

Multiphoton dissociation of some aromatic molecules. Formation of atomic carbon in the $2p^2\ ^1S_0$ excited state

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Abstract. Carbon atoms in the high energy metastable state $2p^2\ ^1S_0$ have been detected for the first time in multiphoton dissociation of some aromatic molecules, using tunable laser light in the region of 380 to 393 nm. The detection is based on the two-photon resonances $2p\ ^1S_0 \rightarrow \rightarrow 3p\ ^1D_2$ and $2p\ ^1S_0 \rightarrow \rightarrow 3p\ ^1S_0$ three-photon ionization of atomic carbon, following the dissociation of the molecule, during the same laser pulse. The results are of particular interest in the field of nonlinear photochemistry.

Keywords. Multiphoton ionization; multiphoton dissociation; carbon two-photon transitions; benzene derivatives.

1. Introduction

Tunable wavelength laser radiation is currently used to excite various states of atoms and molecules. By means of multiphoton excitation it is possible to introduce selectively a considerable amount of energy into the atom or molecule causing its selective photoionization (Hurst *et al* 1979; Johnson and Otis 1981; Antonov *et al* 1984). Molecules in intermediate excited states can undergo various photophysical and photochemical transformations. Photodissociation, which competes with photo-absorption and photoionization processes, is of basic interest (Johnson and Otis 1981; Gedanken *et al* 1982; Antonov *et al* 1984; Gobeli *et al* 1985).

Neutral atoms may be formed in the multiphoton dissociation (MPD) of molecules. Examples are the metal carbonyls and organometallics (Gedanken *et al* 1982; Gobeli *et al* 1985) while carbon atoms in the lowest $^3P_{0,1,2}$ and 1D_2 states have been detected in the MPD-ionization spectra of aromatic molecules (Whetten *et al* 1983; Bolovinos *et al* 1986; Ioannidou and Christodoulides 1990), using nanosecond laser pulses with wavelengths shorter than 341 nm.

The ground configuration of carbon, $1s^2 2s^2 2p^2$, contains the 1S_0 term, which lies $21,648\text{ cm}^{-1}$ (2.684 eV) (Baskin and Stoner 1975) above the ground 3P_0 state. Therefore the question arises as to whether $C(^1S_0)$ is one of the fragments in the MPD of organic molecules. The question becomes more interesting if we add that the photolysing laser wavelength should not be in the deep UV region but as close to the visible as possible. The presence of the atoms can be seen by detecting the proper atomic lines. Examination of the carbon energy levels (Baskin and Stoner 1975) shows that the two-photon transition $2p\ ^1S_0 \rightarrow \rightarrow 3p\ ^1P_1$ needs laser light of wavelength 423.54 nm; however, this transition is identity-forbidden because of the 0–1 J rule. The allowed transitions that follow at lower wavelengths, are the two-photon resonances $2p\ ^1S_0 \rightarrow \rightarrow 3p\ ^1D_2$ ($\lambda_1 = 392.33\text{ nm}$) and $2p\ ^1S_0 \rightarrow \rightarrow 3p\ ^1S_0$ ($\lambda_2 = 382.09\text{ nm}$);

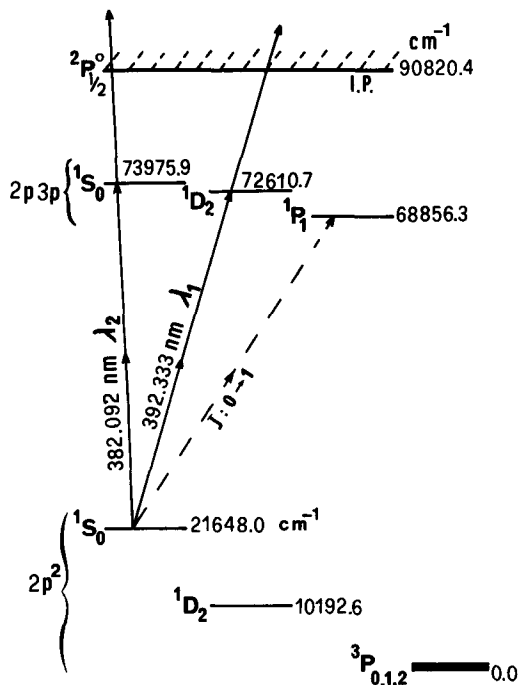


Figure 1. Energy levels of the carbon atom, showing the two-photon resonances λ_1, λ_2 . The transition $J = 0 - 1$ is TP identity forbidden.

a third photon is needed to overcome the ionization potential (IP) of atomic carbon. In figure 1 we show these “ $2R + 1$ ” schemes. Thus we have tried to detect the carbon lines λ_1 and λ_2 of figure 1 using a single pulsed laser source which would photolyze the organic compound and probe the carbon atoms. The molecules we chose to study are various benzene derivatives.

