of the samples studied show continuous absorption in the UV region and difference in the photon energy between the H and D atom production is about $25\,cm^{-1}$, the same photolysis probability in this spectral region could be assumed. Also, the photon energy around 243 nm is larger than $40,000\,cm^{-1}$, from which it can be assumed that the contribution from this $25\,cm^{-1}$ difference to the translational energy release should be negligible.

4. Discussion

4.1. H from $(CH_3)_2CO$

The major primary photochemical process from acetone has been known to produce acetyl and methyl radicals upon absorption of the UV light. The quantum yield of this channel was measured to be 0.76 at 250 nm [6]. A possible minor channel would be the H atom production channel.

$$(CH_3)_2CO \rightarrow CH_3 + CH_3CO, \quad \Delta H = 353.6\,kJ/mol \qquad (1)$$

$$(CH_3)_2CO \rightarrow CH_2COCH_3 + H, \quad \Delta H = 411.3\,kJ/mol \qquad (2)$$
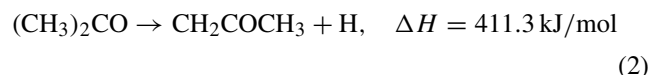
The measured translational energy release of the H atom channel is 85.9 kJ/mol, which is larger than the available energy for the reaction (2), 82.2 kJ/mol (the photon energy, 493.5 kJ/mol — the dissociation energy for channel (2)). Thus, the channel (2) cannot be opened by the one photon process at 243.2 nm. The acetyl radical may further decompose to yield methyl radical and CO or H and ketone.

$$CH_3CO \rightarrow CH_3 + CO, \quad \Delta H = 48\,kJ/mol \qquad (3)$$

$$CH_3CO \rightarrow CH_2CO + H, \quad \Delta H = 181\,kJ/mol \qquad (4)$$

Recent studies on photodissociation at 248 nm identified the acetyl radical and secondary unimolecular dissociation into methyl and CO [4]. The rate of decomposition depends upon internal energies of the acetyl radical and the lifetimes were estimated by the RRKM theory. The energy partitioning in the reaction (1) was successfully modeled by the impulsive model, which shows the internal energy of the acetyl radical is 36% of the available energy. The available energy of channel (1) at 243.2 nm is 139.9 kJ/mol much less than the dissociation energy of H from CH_3CO. Thus, the reaction (4) cannot occur even though all the available energy appears in the internal energy of the acetyl radical. Therefore, it can be concluded that the H atom should be generated at least by the two photon process. Then, there may be two possibilities on the H atom production mechanism. The one possibility is a sequential two photon absorption, that is, an absorption by acetone followed by an absorption by the acetyl radical

and the other is a simultaneous two photon absorption by acetone.

A simultaneous two photon absorption by acetone at 243.2 nm excites the molecule into a Rydberg state producing methyl and acetyl radicals. In this case, the acetyl radical may have large internal energy and subsequently undergo the reactions (3) and (4). The reaction (3) proceeds via a simple C–C bond rupture, whose dissociation dynamics was successfully modeled by the statistical theory. However, there should be a configuration change during the course of the reaction (4) to produce the planar CH_2CO molecule. Thus, the potential energy surfaces along the reaction coordinate for the reaction (4) were obtained by simple ab initio molecular orbital calculations using the UHF/6-31G (d,p) basis. The calculations were performed under the HF level to understand the general shape. The potential energy curve along the intrinsic reaction coordinate and the transition state geometry of the acetyl radical is presented in Fig. 3. At the transition state, the planar ketone moiety is already formed with a stretched H atom ($r = 1.610\,Å$), which leaves the acetyl radical beyond the transition state. The internal energy of the acetyl radicals produced from the reaction (1) is estimated to be about 36% of the available energy and thus the available energy of the reaction (4) is 380 kJ/mol including one more photon energy at 243 nm. Assuming the dissociation of the acetyl radicals into H and ketone statistically occurs, a statistical prior calculation was performed [7,8]. In this calculation, the available energy is assumed to be equally distributed among all degrees-of-freedom of the products. Then, the translational
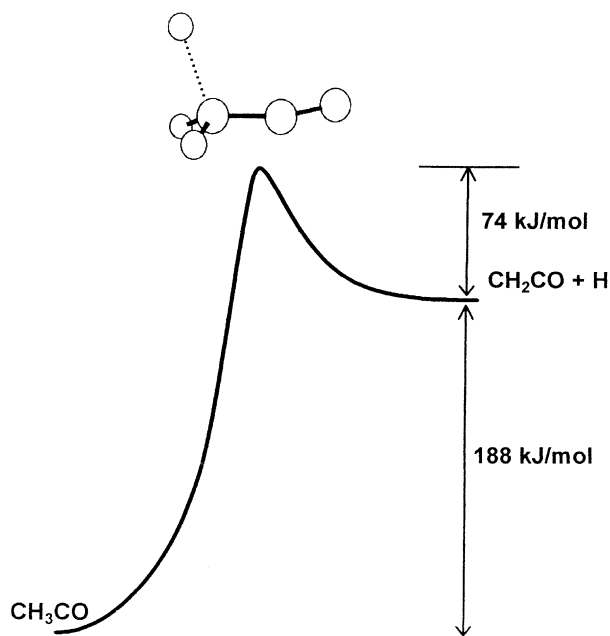

