

Free Electron Treatment of Diels-Alder's Reaction

Sadhan Basu

Citation: *The Journal of Chemical Physics* **23**, 1548 (1955); doi: 10.1063/1.1742356

View online: <http://dx.doi.org/10.1063/1.1742356>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/23/8?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[A quantum chemistry study of Diels–Alder dimerizations in benzene and anthracene](#)

J. Chem. Phys. **131**, 024313 (2009); 10.1063/1.3159542

[Diels–Alder reactions: An assessment of quantum chemical procedures](#)

J. Chem. Phys. **106**, 8727 (1997); 10.1063/1.473933

[Combined quantumchemical and MM approach to the endo/exoselectivity of DielsAlder reactions in polar media](#)

AIP Conf. Proc. **330**, 145 (1995); 10.1063/1.47869

[Solvent effects on DielsAlder reactions: ab initio versus density functional theory](#)

AIP Conf. Proc. **330**, 76 (1995); 10.1063/1.47855

[Mechanism of the Diels—Alder Reactions of Butadiene](#)

J. Chem. Phys. **46**, 4920 (1967); 10.1063/1.1840657



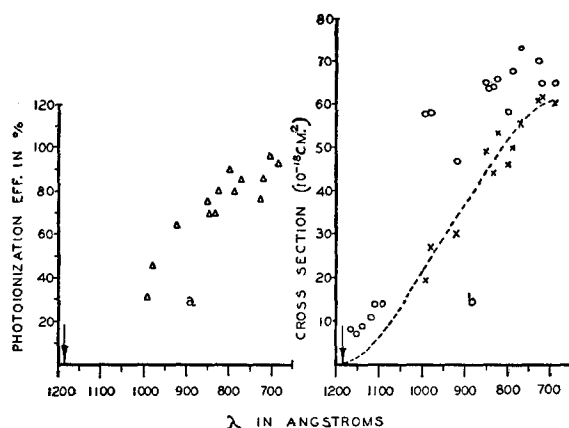


FIG. 1. (a) Photoionization efficiencies of C_2H_4 . (b) Absorption and photoionization cross sections of C_2H_4 . \circ Absorption cross sections. \times Ionization cross sections. All data were taken with 3-cm ionization chambers and a 5 Å resolution (see reference 1). The first ionization potential of 10.46 ± 0.05 eV is shown by the arrow.

from electron impact measurements. The ionization efficiencies of C_2H_4 in percent or ion pairs per 100 absorbed quanta are shown in Fig. 1(a). From these efficiencies and the measured absorption coefficients, the ionization cross sections were calculated. In Fig. 1(b) both the absorption and ionization cross sections are presented. The error in the absorption cross sections was estimated to be within ± 10 percent, while that for the ionization cross sections was ± 20 percent. It should be noted that the absorption for wavelengths shorter than 850 Å was large, corresponding to absorption coefficients of the order of 1500 cm^{-1} . The dotted line indicates the contour of the ionization continuum established by these data. Although no ionization cross sections were obtained for wavelengths longer than 991 Å, the extension of the curve to the ionization limit seemed justified by the trend of the total absorption cross sections.

In the case of C_2H_2 the onset of ionization occurred at 1100 ± 5 Å corresponding to 11.25 ± 0.05 eV, again in agreement with the electron impact value of 11.4 ± 0.1 eV by Lossing, Tickner, and Bryce⁷ and the spectroscopic value of 11.35 ± 0.01 eV obtained by Price.⁸ Since the most likely impurity in the tank C_2H_2 used was acetone, with an ionization onset at 1279 Å,⁶ the existence of a sharp onset at 1100 Å indicated that the gas sample was free from this impurity. The possibility of the presence of small amounts of other impurities cannot be entirely ruled out, although it was felt that their effects in this investigation were small. The ionization efficiencies of C_2H_2 are shown in Fig. 2(a) and the corre-

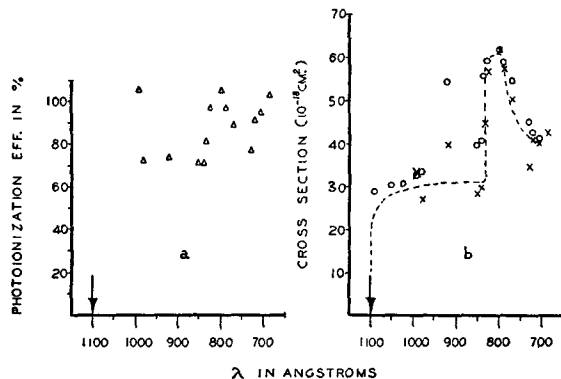


FIG. 2. (a) Photoionization efficiencies of C_2H_2 . (b) Absorption and photoionization cross sections of C_2H_2 . \circ absorption cross sections. \times ionization cross sections. All data were taken with 3-cm ionization chambers and a 5 Å resolution (see reference 1). The first ionization potential of 11.25 ± 0.05 eV is shown by the arrow.

