High resolution (3+1) REMPI and dissociation of acetone via 3p←n Rydberg transitions

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Measurements of multiphoton ionization and dissociation of acetone are reported in the wavelength range 490.0-510.0 nm at 1 nm intervals. To our knowledge there are no available results of (3+1) REMPI on acetone in this region. The experiments were performed using an Nd:YAG-OPO (optical parametric oscillator) laser system coupled to a time-of-flight mass spectrometer. The experimental results show two dissociation channels of the acetone ion, leading to the products (CH_3CO^+) and (CH_3^+), the channel $CH_3COCH_3^+ \rightarrow CH_3CO^+ + CH_3$ being the most favored. The acetone and acetyl ions are observed in the entire wavelength range investigated. Finally, the three-photon resonance multiphoton spectrum of the acetone *3p←n Rydberg* transition is also reported.

Keywords: REMPI; acetone; Rydberg states; Rydberg transition.

En este trabajo se reportan medidas de ionización y disociación multifotónica de acetona en la región comprendida entre 490.0 y 510 nm a intervalos de 1 nm. Por primera vez se observa el proceso (3+1) REMPI en esta región del espectro para la molécula de acetona. Los experimentos fueron llevados a cabo usando un sistema láser Nd:YAG-OPO acoplado a un espectrómetro de masas de tiempo de vuelo. Los resultados experimentales muestran que el ión acetona se disocia a través de los canales $CH_3CO^+ + CH_3$ y $CH_3^+ + CH_3CO$, siendo más favorable el primero de estos canales. Finalmente, presentamos el espectro multifotónico de la transición *3p←n Rydberg* para la acetona.

Descriptores: REMPI; acetona; estados de Rydberg; transiciones de Rydberg.

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1. Introduction

When a molecule is excited by multiphoton absorption, ionization and dissociation may occur. Ion yield spectroscopy provides a very detailed picture of the fragmentation processes following multiphoton excitation. The observation of the resulting ions is very informative as to the nature of the excited and ionized states and the dynamics of fragmentation processes. Lasers combined with time-of-flight mass spectrometry are an excellent tool for examining the behavior of molecules excited by one or more photons by monitoring the ion yield of all ion fragments (total yield mode) or of the single ion channel (partial yield mode) as a function of photon energy.

Acetone is the most frequently studied molecule of its type. Being the simplest carbonyl molecule, it presents *Rydberg* states of particular interest in ion-electron reaction studies. In this paper, for the first time to our knowledge, both partial yield and total yield mode are presented for the three-photon resonant excitation of the *3p ← n Rydberg* transition and four-photon ionization spectra for acetone in the wavelength range from 490.0 to 510.0 nm.

The *3p-Rydberg* [1-3] state has been studied using single-photon absorption multiphoton ionization as well as two-photon resonance. Philis *et al.* [4] resolved the *3p-Rydberg* vibrationally and determined the a_2 torsional mode by two-photon resonant multiphoton ionization. Kandu *et al.* [2] studied the methyl effects on acetone *3p-Rydberg* spectra and determined the torsional fundamental frequencies of the a_2 and b_1 modes of the *3p-Rydberg* state. There are also relevant studies where the assignments for the vibrational levels of the *3p-Rydberg* state are reported [1-3]. Other theoretical and experimental studies [5-6] reported the excitation energy of the *3p-Rydberg* states: $3p_x$ (∼7.35 eV), $3p_y$ (∼7.41 eV), $3p_z$ (∼7.45 eV).

2. Experimental

The experiments were performed using laser-time of a flight mass spectrometry system. Partial measurements of photoionization and photodissociation of acetone and the detailed description of the apparatus have been reported elsewhere [7-9].

A schematic diagram of the experimental apparatus is presented in Fig. 1. The experimental set up consists, basically, of the sample injection system, an Nd:YAG-OPO laser, and the time of flight spectrometer.