Fig. 3. Potential energy curve along the minimum energy path obtained by ab initio calculations for the H atom elimination reaction from the acetyl radical. The transition state geometry is depicted on top of the potential energy maximum.

energy distribution is simply proportional to the number of accessible ro-vibrational states of the products at the energy, $E = E_{av} - E_t$ (products). The average translational energy release obtained from the prior calculation is 37 kJ/mol, which is much smaller than the translational energy release observed from the spectra. Thus, a dynamical effect in the exit channel should be involved in the dissociation of the acetyl radicals. When the exit channel barrier exists in the reaction coordinate as can be seen in Fig. 3, it is generally known that this energy of the reverse barrier is mostly transformed into the product translation. The calculated reverse barrier is 74 kJ/mol comparable to the measured translational energy release in the H atom channel. Considering the accuracy of the calculation, they are in good agreement.

Recent femtosecond studies, on the other hand, demonstrated the fast decay of the excited acetone arising from the C–C bond rupture, whose lifetime is about few tens of femtoseconds [5]. Thus, the probability of the simultaneous two photon absorption may be relatively small by the present nanosecond light pulse. In addition, the lifetime of the acetyl radical produced from photodissociation was measured to be about 500 fs when the internal energy in the acetyl radical is estimated in the range of 155–190 kJ/mol. Assuming 36% of the available energy in the acetyl radical, that is, 50 kJ/mol at 243.2 nm, as estimated from the impulsive model, the lifetime would be much longer, about hundreds of picoseconds because the rate of decomposition exponentially decreases with the internal energy. Therefore, it seems likely that the H atom is produced from the acetyl radical by absorption of another photon at 243.2 nm. The absorption spectra of the acetyl radical produced from several precursors show continuous absorption in UV, which peaks at around 210 nm and extends up to 250 nm [9]. The absorption cross section was measured to be about 10^{-17} cm^2 at 210 nm much larger than that of acetone. The transition could be assigned if there would be some theoretical calculations but the similar $n \rightarrow \pi^*$ transition at this wavelength as in acetone can be assumed. Then, from the estimated total energy (kinetic and internal) of the acetyl radical, 70 kJ/mol and the one photon energy at 243.2 nm, the fraction of the available energy in translation in the H atom channel is 0.15. Although oversimplified, the impulsive model predicts the fraction of the available energy in product translation to be 0.94, much larger than the measured translational energy in the present study. The H atom release from the acetyl radical may take place in the hot ground electronic state after internal conversion and the energy of the reverse barrier may be transformed into the translational energy of the H atom.

However, the detailed mechanism of the H atom production from acetone at 243 nm cannot be precisely determined at present. In order to distinguish the possible mechanisms mentioned in the above discussion, theoretical investigations on the ground as well as electronically excited states of the acetyl radical should be required. In addition, the translational energy releases measured at other photolysis wavelengths may help clarifying the photodissociation dynamics.

4.2. H and D from CH₃COOD

Photodissociation dynamics of acetic acid has been studied in UV [10–12] and the quantum yield of OH production was measured to be 0.55 at 222 nm [13]. The H atom can be generated by the following primary process.

