

Multiphoton dissociation/ionization of benzene, pyridine, and diazabenzenes. Detection of an atomic carbon transition

A. Bolovinos,^{a)} S. Spyrou, and A. C. Cefalas

National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute, 48 Vas. Constantinou Avenue, Athens, Greece

J. G. Philis and P. Tsekeris

Physics Department, University of Ioannina, Ioannina, Greece

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Multiphoton ionization (MPI) of polyatomic molecules by high intensity laser radiation is usually accompanied by intense fragmentation even down to atomic ions, like C^+ in benzene.¹ This mechanism (ionization first and fragmentation afterwards) was observed in molecules containing light atoms only. In molecules with one or more heavy atoms, like organometallics or metal carbonyls, it is observed that fragmentation producing neutral (metal) atoms is more probable than MPI, when weakly focused laser light of convenient vis-UV wavelengths is used.²⁻⁴

Recently, extensive multiphoton fragmentation was reported for some strongly bound molecules (benzene, benzaldehyde, fluorobenzene and perfluorobenzene) yielding neutral carbon atoms.⁵ This occurred during a 5 ns, 30–300 μJ UV laser pulse and produced carbon atoms in their ground

$^3P_{0,1,2}$ and first metastable 1D_2 levels. Atomic lines appeared as two-photon resonances on the three-photon carbon ionization spectrum in the 279–320 nm laser wavelength range.

In the present study, using laser light in the ~ 340 nm region, we have observed another atomic carbon transition, in the multiphoton dissociation/ionization of another related group of molecules, that of benzene, pyridine, and the three diazabenzenes. Specifically we detected the $\dots 2p^2 \ ^1D_2 \rightarrow \dots 2p3p \ ^1P_1$ transition as a two-photon resonance in the three-photon ionization of carbon atoms [Fig. 1(a)].

The experimental setup and procedure is described in detail elsewhere.⁶ Sample pressure in the static cell was ~ 0.5 Torr. The output of a dye laser, pumped by a XeCl excimer laser, was focused between two parallel electrodes by a 4 cm focal length lens. Pulse duration was ~ 10 ns, pulse energy

