MPI spectroscopy in the region of the 3p Rydberg state of some cycloketones

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Abstract

The two-photon resonance three photon ionization spectra of cyclopentanone, cyclohexanone and cycloheptanone in the region of the 3p Rydberg state have been recorded, analysed and compared with the one-photon absorption spectra. A new 3p origin is identified for cyclopentanone. The absence from the MPI spectra of a sharp spectral feature that is observed in the absorption spectra is discussed. Photochemical generation of acetaldehyde is observed at high laser intensities and possible mechanisms for this are considered.

1. INTRODUCTION

The resonance-enhanced multiphoton ionization (REMPI) spectroscopy [1] is one of the most sensitive techniques for the detection of molecular Rydberg states, particularly in the presence of iso-energetic valence states. The valence states are usually dissociative and thus they cause no detectable resonance enhancement of the ionization signal unlike the longer lived Rydberg states.

In this work we present the two-photon resonant three-photon ionization, (2+1) REMPI spectra of cyclo-pentanone, -hexanone and -heptanone, measured in a static cell in the one-photon range of 375-349 nm, and compare them with the one-photon absorption spectra in the range of 190-170 nm. In a recent publication [2] we have identified the 3p Rydberg region of these cyclic ketones and have assigned one 3p origin for each molecule and a tentative second one in two of them. The (2+1) REMPI were measured in the hope of completing the assignment of these transitions as, to date, all three 3p Rydberg origins have been definitively identified only in the case of the C_{2v} ketones methanal and propanone. For methanal these are at 64276(z), 65451(y), 67109 (x) cm⁻¹ [3] and for propanone at 59371 (x), 59744 (y), 60103 (z) cm⁻¹ [4].

Under C_{2v} symmetry the one photon transitions to the $3p_y$ and $3p_z$ orbitals are allowed, but not that to the $3p_x$ one, from the highest occupied molecular

orbital n_0 which is localised on oxygen and is of almost pure 2p composition. In methanal the $3p_x$ transition was identified through analysis of vibronic structure and for propanone through (2+1) REMPI in which case the transistion is allowed. In the case of ethanal two 3p origins have been identified at 60166 and 62500 cm⁻¹ [5], the latter being thought to be accidentally degenerate. This work was undertaken in order to investigate the extent of the p orbital splitting induced by the molecular core and its relationship to molecular symmetry in the cyclic molecules as well as to compare their spectra with those of the acyclic systems.

2. EXPERIMENTAL

The one photon absorption spectra were recorded with a resolution of 0.25 nm using a "double beam" system which allows us to measure the corresponding absorption cross sections. The apparatus consists of a UV-VUV 1 m Rank-Hilger 776 monochromator (linear dispersion 1.66 nm/mm), a hydrogen light source, a double-beam chamber and an electronic detection system from McPherson and a gas handling system. The measuring procedure is presented in detail elsewhere [6].

For the MPI spectra we used a home made XeCl Excimer laser (constructed at the Institute of Electronic Structure and Laser, Crete) producing .50 mjoule pulses of 12 nsec duration. This laser pumped a home made dye laser with .0.1 Å resolution. We used the DMQ dye in dioxane (or toluene/ethanole). The laser light was focused in the static cell with an f=10 cm lens. The vapour pressure of the samples was 1-2 mbar. For wavelength calibration we recorded, simultaneously with the MPI signal, the optogalvanic (OG) signal from an U/Ar hollow-cathode lamp (Oriel). Both MPI and OG signals were processed by two gated integrators (BCI 101, FORTH).

3. **RESULTS AND DISCUSSION**

The one photon absorption and the corresponding (2+1) REMPI spectra are presented in the same diagram for each molecule. The MPI spectra have not been corrected for the laser intensity, the profile of which is shown with a broken line in figure 1. The broad ionization background under the peaks in all MPI spectra is due to the nonresonant three-photon ionization of the molecules. This was checked by observing the increase of the intensity ratio of the spectral peaks to the background as the laser intensity decreased. Because of the broadness of the spectral lines the wavelength accuracy of the MPI spectrum is \pm 1Å (introducing a \pm 16 cm⁻¹ accuracy to the two photon resonances).

Cyclopentanone

From the spectrum in figure 1 we see that the MPI structure extends to longer wavelengths than the intense one-photon structure. Thus the MPI data allows us to assign an origin to the peak at 365.1 nm (= 182.55 nm in the one-photon spectrum) where there is very weak and unanalysable structure in the one-photon spectrum. This peak is proceeded by hot structure at longer

wavelengths and taking the laser intensity variation into consideration it is clear that this origin is by far the most intense peak in the band.