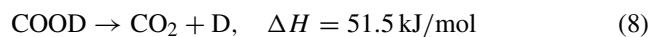$$CH_3COOD \rightarrow CH_2COOD + H, \quad \Delta H = 420 \text{ kJ/mol} \quad (5)$$
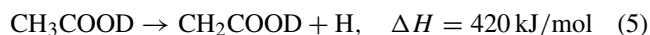
The available energy at 243.2 nm is 73.5 kJ/mol and the measured translational energy release in the H atom channel is 66.5 kJ/mol, which is 0.90 of the available energy. A simple impulsive model predicts this fraction to be 0.94. Thus, one may suppose the H atom is directly dissociated from the parent molecule by one photon absorption to the repulsive part of the potential surface. However, the power dependence study revealed a linear slope of 4.5 ± 0.3 (not shown) in the log–log plot of the signal intensities versus the laser power, implying more than one photon process for the reaction to take place. Since the major dissociation channel should be OD production channel, the H atom may be generated from the acetyl radical as in acetone.

$$CH_3COOD \rightarrow CH_3CO + OD, \quad \Delta H = 465.5 \text{ kJ/mol} \quad (6)$$

Assuming the same fraction in the internal energy of the acetyl radical as that from the 218 nm photolysis [10], the internal energy of the acetyl radical is 15 kJ/mol at 243.2 nm. Since the internal energy of the acetyl radical in this case is smaller than that from acetone dissociation (50 kJ/mol), the lifetime of the acetyl radical should be even longer than that from the acetone dissociation. Very recently, Owruntsky and Baronavsky actually measured the lifetime of the acetyl radical produced from the 194.5 nm photodissociation of acetic acid to be about 5 ps where the internal energy in the acetyl radical is about 85 kJ/mol [14]. They also measured the lifetime of the excited acetic acid shorter than 200 fs. Since the OD is produced by the impulse between the C and O atoms, the lifetime of the excited acetic acid would be assumed to be in the femtoseconds range. Thus, it is likely as in acetone that the H atom is produced from absorption of another photon by the acetyl radical at 243.2 nm. In this case, the translational energy release would be similar to the acetone dissociation case, which is 0.13 in this study. As in the acetone dissociation case, however, a simultaneous two photon absorption and sequential cleavages of the C–O and C–H bonds can be assumed. In this case, the measured translational energy release, 66.5 kJ/mol, may again reflect the reverse barrier height, 74 kJ/mol producing CH₂CO from the acetyl radical.

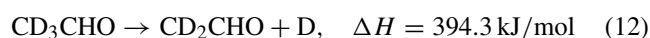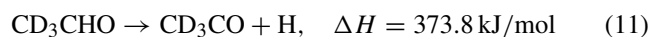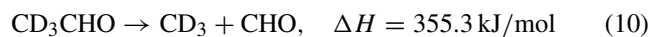The C–C bond breaking was identified as a minor channel in the photodissociation at 218 nm [10]. The resulting COOD
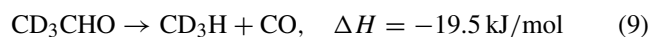
further dissociates into $CO + OD$ or $CO_2 + D$. Thus, the D atom should be generated by the following process.

$$CH_3COOD \rightarrow CH_3 + COOD, \quad \Delta H = 360 \, kJ/mol \quad (7)$$

$$COOD \rightarrow CO_2 + D, \quad \Delta H = 51.5 \, kJ/mol \quad (8)$$

The available energy in (7) is 133.5 kJ/mol at 243.2 nm, which is distributed in the methyl and carboxyl radicals. Although COOD only needs 51.5 kJ/mol to be dissociated into CO_2 and D, the measured translational energy of the D atom is 87 kJ/mol implying one more photon is needed for the reaction (8) to take place. Thus, as in acetone, fast C–C bond rupture in femtosecond time scale followed by absorption of another photon at 243.2 nm by COOD may produce the D atoms. Although there have been no absorption spectra of COOH in UV, the similar $n \rightarrow \pi^*$ transition at this wavelength due to the carbonyl group can be assumed. If the molecules simultaneously absorb two photons and dissociate into $CH_3COO + D$ or $CH_2COOD + H$, then the resulting H (D) atoms would have larger kinetic energies because the available energy is much larger. As an alternative, the simultaneous two photon absorption can sequentially break the C–C and O–D or C–O and C–H bonds. In this case, the probability of the two photon absorption would be small because the first bond breaking process is impulsive, which is in the order of femtoseconds. However, more of the theoretical and experimental studies would be needed to clarify the detailed dissociation dynamics.

