Theoret. chim. Acta (Berl.) 3, 238—240 (1965)

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Free Electron Model and Photoionization of π-Electrons from Aromatic Hydrocarbons

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Using the free electron wave function it has been shown that the propability of photoionization of a π-electron from aromatic hydrocarbons should be maximum if the incident photon has energy sufficient to ionize and to leave an additional momentum $p = \sqrt{5\, K\hbar^2/2}$ to the escaping electron. This momentum further appears to be independent of the ring size.

Mit Hilfe der Wellenfunktionen des Modells freier Elektronen wird gezeigt, daß die Wahrscheinlichkeit für die Photoionisation eines π-Elektrons aus einem aromatischen Kohlenwasserstoff maximal sein sollte, wenn das auftreffende Photon eine Energie mitbringt, die ausreicht, um die Ionisation herbeizuführen und auf das Elektron ein zusätzliches Moment $p = \sqrt{5\, K\hbar^2/2}$ zu übertragen. Dieses Moment scheint unabhängig von der Ringgröße des aromatischen Systems zu sein.

Employant la fonction d'onde de l'électron libre, on montre que la probabilité de photoionisation d'un électron π des hydrocarbures aromatiques devrait être maximale si le photon incident a l'énergie pour rendre un électron libre *à* $p = \sqrt{5\, K\hbar^2/2}$ de moment. Ce moment ne semble pas dépendre du périmètre du système cyclique.

Although the ionization potentials of a number of aromatic hydrocarbons have been determined by photoionization method, [*4*] the photoionization process itself has been very little studied either experimentally or theoretically. Theoretical analysis is greatly hampered because of the incompleteness of our knowledge of molecular wave functions. Of late free electron wave functions for the π-electrons have been successfully used in the calculation of magnetic susceptibility of aromatic hydrocarbons [*1*] and the doublet splitting in hydrocarbon ions. [*2*] The object of the present investigation was to use free electron wave function in the analysis of photoionization process of π-electrons from aromatic hydrocarbons.

The perturbation energy of a charge ε of velocity v near $z = 0$ in the field of light wave travelling in the z-direction and x-polarized is given by

$$U' = \frac{\varepsilon}{2\,\mu\omega} E_x^0\, p_x = \frac{\varepsilon}{2\,\mu\omega} E_x^0 \left(- i\hbar \frac{\partial}{\partial x} \right) \tag{1}$$

assuming that the incident light waves of frequency ω are so long that they are practically constant in phase over the initial orbit of the electron to be liberated. Let the wave function in the initial state be Ψ_i. In the final state the electron may speed away with a momentrum p in a direction Θ with respect to x-direction so that $p_x = p \cos \Theta$. The Ψ-function of the final state normalised to unity is then written as

$$\Psi_f = \frac{e^{i(\mathbf{p} \cdot \mathbf{r})/\hbar}\, e^{il\varphi}}{(\mathrm{vol})^{\frac{1}{2}}} \tag{2}$$

in a given volume, assuming that in the photoionization process the energy and the z-component of the angular momentum is conserved. The matrix element of U' between the two states becomes

$$U'_{if} = \int \Psi_i \, U' \, \Psi_f \, d\tau \ . \tag{3}$$

Now $pr = pr \cos \theta$ (in polar coordinate) $= pz$ (in cylindrical coordinate). If we use for Ψ_i the wave function given in the previous paper [*2*], i.e.

$$\Psi_i = N K^{\frac{1}{2}} z e^{-Kz^2/2} \, C^{\eta/2} \, r \eta \, e^{-Cr^2/2} \, e^{il\varphi} \tag{4}$$

then the integration (3) can be performed in cylindrical coordinate yielding

$$| U_{if} |^2 = \frac{\varepsilon^2}{4 \, \mu^2 \, \omega^2} \, | E_x^0 |^2 \, \frac{\cos^2 \Theta}{\text{vol}} \cdot \frac{2^{\eta+6} \, \pi^{\frac{7}{2}} \, \Gamma_{(\eta/2+1)}}{C \, \Gamma_{(\eta+1)}} \, \frac{p^4 \, e^{-p^2/k\hbar^2}}{h^2 \, k^{\frac{3}{2}}} \tag{5}$$