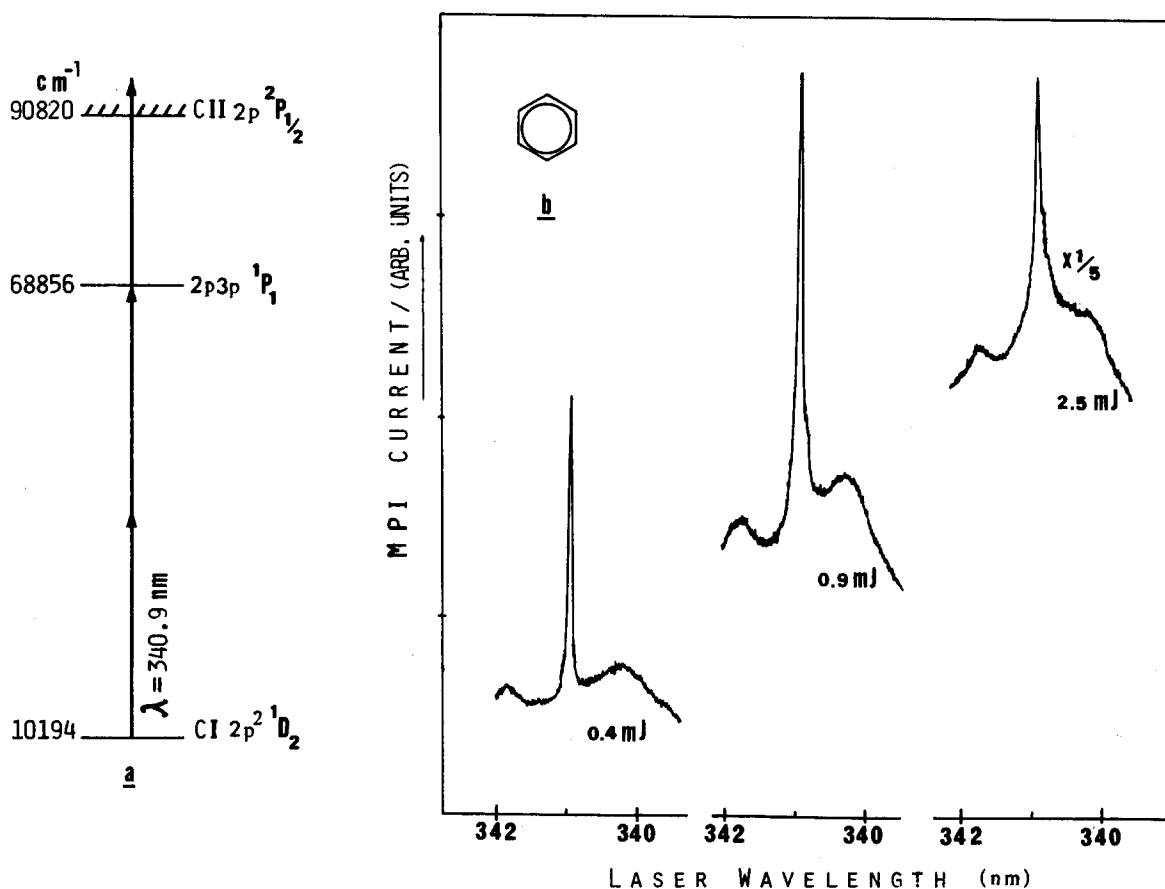


FIG. 1. (a) Energy diagram (Ref. 13) of the observed atomic carbon transition. (b) Multiphoton dissociation/ionization of benzene at different laser powers. The zero MPI signal level is the same for all cases. Signal scale is the same for the 0.4 and 0.9 mJ spectra, while it is reduced five times for the stronger 2.5 mJ signal.