4.3. H and D from CD_3CHO

In the above discussion, it is suggested that the H atom from acetone is produced from sequential breaking of the C–C followed by the C–H bond. Although it is a minor channel, acetaldehyde has also been known to produce the acetyl radical upon UV absorption. The primary photochemical processes are

$$CD_3CHO \rightarrow CD_3H + CO, \quad \Delta H = -19.5 \, kJ/mol \quad (9)$$

$$CD_3CHO \rightarrow CD_3 + CHO, \quad \Delta H = 355.3 \, kJ/mol \quad (10)$$

$$CD_3CHO \rightarrow CD_3CO + H, \quad \Delta H = 373.8 \, kJ/mol \quad (11)$$

$$CD_3CHO \rightarrow CD_2CHO + D, \quad \Delta H = 394.3 \, kJ/mol \quad (12)$$

Among them, the direct β-cleavage has not been reported although the reaction (12) is energetically possible at 243 nm. The quantum yield of the major processes (9) and (10) was measured altogether to be about 0.75 in UV and the reaction (9) becomes more important at the shorter wavelength [15]. The time resolved measurement showed direct formation of CHO from (10) as well as indirect formation of CHO from the secondary reaction, $CH_3CO \rightarrow CH_2 + CHO$ was suggested [16]. Although the photodissociation of acetaldehyde has been extensively studied [17–19], studies on the H atom channels are rare.

The H atom can be generated from CHO produced from reaction (10). The available energy from (10) at 243 nm is 138 kJ/mol, which is distributed among the products. The energy distribution has been successfully modeled by a statistical theory [19,20]. Since the measured average rotational energy is about 6 kJ/mol [19] and the reverse barrier of the reaction is about 24 kJ/mol [20], the rough estimate, probably the upper bound of the internal energy of the CHO radical is about 36 kJ/mol assuming the equal energy distribution among the vibrational states of the CHO and the methyl radicals. This energy is smaller than the critical energy, 77 kJ/mol, of the dissociation of CHO into CO and H implying that one more photon is required to produce H. The log–log plot of the signal intensities versus laser powers shows the linear slope of 4.2 ± 0.3 (not shown) in this case confirming the two photon processes. Here, we again calculated the potential energies along the reaction coordinate similar to Fig. 3 and obtained the critical energy of 77 kJ/mol with the reverse barrier of 35 kJ/mol. Thus, the measured translational energy release of 73 kJ/mol would be the reverse barrier plus the remaining available energy transformed into the translational energy of the products.

Although it is a minor channel, the H atom can also be produced by the reaction (11). Upon UV absorption, the $n \rightarrow \pi^*$ transition leads the molecule to the excited singlet surface. It has been known that the radical products, CD_3 and H are produced from the triplet surfaces via intersystem crossing [21]. The triplet surface is lower than the dissociation limit, $CD_3CO + H$ with the reverse barrier of 58 kJ/mol. The available energy for the reaction (11) is 119 kJ/mol, which is distributed to the various degrees-of-freedom of the products. The translational energy release of the H atom channel, which was measured to be 73 kJ/mol would be in this case the reverse barrier for the reaction plus the statistical partitioning of the remaining excess energy.

The D atoms can be produced from the acetyl radical produced from the reaction (11). The excess energy for the reaction (11) at 243 nm is 119 kJ/mol, which is not enough to release the D atom from the acetyl radical. Therefore, at least two photons should be needed to produce the D atoms at 243 nm. Now, several possible mechanisms for the D atom production can be proposed. One is a simultaneous two photon absorption at 243 nm by acetaldehyde and direct release of H and D atoms. In this case, since the dissociation is known to be impulsive, the translational energy release should be much larger than the measured (Table 1). If the dissociation thermally takes place after internal or intersystem crossing to the lower electronic state, statistical energy distribution among the products would be expected. In addition, the H/D ratio would be close to 1/3 in this case. However, the measured H/D ratio is about 3 implying that the reaction is not statistical. Another possible mechanism is the simultaneous two photon absorption and sequential breaking of the C–H and C–D bonds. In this case, the first step, that is, the H atom release is impulsive and the translational energy of the H atom should be much larger than the measured

or at least very high energy component would be observed in the measured Doppler profiles of the H atom spectra. The absence of such a high speed component of the H atom may exclude the simultaneous two photon absorption mechanism. The last possible mechanism is sequential absorption of two photons as in the dissociation of acetone, that is, one photon absorption by acetaldehyde leading to the reaction (11) followed by absorption of another photon by the acetyl radical releasing the D atom. In this case, the D atom should be produced by exactly the same mechanism as the acetone dissociation.

5. Summary

The H atom channels from photodissociation of acetone, acetaldehyde, and acetic acid at 243.2 nm have been investigated. From the measured translational energy releases, it has been found that the H atoms are produced from acetyl radicals by absorption of one more photon at 243.2 nm. A further investigation is needed to know whether the H atom is released from the electronically excited state or from the ground state of the acetyl radical after internal conversion.

Acknowledgements

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