sponding absorption and ionization cross sections in Fig. 2(b). A dotted line again has been used to indicate the contour of the continuum. It was observed that a distinct break in this curve occurred at about 827 Å. This increase in the ionization cross section may be due to a second ionization continuum beginning at about 15 eV. There appears to be no published information concerning the existence of this second continuum. Price⁸ reported, on the basis of absorption spectra, that continuous absorption in C_2H_2 began at about 1050 Å and decreased toward shorter wavelengths becoming very weak between 800 Å and 150 Å. This is not substantiated by these results, since relatively large cross sections were observed near 800 Å. The present data show, however, that the absorption does decrease rapidly for wavelengths shorter than 750 Å.

† The aid of the Office of Naval Research is gratefully acknowledged.

- ¹ Wainfan, Walker, and Weissler, *Phys. Rev.* (to be published).
- ² W. C. Price and W. T. Tuttle, *Proc. Roy. Soc. (London)* **A174**, 207 (1940).
- ³ W. C. Price and A. D. Walsh, *Trans. Faraday Soc.* **41**, 381 (1945).
- ⁴ M. Zelikoff and K. Watanabe, *J. Opt. Soc. Am.* **43**, 756 (1953).
- ⁵ G. Moe and A. B. F. Duncan, *J. Am. Chem. Soc.* **74**, 3136 (1952).
- ⁶ K. Watanabe, *J. Chem. Phys.* **22**, 1564 (1954).
- ⁷ Lossing, Tickner, and Bryce, *J. Chem. Phys.* **19**, 1254 (1951).
- ⁸ W. C. Price, *Phys. Rev.* **47**, 444 (1935).

Free-Electron Treatment of Diels-Alder's Reaction

SADHAN BASU

Department of Chemistry, University of Calcutta,
92 Upper Circular Road, Calcutta 9, India

(Received May 2, 1955)

MOLECULAR orbital calculations have been successful in predicting the reactivities of a number of complicated organic molecules; especially the theoretical calculations of Brown¹ have agreed well, at least qualitatively, with the experimental results of a large number of Diels-Alder's reactions. Of late, free electron wave functions^{2,3} have been used in predicting the spectral transition in the case of a number of conjugated compounds and the calculated frequencies have been found to agree with the experimental values better than those of MO method in some cases. It has been shown by Basu⁴ that the free electron model can be used effectively in explaining the orientation of substituents in aromatic molecules. The object of the present investigation is to show that free-electron model can also be used effectively in explaining Diels-Alder's reactions.

The formation of maleic anhydride addition product consists in localizing two π electrons of the conjugated system with the formation of two σ C-C bonds. The fundamental assumption of Brown¹ is that, the ease of formation of an addition product at a pair of carbon atoms of the conjugated system depends on the energy required to localize two of the π electrons upon atoms, say m and n , provided they are suitably oriented. In the case of aromatic hydrocarbons the latter provisions mean that m and n must be para to each other. This energy quantity is termed para localization energy, P , and is given by

$$P = 2\alpha + E_r - E, \quad (1)$$

where E is the total π -electron energy of the original conjugated system, 2α the energy of two isolated π electrons and E_r the total π -electron energy of one or more conjugated systems left after two π electrons are localized in two suitably oriented atoms. The total π -electron energy of the parent and residual molecules were calculated by Brown by MO method. These quantities may be calculated by the free electron network model.^{5,6} For these purposes the conjugated system is divided into a number of segments; the free-electron wave function in each segment is then expressed in the form

$$a \cos \omega x + b \sin \omega x \quad (2)$$

where x is expressed in unit of l , the C-C bond length, and ω

TABLE I. Para localization energies.^a

Compound	Positions	P	$P'(-\gamma)$	k_a
Benzene	1:4	$2\alpha + 3.560 K$	2.67	$ca 10^{-16}$
Naphthalene	1:4	$2\alpha + 1.604$	2.40	$ca 10^{-8}$
Anthracene	1:4	$2\alpha + 1.599$	2.34	$ca 10^{-7}$
	9:10	$2\alpha - 0.353$	2.07	1
Naphthacene	1:4	$2\alpha + 1.601$	2.33	...
	5:12	$2\alpha - 0.357$	2.01	30
Pentacene	1:4	$2\alpha + 1.595$	2.33	...
	5:14	$2\alpha - 0.361$	1.99	90
	6:13	$2\alpha - 0.368$	1.94	1600
Phenanthrene	1:4	$2\alpha + 1.615$	2.47	...
Triphenylene	1:4	$2\alpha + 0.205$
Perylene	1:12	$2\alpha + 2.388$	2.60	...