2. Experimental

Resonance multiphoton ionization (REMPI) studies were performed in the gas phase using a parallel-plate ionization chamber. The dye laser (Sopra LCR1 oscillator-amplifier) pumped by a Sopra 804C N_2 laser was operated in the spectral region 380–393 nm using a solution of BBQ dye in ethanol/toluene, with a maximum energy of $\approx 100 \mu\text{J}/\text{pulse}$. The dye laser beam was focused ($f = 6 \text{ cm}$ lens) between the plates of the chamber. These plates were held at a potential difference of 40 V. Laser power (at maximum) was $\approx 17 \text{ kW}$ resulting to a power density at the focal point of $\approx 6 \cdot 10^8 \text{ W}/\text{cm}^2$. Neutral fragments were detected by the wavelength dependence of the REMPI current. MPI or REMPI signals were also present due to the parent (target) molecules.

3. Results and discussion

Our results are summarized in table 1. The two atomic carbon transitions λ_1, λ_2 predicted in figure 1, are indeed detected in a number of molecules. The formation

of $C(^1S_0)$ is efficient in polyfluorobenzenes $C_6H_{6-n}F_n$ ($n \geq 3$), benzaldehyde, and 4-fluorobenzaldehyde.

Figure 2 is the MPD/MPI spectra of benzaldehyde, 4-fluorobenzaldehyde and *p*-tolualdehyde. The dissociation of the first two molecules (figures 2a and b) is revealed by the atomic carbon lines λ_1, λ_2 originating from the $2p^2\ ^1S_0$ level. The laser wavelength (393–380 nm) is in the region of the first singlet–triplet $^3n\pi^*$ molecular transition of these molecules. The λ_1, λ_2 lines are not detected in *p*-tolualdehyde.

In figure 3 we present part of our experimental results for the fluorinated benzene derivatives. For these molecules the carbon resonances λ_1, λ_2 are not the only lines observed. The other features are rovibronic bands of a molecular fragment. These features are not due to CH since the same pattern is observed in C_6F_6 . A mass analysis can give a definite assignment on these fragments.

The continuum backgrounds (figures 2 and 3) follow the dye laser gain. The BBQ dye gain is given in figure 2 by the broken line and is approximately the same in figure 3. The only exception for the dye gain is in the lowest spectrum of figure 3. Figure 3c is the case with the target molecule C_6HF_5 and in the lowest spectrum the power of the pumping N_2 laser is about half compared to all the other cases.

Special care was taken to prevent any contamination from previous samples in the ionization chamber. The nonappearance of the carbon transition in a number of compounds studied (table 1) shows that the observed lines are not due to signals coming from irradiation of the plates-chamber or the entrance–exit windows of the chamber. Further tests were done using benzene and the REMPI spectrum was found to be similar to the $3s$ Rydberg $^1E_{1g}$ transition (Johnson 1975, 1976) with no other extra features.

The negative results for some molecules of table 1 do not imply that the dissociation mechanisms are not present in these molecules. Carbon atoms may be formed in the lower $^3P_{0,1,2}$ or 1D_2 terms. The BBQ dye laser wavelength is not proper to probe transitions originating from these lower carbon states. For any given molecule various

Table 1. Spectroscopic features observed in the MPD/MPI spectra of some aromatic molecules. Dye laser region is 393–380 nm.

Molecule	$C(^1S_0 \rightarrow ^1D_2)^a$	$C(^1S_0 \rightarrow ^1S_0)^b$	Other features-comments
C_6H_5CHO	Yes	Yes	^c
$4-C_6H_4FCHO$	Yes	Yes	^c
$4-C_6H_4(CH_3)CHO$	No	No	^c
$C_6H_5C(CH_3)O$	No	? n.l.	^c Not reproducible
C_6H_5F	No	No	$3s$ Rydberg ^d
$1,2-C_6H_4F_2$	Yes, n.l.	Yes, n.l.	$3s$ Rydberg
$1,3-C_6H_4F_2$	Yes, weak	Yes, weak	$3s$ Rydberg
$1,4-C_6H_4F_2$? n.l.	? n.l.	^c Spectrum noisy
$1,3,5-C_6H_3F_3$	Yes	Yes	^c And other fragment
$1,2,3,5-C_6H_2F_4$	Yes	Yes	^c And other fragment
$1,2,4,5-C_6H_2F_4$	Yes	Yes	^c And other fragment
C_6HF_5	Yes	Yes	^c And other fragment
C_6F_6	Yes	Yes	^c And other fragment
$C_6H_5SiH_3$	No	No	^c Si lines "2R + 1"
$1,2-C_4H_4N_2$	No	No	Valence $S_0^* \rightarrow S_1$
$1,4-C_4H_4N_2$	No	No	Rydberg ^e

^a Peak detected at 392.4 nm; ^b Peak detected at 382.1 nm; ^c Continuum background following the dye gain; ^d As in Krogh-Jespersen *et al* 1979; ^e As in Turner *et al* 1978; n.l. – noise level.