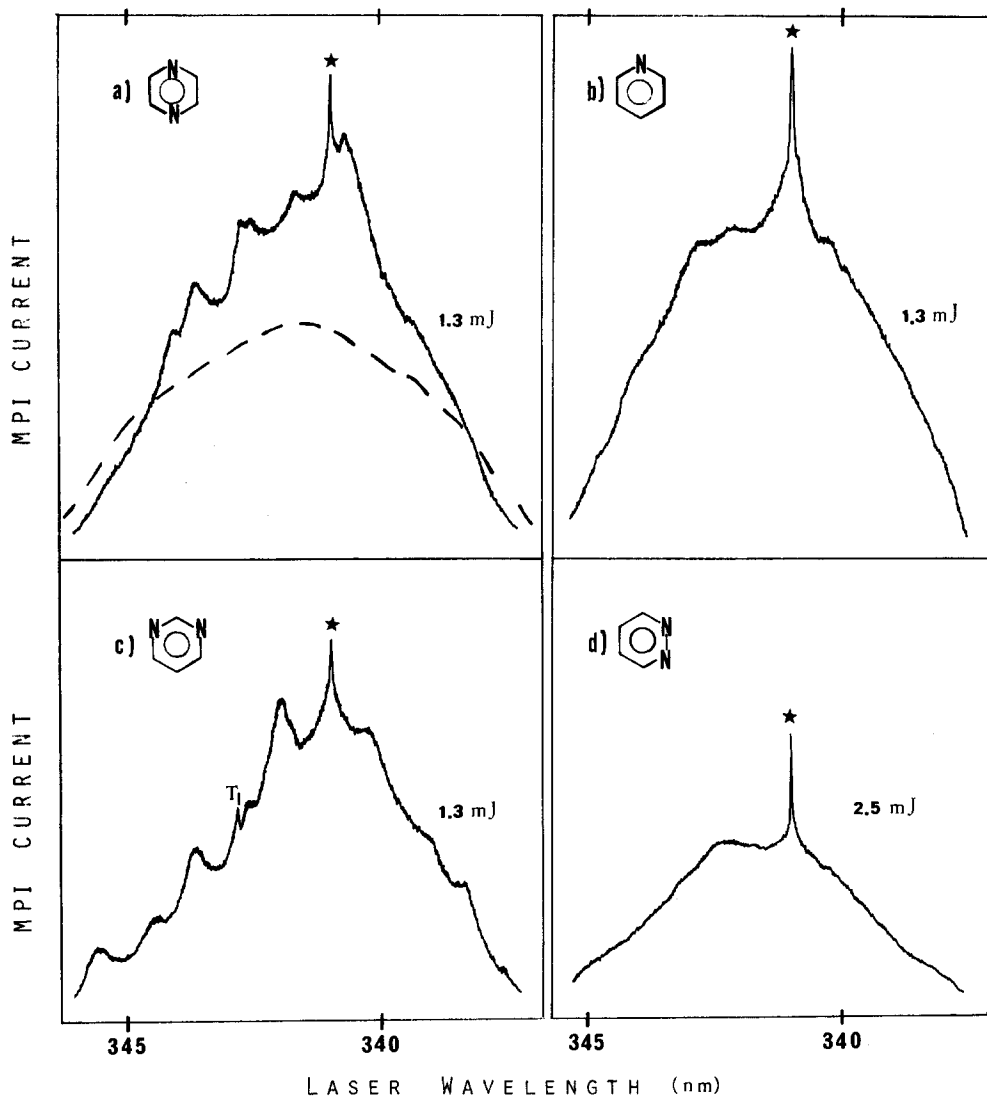


FIG. 2. Multiphoton dissociation/ionization of (a) pyrazine, (b) pyridine, (c) pyrimidine, and (d) pyridazine. * indicates the carbon resonance. Broken curve in (a) is the dye profile.

up to ~ 2.5 mJ, and bandwidth ~ 0.01 nm. The dye used was *p*-terphenyl/dioxane.

The MPI spectra of the studied molecules are presented in Figs. 1(b) and 2. All of them show a continuous nonresonant background, which follows the wavelength dependence of the laser intensity, and some more or less distinct structure. Their most characteristic feature is a sharp peak, appearing at 340.93 ± 0.06 nm in all cases, which can be attributed to the above-mentioned carbon transition. As we see in the case of benzene [Fig. 1(b)] the ratio of the atomic resonance to the nonresonant background is higher for lower laser power, in agreement with previous observations.⁵

In order to certify that this peak is not due to any impurity in our samples or in the cell, we used samples from different suppliers plus we applied the same experimental procedure with an empty cell and with samples of *s*-triazine ($C_3H_3N_3$) or air. In the last three cases no such peak was detected. The structure we observed in the *s*-triazine spectrum is attributed to vibrations of $3s$ Rydberg state (see Ref. 7 for the MPI supersonic jet spectrum). The fewer carbons of *s*-triazine or the possibility that this molecule gives HCN fragments under laser irradiation may be the reasons we did not detect the carbon atomic transition. The possibility of

HCN production can be supported from the *s*-triazine photodissociation into three HCN molecules, when irradiated with laser light at 248 and 193 nm.⁸

Except the carbon peak there are some additional, distinctly broader, MPI transitions appearing mainly in the spectra of pyrazine and pyrimidine [Figs. 2(a) and 2(c)]. They can be attributed to the vibrational structure of the $3p$ Rydberg state which has a 0-0 energy of 6.838 eV in pyrazine⁹ and 6.977 eV in pyrimidine.¹⁰ Such an assignment is in agreement with the structure observed in their VUV absorption spectra.^{9,10}

Finally, in the pyrimidine spectrum [Fig. 2(c)] there is another weaker but quite sharp resonance T_1 at $\lambda = 342.8$ nm, which does not show up in the other molecules. Moreover, the pyrimidine one-photon absorption spectrum¹⁰ does not show any transition at $\lambda/2$. On the other hand, the $^3B_1(n \rightarrow \pi^*)$ triplet state origin was assigned at $28\,530\text{ cm}^{-1}$ from vapor phase phosphorescence measurements.¹¹ Based on these facts we tentatively attribute the 342.8 nm ($29\,163\text{ cm}^{-1}$) peak to the one-photon excitation, and subsequent ionization by two more photons, of the $6a'_0$ (630 cm^{-1}) vibration of this triplet state. Its sharpness supports further such an assignment, because of the longer lifetime of the

lower triplet state. An analogous singlet-triplet transition was observed also in the MPI spectrum of pyrazine.¹² Unfortunately, the 28 530 cm⁻¹ origin of the ¹A₁→³B₁ transition was outside the wavelength range of the dye used.