The quantum defect δ of this peak is 0.66, using the recently determined ionization potential of 74800 cm⁻¹ [2]. The one-photon spectrum shows another 3p origin at 178.52 nm ($\delta = 0.58$), arrowed in figure 1, and a third was tentatively assigned at 177.64 ($\delta = 0.56$). Neither of these one-photon origins



Figure 1. Cyclopentatnone: a) One-photon absorption and b) Two-photon resonance, three-photon ionization spectrum. The dye laser profile is shown with the broken line.

appears in the MPI spectrum, which is not suprising for the 177.64 nm peak as it lies on the limit of the dye. The absence of the 178.52 nm peak is remarkable though. Certainly we expect to observe all three 3p origins as they have all similar intensity in the propanone MPI studies [4]. The vibrational analysis of the MPI band is presented in Table 1.

IABLE I				
Vibrational	Energies an	d Assignments	for Cyclopentanone	
Laser λ	2vvac	$\Delta v(2v_{vac})$	Assignment	
Å	(cm ⁻¹)	cm ⁻¹		
3667	54125	239	2 ⁰ ₁ (239)	
3658	54659	105	1 ⁰ ₁ (105)	
3651	54764	0	0-0	
3632	55050	286	3 ¹ ₀ (450)	
				C=O bend
(3630)	(55080)	(316)	4 ¹ ₀ (472)	

Laser λ Å	2v _{vac} (cm ⁻¹)	$\Delta v(2v_{vac})$ cm ⁻¹	Assignment
3613	55340	576	6 ¹ ₀ (580)
3593	55648	884	10_0^1 (892) or $6_0^1 4_0^1$
3577	55897	1133	15 ¹ ₀ (1151)
3569	56022	1258	28 ¹ ₀ (1748), C=O stretch
3564	56100	1336	6 ¹ ₀ 8 ¹ ₀
3556	56227	1463	$6_0^1 \ 10_0^1 \text{ or } 6_0^2 \ 4_0^1$
3551	56306	1542	$28_0^1 \ 3_0^1$
3542	56449	1685	6 ¹ ₀ 15 ¹ ₀
3527	56689	1925	$6_0^2 8_0^1$

Numbering of different vibrations and their ground state frequencies (numbers in parentheses) are taken from [7].

Cyclohexanone and Cycloheptanone

The absorption and MPI spectra of cyclohexanone and cycloheptanone are shown in Figures 2 and 3 respectively. We can see here also that the most intense peak of the absorption spectrum, denoted by an arrow at 178.66 nm in cyclohexanone and at 177.21 nm in cycloheptanone, is absent in MPI spectra. The absence of such an intense peak in the MPI spectra of all three molecules cannot be attributed to different selection rules for the one-and two-photon processes, since both excitation schemes are allowed in these low symmetry (C₂, C₈ and C₁ respectively) [7,8,9] configurations.

The peaks at 182.55 nm and 178.52 nm in cyclopentanone, at 179.86 nm and 178.66 nm in cyclohexanone and the peaks at 179.47 nm and 177.21 nm in cycloheptanone are assigned as transitions to two different components of the 3p Rydberg orbital [2]. The explanation for the absence of the second transition in the MPI spectra is not obvious, if such an assignment is correct.

Maybe the second peaks are in fact molecular valence transitions and not Rydberg transitions. This would certainly account for their different appearence in the two spectroscopic techniques for the reasons given above, but leaves the problem of which valence transitions are they and what has happened to the Rydberg transitions. Old theoretical calculations [11] predict several transitions from the n or σ MOs to different σ^* , π^* MOs in these energy ranges.



Figure 2. Cyclohexanone a) Onephoton absorption and b) Twophoton resonance, three-photon ionization spectrum. The arrow shows the position of missing peak



Cycloheptanone Figure 3. a) absorption One-photon and b) Two-photon resonance, threephoton ionization spectrum. The position arrow shows the of missing peak

The proposed vibrational analysis for cyclohexanone is given in Table 2. The

TABLE 2 Vibrational	Energies and	Assignments	for Cyclohexanone
Laser λ Å	2v _{vac} (cm ⁻¹)	$\Delta v(2v_{vac})$ cm ⁻¹	Assignment
3663	54584	1018	16 ⁰ ₁ (1019)
3662	54599	1003	15 ⁰ ₁ (993)
3652	54749	853	11 ⁰ ₁ (841)
3645	54854	748	10 ⁰ ₁ (752)
3617	55278	324	3 ⁰ ₁ (313)
3603	55493	109	1 ⁰ ₁ (107)
3596	55602	0	0-0
3578	55881	279	3 <mark>0</mark>
3567	56054	452	7^1_0 (491)