The acetone beam was prepared by vaporizing liquid acetone (J.T. Baker, 99.5%) about 25°C and mixed with 1.0 atm of helium carrier gas. The gas mixture was expanded through a pulsed valve with an 800 μm nozzle diameter, collimated by a skimmer of 1 mm of diameter, then introduced into the ionization region. The laser is aligned in such a way that the molecular beam, the accelerating field, and laser beam are perpendicular to each other and intersect at the center of the electrodes. In order to insure that the laser beam and the

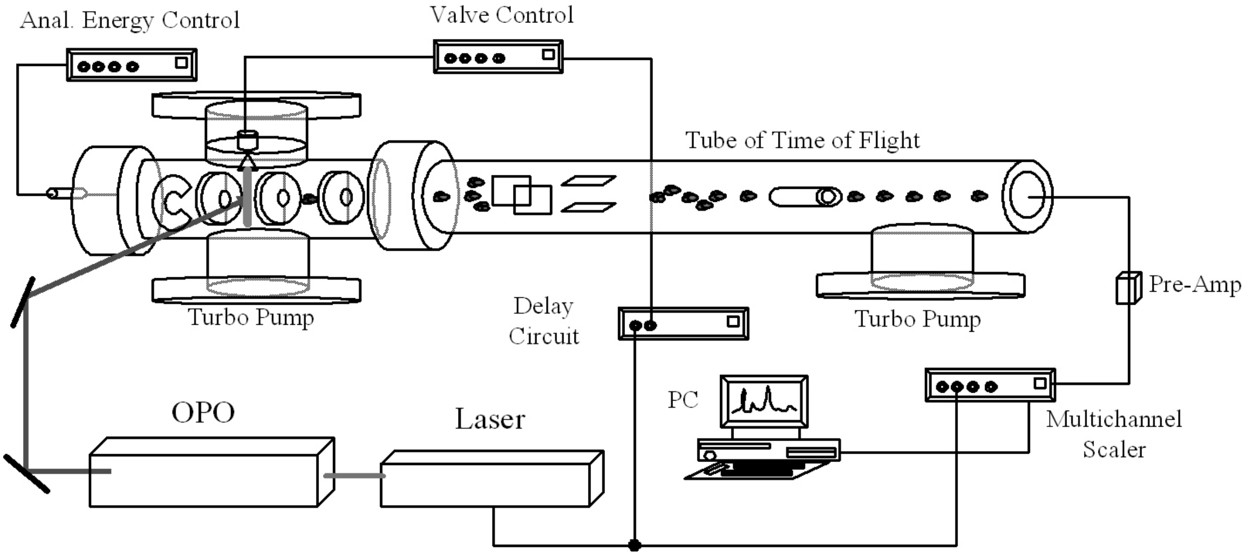

FIGURE 1. Experimental arrangement.

molecular beam coincide in time at the center of the electrodes plates of the TOF spectrometer, and that the detection and recorder system get ready to count the ions generated by the interaction between photons and molecules, a home-built delay circuit was used. The interaction between the two beams was achieved in the following sequence: the first laser pulse produces a TTL signal which is introduced into the delay circuit, and this generates a second TTL with a delay that can be changed to optimize the ion signal. This, in turn, is used as a trigger to open the nozzle. In our system, the delay is about 98.7 ms and allows the first molecular pulse to interact with the second laser pulse, which initializes another cycle. As has been pointed out in Ref. 10, the open time of the valve is 400 μs and pulse frequency is 10 Hz, same as the laser. The TTL of the laser is also used to start the Multichannel Scaler (Turbo-MCS, EG&E ORTEC) recorder.

Using an Optical Parametric Oscillator, OPO, pumped by the third harmonic of the Nd:YAG laser, laser pulses of high intensity, tunable in the range of 450-680 nm and with a resolution of 0.2 cm^{-1}, can be generated. In this study, we used output power from a 10 to 20 mJ/pulse in the 490.0-510.0 nm range. The laser beam was focused onto the interaction region by a quartz lens of focal length 150 mm. The direction of the laser polarization was set parallel to that of the axis of the mass spectrometer. The energy per pulse was measured at the exit of the TOF with a power energy meter.