The probability per unit time of the ionization process is given by the general formula [*3*]

$$\mathscr{P}_{if} = \frac{2\,\pi}{\hbar} \, | U_{if} |^2 \, \varrho_E \, t \tag{6}$$

where ϱ_E is the density distribution of the final states for free particles of energy E and momentum p in a large volume (vol) and is given by

$$\varrho_E = \frac{4\,\pi \mu \, p}{h^3} \, (\text{vol}) \ . \tag{7}$$

If we consider only the escaping electrons in the direction of a solid angle $\delta\Omega$, we have to replace $4\,\pi$ by $\delta\Omega$. The differential probability of the electron escaping with momentum p in the solid angle $\delta\Omega$ during t thus becomes

$$\delta\mathscr{P} = \delta\Omega \, \cos^2 \Theta \, \frac{\varepsilon^2}{\mu\omega^2} \, \frac{2^{\eta+6} \, \pi^{\frac{9}{2}} \, | E_x^0 |^2 \, \Gamma_{(\eta/2+1)}}{C \, \Gamma_{(\eta+1)}} \, \frac{p^5 \, e^{-p^2/k\hbar^2}}{h^6 \, k^{\frac{3}{2}}} \ . \tag{8}$$

The differential cross section for the process of photoionization is $\delta\mathscr{P}$ divided by the number of photons incident per cm² during t, namely $\frac{ct}{8\,\pi} \, \frac{| E_x^0 |^2}{\omega\hbar}$. The total cross section $\mathscr{S}$ is obtained by writing $\frac{4\,\pi}{3}$ in place of $\delta\Omega \cos^2 \Theta$, yielding

$$\mathscr{S} = \frac{2}{3} \, \frac{\varepsilon^2}{\mu \, \omega \, c} \, \frac{2^{\eta+6} \, \pi^{\frac{9}{2}} \, \Gamma_{(\eta/2+1)}}{C \, \Gamma_{(\eta+1)}} \cdot \frac{p^5 \, e^{-p^2/k\hbar^2}}{h^5 \, k^{\frac{3}{2}}} \ . \tag{9}$$

The probability of ionization, eq. (6), has a rather sharp maximum for $p = \sqrt{\frac{5}{2} K h^2}$, that is when the incident photon is large enough not only to ionize but also to leave an additional momentum $= \sqrt{\frac{5}{2} K \hbar^2}$ to the escaping electron. Further since the the additional momentum depends on K which is equal to $\sqrt{\frac{4\,\pi^2 \, mk}{h^2}}$ and is independent of the size of the ring, this should be constant for hydrocarbons of any size.

From the values of k given in the previous paper [*1*], the kinetic energy of the escaping electron ($p^2/2\,m$) is estimated to be about 8 ev. The orbital energy of an electron (whose magnitude is equal to the ionization energy) is given as

$$\begin{aligned} E &= E_z + E_r + E_\varphi \\ &= \frac{3}{2} \cdot \frac{h}{2\pi} \sqrt{\frac{k}{m}} + \frac{h^2}{8\pi^2 m R^2 \alpha} + \frac{h^2}{8\pi^2 m R^2} l^2 f(\alpha^2 l^2) \, . \end{aligned}$$

which for the topmost filled level of benzene comes out to be about 14 ev. Thus we conclude that the photoionization probability of an electron from the topmost filled level of benzene is maximum when the incident photon has energy sufficient to ionize the molecule and leave 4/7 th of the ionization energy to the escaping electron as kinetic energy.

It is to be rembered that the free electron model is still an one electron approximation and the conclusions may hold approximately for the ionization of a π-electron from the topmost filled orbital only. Further, the free electron model is a poor approximation for absolute energy calculation as will be evident from the calculated ionization energy of 14 ev as compared to the experimental value of about 10 ev.

References

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(Received April 4, 1965)