Laser λ Å	2v _{vac} (cm ⁻¹)	$\Delta v(2 v_{vac})$ cm ⁻¹	Assignment
3559	56180	578	8_0^1 (665), C=O bend
3543	56433	831	11 <mark>0</mark>
3539	56497	895	7_0^2
3535	56561	959	15 <mark>0</mark>
3524	56737	1135	8 <mark>0</mark>
3518	56834	1232	35 ₀ ¹ (1709), C=O stretch

Numbering of different vibrations and their ground state frequencies (numbers in parentheses) are taken from [10].

MPI spectrum of cycloheptanone does not show clear enough structure and thus we assign only the 0-0 band at 358.8 nm. The proposed 0-0 bands in the MPI spectra of these two molecules are in agreement with the corresponding peaks of the absorption spectra. The vibrational assignment for all three molecules is based on the work of Cornish and Baer [12] for their 3s Rydberg state. We follow their assignment since the geometry of the non-bonding 3s and 3p Rydberg states is expected to be similar.

From these tables we see a large reduction in the excited state value of the C=0 stretch vibration (ground state values are given in parenthesis). As it is mentioned also in the case of the 3s Rydberg state [12], this reduction means that the C=0 double bond becomes weaker in the excited state and the bond takes characteristics of a single C-0 one. On the other hand the assignment for the C-H modes in the excited state is based on the fact that the C-H bond in not greatly affected by the removal of the oxygen lone pair electron and thus the vibrational frequency values are expected to be very close to those for the ground state.

In all cases, although the spectra have not been taken with constant laser intensity, the most intense peaks are those corresponding to the 0-0 transition which implies that the transition to the 3p Rydberg state is a vertical one.

Photofragmentation

By increasing the dye laser intensity (.1 mjoule) new features appeared clearly in the MPI spectra of cyclopentanone and cycloheptanone. These are the new sharp lines of Fig. 4 and their appearance at the same position in the spectra suggests that they correspond to transitions of the same molecule. From the literature we found that they correspond to the two photon resonant three-photon ionization spectra of the 3s Rydberg of acetaldehyde [13]. This is further confirmed from the MPI spectra, in the same wavelength region, of some methyl derivatives of cyclopentanone and cyclohexanone, where all the previously reported [13] transitions to the 3s Rydberg state of acetaldehyde are clearly recorded [14].

Because of the high two-photon cross section of acetaldehyde (three orders of magnitude larger than that of typical organic compounds [15]) such a signal might be due to impurities of the samples. To exclude this we checked our



The MPI spectra Figure 4. cyclopentanone and of cycloheptanone recorded with laser higher intensity. The lines shaded corresponds to the 3s transition of acetaldehyde

samples with gas chromatography and we found no evidence of acetaldehyde existence.

The photochemical properties of ketones (and cycloketones) have been extensively studied. It is well known that the excitation of the (n,π^*) state be followed by fragmentation of the can molecule, a process often referred to as a Norrish type reaction [16], producing an unsaturated aldehyde or alternatively a ketone. In case we have an excitation from the our nonbonding n type orbital too, but contrary to what has been described above, the molecules are now ionized after being in resonance with an excited Rydberg state, which lies much higher than the lowest excited valence state. The way through which acetaldehyde is formed is not obvious under these conditions.

May be the cyclopentanone (and cycloheptanone) cation undergoes an alpha-bond cleavage to form the linear acylium ion followed by hydride shifts and cleavage of the 2,C - 3,C thus a cyclopropylene cation bond producing and acetaldehyde as shown in the diagram of Fig. 5. In addition it is well known that the alphacyclopentanone for bond cleavage and cycloheptanone easier than that of is cyclohexanone and this supports the fact we have generation not observed clearly any of acetaldehyde in the case of cyclohexanone. Further investigation using other techniques, like mass spectroscopy, will be very helpfull in explaining the mechanism of acetaldehyde formation.



Figure 5. Proposed mechanism for acetaldehyde formation

4 **CONCLUSIONS**

The one-photon absorption and the 2+1 MPI spectra of cyclopentanone cyclohexanone and cycloheptanone in the region of the 3p Rydberg transition were recorded and analysed. A reassignment of the corresponding 0-0 transition for the cyclopentanone is proposed and the absence from the MPI spectrum of a sharp one-photon absorption peak is discussed. At higher laser intensities the formation of acetaldehyde was observed through its characteristic MPI spectrum.

5. REFERENCES

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