The products of the multiphoton ionization and dissociation were analyzed and collected using a time-of-flight spectrometer. The cations were accelerated to 4 keV by three parallel electrode-plates, so that they were spatially focused through a 1 m free-field region. The TOF system was pumped by two turbo molecular pumps with a pumping rate of 450 l/s, both backed up by an oil-free scroll pump. The first turbo molecular pumps are located below the interaction region while the second is in the detection region. The base pressure in the TOF spectrometer is about 4×10^{-8} torr. When the pulsed valve is open, the pressure decreases to 8x10^{-5} torr and returns to the base pressure when closed. Photoelectrons were extracted from the interaction region with a field of 1 V/cm and focused into the entrance of the hemispherical electron analyzer (COMSTOCK-901B). The analyzer was operated in a constant transmission mode (10 eV), and the electron signal was detected using a channel electron multiplier. For the calibration of laser wavelength and electron energy analyzer, we measured the photoelectron spectrum resulting from the multiphoton ionization from Xe to $Xe^+(^2P_{3/2})$ and $Xe^+(^2P_{1/2})$ previously measured by Bajic and Compton *et al.* [10] at 499.05 nm. Due to the pulsed laser and the size of the energy analyzer, our electron energy resolution is not very good, $\sim$ 160 meV.

The ions $CH_3COCH_3^+$, CH_3CO^+ and CH_3^+ produced by the interaction between the laser and molecular beam are detected using a channeltron multiplier detector. The signal from the detector is amplified using a fast amplifier and TOF. The spectra were recorded using a Multichannel Scaler recorder (Turbo-MCS, EG&E ORTEC) and were stored on a PC. The dwell time used on the MCS was 20 ns; typically 1000 channels were recorded, and a TOF spectrum usually represents 2000 laser pulses.

To calculate the resolving power of the time-of-flight spectrometer, we used (4+1) REMPI of xenon at 499.05 nm. Xenon was chosen because its mass spectrum is well known and it presents a considerable number of isotopes. The resolution *($t/2\Delta t$)* of this mass spectrometer was 490.

3. Results and discussion

3.1. Fragmentation of acetone cation

We obtained the partial and total yield for multiphoton ionization and dissociation of acetone for the following ionic species: CH_3^+, CH_3CO^+, and $CH_3COCH_3^+$ from 490.0 to

510.0 nm. Figure 2 shows the time-of-flight spectrum of acetone at 502.00 nm. The total ion yield shows three prominent peaks: m/e = 15, 43 and 58 which correspond to CH_3^+, CH_3CO^+ and $CH_3COCH_3^+$, respectively. The ions CH_3CO^+ and $CH_3COCH_3^+$ are observed for all the wavelengths used in this study even at low energy per pulse of the laser (8 mJ/pulse). These observations, we allow, assume that the 3p-Rydberg state has relatively little depth.

Galasso and Merchan [5-6] previously reported the excitation energy of the *3p-Rydberg* states: $3p_x$ (~7.35 eV), $3p_y$ (~7.41 eV), $3p_z$ (~7.45 eV), and the ionization potential of acetone is 9.7 eV [11]. The photon energy used in this experiment for the multiphoton ionization of the acetone is in the range 2.53 to 2.43 eV; therefore, we assume that the ionization of the acetone is via the (3+1) resonant multiphoton ionization process; three-photons to excite to the *3p-Rydberg* state, and one photon to ionize the acetone molecule. The absorption of four photons by neutral molecule leaves the acetone ion with an excess energy of ~0.4 eV, which is sufficient to dissociate the molecular ion according to the following:

$$CH_3COCH_3^+ \rightarrow CH_3CO^+ + CH_3 \qquad (1)$$

$$\rightarrow CH_3CO + CH_3^+ \qquad (2)$$

The above dissociation channels have been reported, leaving the acetone ion with an internal energy between 0.5–8 eV [11]. However, we have observed the fragments CH_3CO^+ and CH_3^+ at excess energies < 0.4 eV.