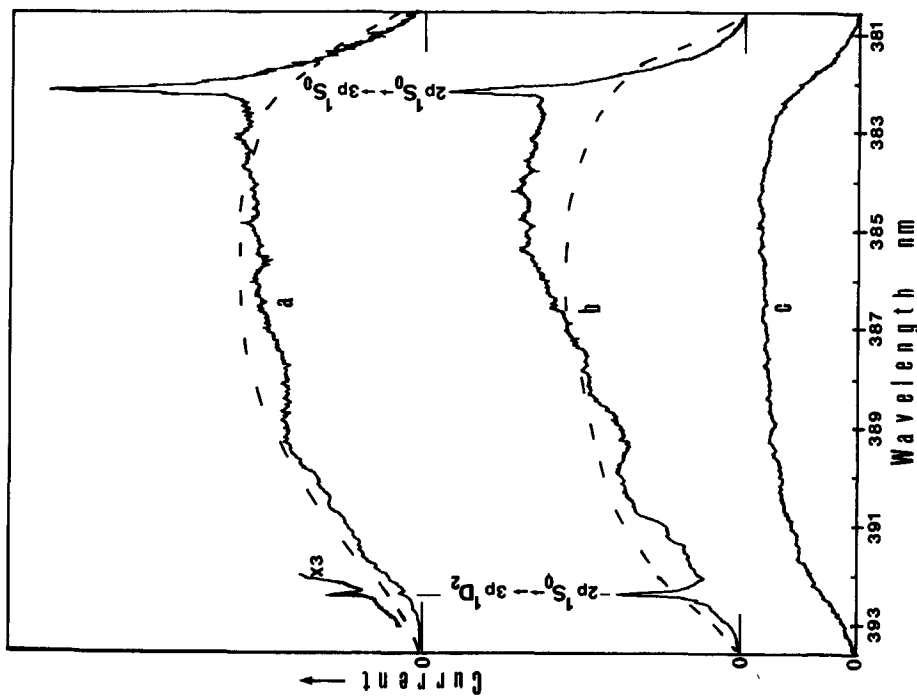


Figure 2. MPD/MPI spectra of (a) C_6H_5CHO , (b) $4-C_6H_4FCHO$, and (c) $C_6H_4(CH_3)CHO$. Lines λ_1, λ_2 are assigned to atomic carbon transitions and are not detected in (c). Broken lines are the dye laser gain.

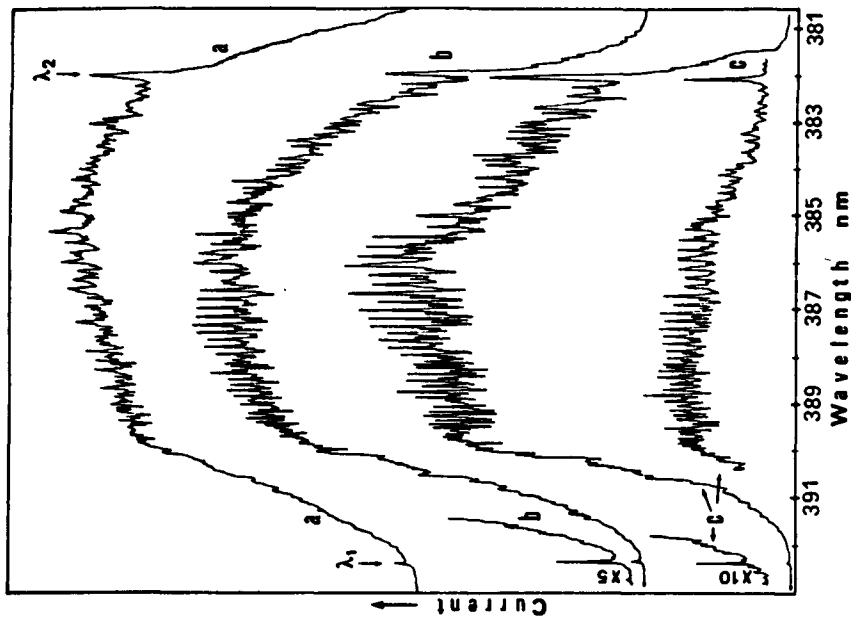


Figure 3. MPD/MPI spectra of (a) $1,3,5-C_6H_3F_3$, (b) $1,2,3,5-C_6H_2F_4$, and (c) C_6HF_5 . Lines λ_1, λ_2 are assigned to C transitions.

fragmentation/ionization pathways may be expected to be important, depending also on the details of the laser pulse, including particularly the wavelength and the flux conditions.

The mechanism for MPD/MPI consists of several steps. Considering the relatively high energy of the $C(2p^2\ ^1S_0)$ state and that atomic carbon is energetically an "expensive" fragment ($\Delta H_f^0 = 171$ kcal/mol), the detection of the λ_1 and λ_2 resonances (energy ≈ 3.2 eV) can be understood by nonlinear photochemistry. Spectroscopic information about the neutral fragments formed by the multiphoton dissociation of the molecules or ion can be obtained whenever one, two or three photons match a fragment's transition.

We conclude that in some aromatic molecules, multiphoton dissociation-ionization with photons of wavelength as low as 393 nm is present and production of $C(2p^2\ ^1S_0)$ is possible.

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