AIP | The Journal of Chemical Physics

FreeElectron Model and Doublet Splitting in Aromatic Hydrocarbon Ions

Sadhan Basu

Citation: The Journal of Chemical Physics **41**, 1453 (1964); doi: 10.1063/1.1726089
View online: http://dx.doi.org/10.1063/1.1726089
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/41/5?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Electronic Interaction in the FreeElectron Network Model for Conjugated Systems. III. Spectra of Hydrocarbons Other Than Even Alternants
J. Chem. Phys. **32**, 1445 (1960); 10.1063/1.1730937

Electronic Interaction in the FreeElectron Network Model for Conjugated Systems. II. Spectra of Aromatic Hydrocarbons
J. Chem. Phys. **25**, 13 (1956); 10.1063/1.1742804

A FreeElectron Model for Discussing Reactivity in Unsaturated Hydrocarbons
J. Chem. Phys. **21**, 174 (1953); 10.1063/1.1698592

Note on the Generalized FreeElectron Model of Conjugated Polycyclic Hydrocarbons
J. Chem. Phys. **21**, 174 (1953); 10.1063/1.1698591

The FreeElectron Model and the Diamagnetism of Aromatic Hydrocarbons
J. Chem. Phys. **20**, 741 (1952); 10.1063/1.1700531

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 169.226.243.112 On: Wed, 03 Dec 2014 15:14:33

main Raman band is 572 cm^{-1} below the origin of the vapor band, and most of this difference is probably due to the crystal field for the following reason. The O–H stretching frequency of HDO in the vapor is 3707 cm^{-1}, whereas in D_2O ice, where there is little coupling of the O–H stretching vibration with other vibrations, the O–H stretching frequency is 3277 cm^{-1}. The crystal field has therefore caused a shift of 3707–3277=430 cm^{-1}. The shift of the ν_1 vibration of H_2O due to the crystal field is not necessarily the same as the shift of the O–H stretching frequency of HDO in D_2O, but it will probably not differ greatly from it. Consequently, it is safe to conclude that most of the difference of 572 cm^{-1} between the frequencies of the H_2O ν_1 vapor band and the ν_1 Raman band in Ice I is due to the crystal field. If most of the difference of 309 cm^{-1} between the H_2O ν_1 vapor band and the ν_1 Raman band in Ice VII is also due to the crystal field, as seems likely, then the crystal field in Ice VII causes very roughly half the shift of the ν_1 vibration from that of the vapor that the crystal field of Ice I causes. This conclusion is of course approximate, but it can be concluded qualitatively with some confidence that the hydrogen bonds in Ice VII, although not so strong as in Ice I, are still strong. More quantitative evidence on the effects of hydrogen bonding unperturbed by coupling effects can be obtained from the infrared spectra of dilute solutions of H_2O in D_2O and of D_2O and H_2O. It is hoped that these experiments will be done in the near future.

ACKNOWLEDGMENTS

We are greatly indebted to Mr. A. Lavergne for help with the high-pressure experiments, and to Dr. L. D. Calvert and Dr. J. E. Bertie for the x-ray diffraction photographs.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 41, NUMBER 5 1 SEPTEMBER 1964

Free-Electron Model and Doublet Splitting in Aromatic Hydrocarbon Ions

SADHAN BASU

Department of Chemistry, University College of Science and Technology, Calcutta-9, India

(Received 4 February 1964)

Doublet splitting in hydrocarbon ions due to spin–orbit interaction arising from electron circulation around the ring has been calculated using a free electron model.

THE semiclassical model proposed by Pauling for ring current in aromatic hydrocarbons has been very useful in the interpretation of diamagnetic anisotropy[1] and the proton magnetic resonance spectra[2] of these compounds. The free-electron model is a quantum mechanical counterpart of Pauling's semiclassical description of mobile electrons. In this model, the pi electrons of an aromatic hydrocarbon molecule are assumed to move freely and independently on the circumference of a circle of radius R. The eigenfunctions ψ_l and eigenvalues E_l are given, respectively,[3] as

$$\psi_l = (2\pi)^{-\frac{1}{2}} \exp(il\phi), \tag{1}$$

$$E_l = \hbar^2 l^2 / 2mR^2, \tag{2}$$

where $l=0, \pm 1, \pm 2, \cdots, R$, the radius of the ring is calculated from the relation $\pi R^2 = N(27/4)^{\frac{1}{2}} R_0^2$, where N=number of rings, R_0=C–C bond distance=1.39 Å. That is, the atoms are assumed to be distributed along the circumference of a circle having the same area as the molecule. In the case of one ring compound, it is more reasonable to calculate R from the relation $2\pi R = nR_0$, n being the number of atoms; that is the so-called perimeter approximation. The integer l in (1) and (2) is called a ring quantum number and has the significance of an "orbital" angular momentum. In this model it is expected that for hydrocarbon monopositive and mononegative ions, the energy levels will split by some sort of spin–orbit interaction between the spin and the "orbital" motion of the unpaired electron.

The free-electron model in its simplest form as given by (1) and (2) can not, however, give rise to any spin–orbit interaction because of the assumption of zero potential field. Following Rudenberg and Parr,[4] the free-electron theory may be modified in the following way to make it more realistic and to estimate the extent of splitting due to spin–orbit interaction. Let us suppose that the unsaturation electron in aromatic

[1] L. Pauling, J. Chem. Phys. **4**, 673 (1936).
[2] H. Bernstein, W. Schnider, and J. A. Pople, Proc. Roy. Soc. (London) **A236**, 515 (1956).
[3] J. R. Platt, J. Chem. Phys. **17**, 484 (1949).
[4] K. Rüdenberg and R. G. Parr, J. Chem. Phys. **19**, 1268 (1951).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 169.226.243.112 On: Wed, 03 Dec 2014 15:14:33

TABLE I. Doublet separation in hydrocarbon ions.