In order to estimate the number of photons involved in the ionization of acetone, we have measured the energy dependence of acetone and acetyl ions at 502.00 nm (Fig. 3). The input energy of the laser covers a range from 12 to 16 mJ. In Fig. 3, the logarithm of the relative intensity of the ion peak is plotted against the logarithm of the relative input laser energy. A fourth dependence is observed for the two cases. This is evidence that acetone absorbs four photons of 502.00 nm to ionize and dissociate through the channel (1).

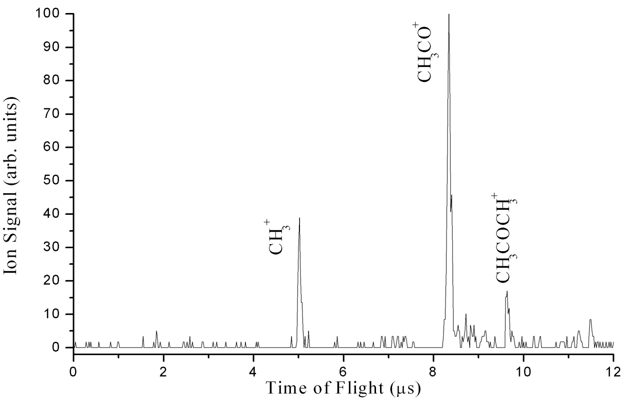

FIGURE 2. Multiphoton ionization time-of-flight mass spectrum of acetone at 502.00 nm

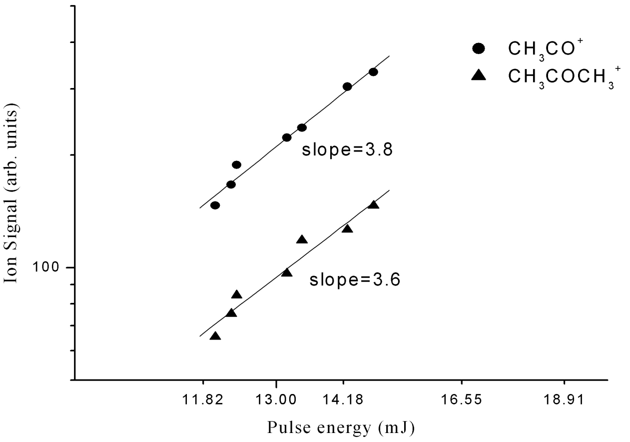

FIGURE 3. Log–log plot of laser energy vs. integrated ion signal for CH_3CO^+ and $CH_3COCH_3^+$.

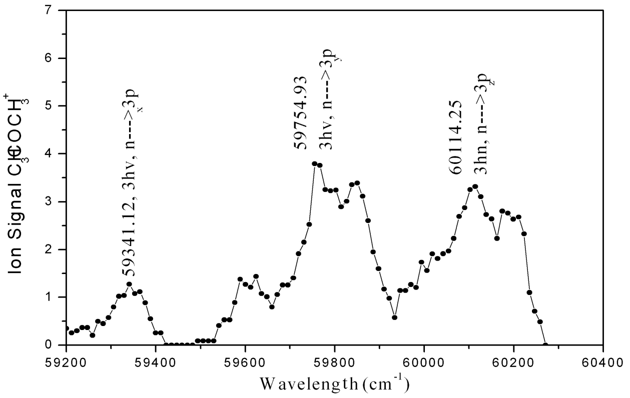

FIGURE 4. Three-photon resonant multiphoton four-photon ionization spectrum in the 59200-60400 cm^{-1} region.

3.2. Photoelectron spectrum

To confirm the number of photons absorbed in the process and to estimate the ionization potential of acetone, we have measured the kinetic energy of ejected electrons at 499 and 502 nm. Figure 5 shows photoelectron spectra of acetone taken at 499 and 502 nm following REMPI through $3p_z$ and $3p_y$ Rydberg states, respectively. According to the energy of the electrons (0.25 eV at 499 nm and 0.16 eV at 502 nm), we can conclude that the ionization potential is around 9.70 eV, as reported by Jackson *et al.* Since at 502 nm (2.47 eV) the (3+1) REMPI process deposits in a acetone molecule a total energy of 9.88 eV, if the electron leaves with a kinetic energy of 0.16 eV then the molecule ionization energy is at least 9.72 eV.