In contrast to the well understood mechanisms of the molecular MPI resonances, the mechanism of neutral carbon production still remains an open question. Possible processes have been mentioned,⁵ but other complementary experimental methods are needed.

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^{a)} Permanent address: Physics Department, University of Ioannina, Ioannina, Greece.

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Fukui function: Spin-density and chemical reactivity

Marcelo Galván, José L. Gázquez, and Alberto Vela

Departamento de Química, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana-Iztapalapa, Apdo. Postal 55-534, 09340 México, D. F. Mexico

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The definition of the frontier or Fukui function as the derivative of the charge density with respect to the number of electrons¹

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v \quad (1)$$

has allowed us to prove the frontier orbital theory,² by assuming that chemical reactions are preferred from the direction which produces maximum initial chemical potential response of a reactant. This in turn implies that the local values of $f(\mathbf{r})$ provide a measure of reactivity. The Fukui function is different for electrophilic, nucleophilic, or free radical attack, and reduces to the classical frontier orbitals when frozen core approximations are imposed.³ That is, the simplest approximation to $f(\mathbf{r})$ is to neglect relaxation effects. In such a case, for an open shell atom, Eq. (1) reduces to³

$$f(\mathbf{r}) \cong \phi_H^*(\mathbf{r})\phi_H(\mathbf{r}), \quad (2)$$

which relates the Fukui function to the density of the highest occupied atomic or molecular orbital. The object of the present work is to establish another approximate relation for $f(\mathbf{r})$ to support its role as a measure of chemical reactivity. We will show through the use of the appropriate Taylor series expansions, and some simplifying assumptions that $f(\mathbf{r})$ can be expressed in terms of the spin density.

It is well known^{4,5} that one can improve the description of the electronic structure of atoms, molecules, and solids by breaking the charge density into spin components. Thus, explicitly indicating the dependence on the number of electrons of a given spin N_\uparrow and N_\downarrow (\uparrow refers to spin up or α , and

\downarrow to spin down or β), in terms of the total number of electrons $N = N_\uparrow + N_\downarrow$, and we shall call the spin number $N_s = N_\uparrow - N_\downarrow$, one can write the total electronic density as

$$\rho(N, N_s, \mathbf{r}) = \rho_\uparrow(N, N_s, \mathbf{r}) + \rho_\downarrow(N, N_s, \mathbf{r}) \quad (3)$$

and the spin density as

$$\rho_s(N, N_s, \mathbf{r}) = \rho_\uparrow(N, N_s, \mathbf{r}) - \rho_\downarrow(N, N_s, \mathbf{r}). \quad (4)$$

Now, since the spin-nonpolarized description amounts to the assumption that there are the same number of spin up and spin down electrons, one could use such electronic configuration as the starting point to reach the actual configuration that distinguishes between the number of electrons of a given spin, for an open shell system. This means that one could propose a Taylor expansion of ρ and ρ_s around $N_s = 0$ for N constant and equal to the total number of electrons. In particular, for ρ_s one has that

$$\begin{aligned} \rho_s(N, N_s, \mathbf{r}) = N_s \left(\frac{\partial \rho_s(N, N_s, \mathbf{r})}{\partial N_s} \right)_N \Big|_{N_s=0} \\ + \frac{1}{6} N_s^3 \left(\frac{\partial^3 \rho_s(N, N_s, \mathbf{r})}{\partial N_s^3} \right)_N \Big|_{N_s=0} + \dots \end{aligned} \quad (5)$$

where we have made use of the fact that ρ_s is an odd function of N_s , which implies that

$$\rho_s(N, N_s, \mathbf{r}) \Big|_{N_s=0}, \quad \left[\frac{\partial^2 \rho_s(N, N_s, \mathbf{r})}{\partial N_s^2} \right]_N \Big|_{N_s=0}, \quad \text{etc.}$$

are all equal to zero.

Now, making some algebraic manipulations in connection with the change from the set of independent variables