No. of rings	R (Å)	l Negative	l Positive	ΔE(cm^{-1}) Negative	ΔE(cm^{-1}) Positive
1	1.32	2	1	0.300	0.280
2	1.78	3	2	0.348	0.176
3	2.18	4	3	0.562	0.155
4	2.58	5	4	0.562	0.289
5	2.81	6	5	0.625	0.395

molecule moves in an axial potential field given as

$$V_z=\tfrac{1}{2}kz^2,$$
$$V_r=\frac{h^2}{8\pi^2 m}\frac{1}{4R^2\alpha^2}\left[\left(\frac{R}{r}\right)^2+\left(\frac{r}{R}\right)^2-2\right], \tag{3}$$
$$V_\phi=0,$$

(k and α are two parameters to be determined from experimental data), where V_z couples the electron to the molecular plane, V_r holds the electron near the radius of the ring, R, and V_ϕ causes a free circulation of the electrons around the ring. Only the last assumption is used in the simple free-electron theory.

The allowed energy values of an electron in such a potential field may be given as

$$E=E_z+E_r+E_\phi, \tag{4}$$

where

$$E_z=(n_z+\tfrac{1}{2})(h/2\pi)(k/m)^{\frac{1}{2}}, \qquad n_z=1, 3, 5, \cdots \tag{5}$$

(since pi-electron wavefunctions must have a node in the molecular plane),

$$E_r=(n_r+1)(h^2/8\pi^2 mR^2\alpha), \qquad n_r=0, 2, 4, \cdots, \tag{6}$$

and

$$E_\phi=(h^2/8\pi^2 mR^2)l^2 f(\alpha^2 l^2), \qquad l=0, \pm 1, \pm 2, \cdots, \tag{7}$$

where

$$1+2\alpha^2 l^2 f(\alpha^2 l^2)=(1+4\alpha^2 l^2)^{\frac{1}{2}}. \tag{8}$$

The separation between the various E_z and E_r levels are much larger than those between the E_ϕ levels. So, in most cases of interest to us, the lowest E_z and E_r level will be filled and the E_ϕ levels will be occupied by electrons progressively, two per level, from $l=0$ onwards. The wavefunction of an electron in such a system may be written as

$$\psi_{10\pm l}$$
$$=NK^{\frac{1}{2}}z\exp(-Kz^2/2)(C^{\frac{1}{2}}r)^\eta\exp(-Cr^2/2)\exp(il\phi), \tag{9}$$

where

$$\eta^2=\frac{1}{4\alpha^2}+l^2, \qquad K=\frac{4\pi^2 mk}{h^2}, \quad \text{and} \quad C=\frac{1}{2R^2\alpha}.$$

This must be multiplied by a suitable spin function Φ.

The spin–orbit interaction operator in an axial coordinate system may be written as[5]

$$H_{s0}=-\frac{\hbar^2}{i(2mC)^2}\left[\sigma_1\left(\frac{\partial V}{r\partial\phi}\frac{\partial}{\partial z}-\frac{\partial V}{\partial z}\cdot\frac{\partial}{r\partial\phi}\right)\right.$$
$$\left.+\sigma_2\left(\frac{\partial V}{\partial z}\frac{\partial}{\partial r}-\frac{\partial V}{\partial r}\cdot\frac{\partial}{\partial z}\right)+\sigma_3\left(\frac{\partial V}{\partial r}\cdot\frac{\partial}{r\partial\phi}-\frac{\partial V}{r\partial\phi}\cdot\frac{\partial}{\partial r}\right)\right], \tag{10}$$

where σ's are the Pauli spin matrices. In the calculation of doublet splitting it can be shown that the integrals of the type[6]

$$\int\Phi^*(10)\sigma_i\Phi\begin{pmatrix}1\\0\end{pmatrix}d\sigma \tag{11}$$

are zero for $i=1$ and 2. For $i=3$ this integral is $+1$ or -1 according to whether we are considering a spin-up or a spin-down case. Consequently, only the third term in (10) will be effective in bringing about a doublet separation; and, in view of our assumption of $V_\phi=0$, the splitting is given by

$$\Delta E=2\left\{\frac{0.0573}{R^4\alpha^2}\left[\frac{1}{4\alpha^2\eta(\eta-1)}-1\right]\right\}(\text{cm}^{-1}), \tag{12}$$

where R is expressed in angstrom units. It has been found that for $\alpha=0.0925$ best agreement is obtained between the experimental and the calculated electronic spectra of aromatic hydrocarbons containing two, three, four, and five fused rings. For the one-ring system, however, α must be given a much higher value of 0.245 to get good agreement with the experimental spectra. With these α's the doublet separation in various hydrocarbon ions were calculated using the relation (12) and are given in the Table I. There is a shred of experimental evidence[7] that the doublet splitting for benzene negative ion is of the order of 1 cm^{-1}. This model may be further refined by assuming a form for V_ϕ similar to that given by Rüdenberg and Parr.[4] It is also important to note that the polynuclear hydrocarbons are replaced in this model by a suitable molecular systems having orbital degeneracy similar to benzene so that the first-order spin–orbit effect does not vanish.

Thanks are due to Prof. C. A. Coulson, Oxford; Dr. S. Dutta Majumder, Calcutta; and Dr. M. Zerner, Harvard for their helpful suggestions and constructive criticisms.

[5] M. Mizushima and S. Koide, J. Chem. Phys. **20**, 765 (1952).
[6] G. Breit, Phys. Rev. **34**, 553 (1929).
[7] H. McConnel, J. Chem. Phys. **34**, 13 (1961).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 169.226.243.112 On: Wed, 03 Dec 2014 15:14:33