3.3. Three-photon 3p-Rydberg spectra of acetone

The three-photon resonance four-photon ionization *3p-Rydberg* spectra are shown in Figs. 4. This figure corresponds to four-photon ionization via *3p-Rydberg* state spectra obtained by monitoring the acetone $CH_3COCH_3^+$ ion signals, in the region from 59200 to 60400 cm^{-1}. In the spectra (Fig. 4) can be observed three maxima corresponding to the

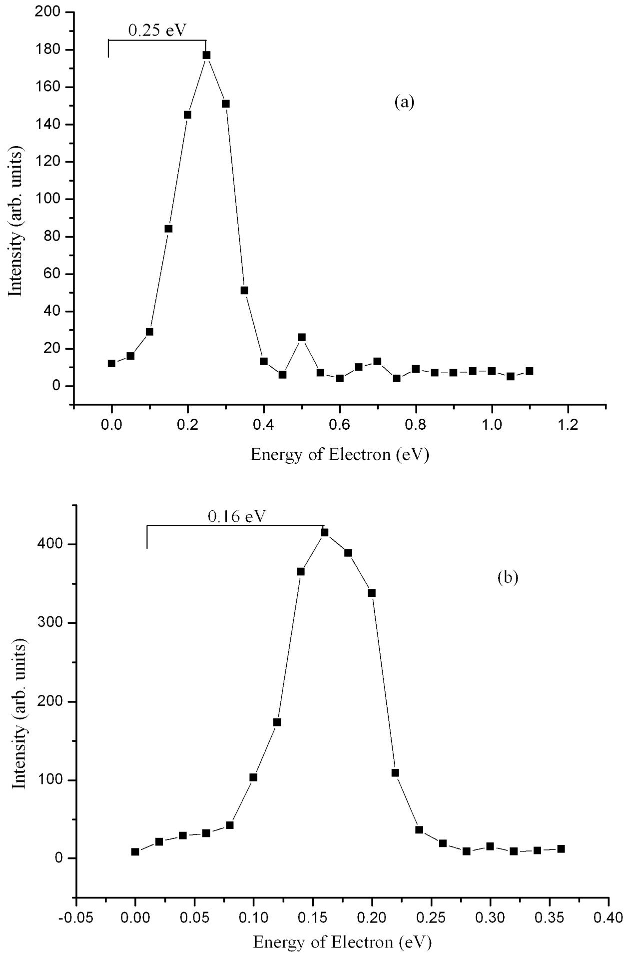

FIGURE 5. Photoelectron spectrum of acetone at: (a) 499 nm and (b) 502 nm.

origin of the three *p-Rydberg* states: $3p_x$ (∼7.35 eV; 59281.7 cm^{-1}), $3p_y$ (∼7.41 eV; 59765.7 cm^{-1}), $3p_z$ (∼7.45 eV; 60088.3 cm^{-1}). These values are in agreement with theoretical results reported by Refs. 5 and 6.

4. Conclusions

Multiphoton ionization and fragmentation studies from 490.00 to 510.00 nm have been performed for the acetone molecule using an optical parametric oscillator system coupled to a time-of-flight mass spectrometer. We have identified two channels of dissociation of the acetone cation; the main one of these channels produces the acetyl ion and another produces methyl radical cation.

We have also measured the origin bands of the$3p_x$←*n* (∼7.35 eV; 59281.7 cm^{-1}), $3p_y \leftarrow n$ (∼7.41 eV; 59765.7 cm^{-1}), and $3p_z \leftarrow n$ (∼7.45 eV; 60088.3 cm^{-1}) transitions through three-photon and four-photon resonant ionization processes, respectively. In the wavelength range used, it is not possible to fully resolve the vibrational transitions due to the $3p_x, 3p_y$ *and 3*p_z *-Rydberg* interaction.

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