^a K stands for $\hbar^2/8m^2$ and k_a , the rate constant, is expressed relative to 9:10 addition to anthracene.

in terms of π . At each junction point of the segments we apply the continuity and conservation condition, and get a number of secular equations which may be solved for ω . The energy is given by

$$E = \frac{\hbar^2 \omega^2}{8m^2 \pi^2} \quad (3)$$

Starting from the lowest state, π electrons are distributed among these energy states, two for each state, and the total π -electron energies are calculated. The π -electron energy of the residual molecule is also calculated similarly; for example, 1:4 addition to anthracene leaves the residual molecules of naphthalene and ethylene, while 9:10 addition leaves two phenyl nuclei.

The para localization energies P calculated for a number of aromatic hydrocarbons are given in Table I along with those calculated by Brown (P') (corrected for overlap) by the MO method.

It may be observed that the calculated values are in the right sequence with the experimental results. As per calculation, benzene and naphthalene do not add maleic anhydride, anthracene undergoes 9:10 addition and naphthacene and pentacene add maleic anhydride at central "meso-position" with increasing ease. The angular ring systems do not undergo maleic anhydride addition at all. Another point that emerges out of the present calculation is that maleic anhydride addition is possible only when the para localization energy is less than the energy (2α) of the two isolated π electrons.

¹ Brown, J. Chem. Soc. 1950, 691.

² Bayliss, J. Chem. Phys. 16, 287 (1948).

³ Kuhn, Helv. chim. Acta. 31, 1441 (1948).

⁴ Basu, J. Chem. Phys. 22, 1952 (1955).

⁵ Rudenberg and Scherr, J. Chem. Phys. 21, 1565 (1953).

⁶ Griffith, Trans. Faraday Soc. 49, 345 (1953).

Simultaneous Transitions in Liquids. A New Kind of Molecular Spectrum

J. A. A. KETELAAR AND F. N. HOOGE
 Laboratory for General and Inorganic Chemistry of the
 University of Amsterdam, Amsterdam, Holland
 (Received June 10, 1955)

SIMULTANEOUS vibrational transitions have recently been observed in mixtures of compressed gases (CO_2) with H_2 , O_2 , and N_2 ,¹ HCl with H_2 ² and in liquid mixtures (CS_2 with Br_2 and I_2).³ Simultaneous vibrational transitions in liquid mixtures are by no means rare as we have observed them in mixtures of CS_2 with such substances as S_2Cl_2 , PCl_3 , PBr_3 , SOCl_2 , PSCl_3 , and CCl_3SCL .

The infrared absorption spectra of these mixtures may be said to furnish examples of a new class of molecular spectra besides Raman spectra and ordinary infrared absorption spectra. The system of bands due to simultaneous transitions with some frequencies forms a complete molecular spectrum, analogous to the

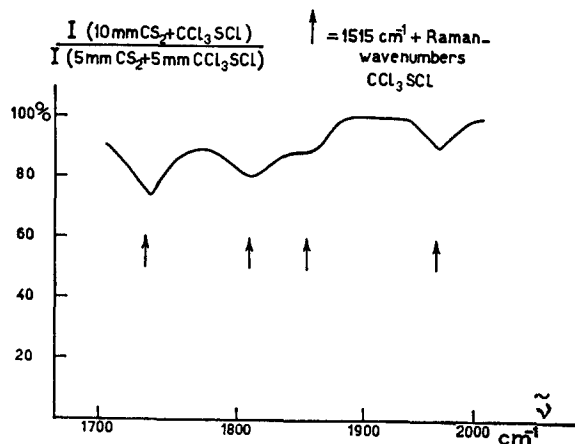


FIG. 1. Simultaneous transition spectrum of CCl_3SCL (perchloromer-captane) with CS_2 . The arrows indicate the positions of Raman lines shifted by 1515 cm^{-1} (ν_3 of CS_2 in liquid state).

Raman spectrum, but shifted to higher frequencies by 1515 cm^{-1} of the ν_3 CS_2 band (liquid state). Only the observable range is restricted by the transparency region of CS_2 between 1500 and 2100 cm^{-1} to molecular frequencies between about 160 and 500 cm^{-1} .

Absorption spectra were recorded for a 10-mm optical path length of mixtures of equal volumes of CS_2 and the second component. The spectra obtained with two superimposed cells of 5 mm thickness, each filled with one of the pure components served as the reference (Fig. 1). Results are given in Table I. The frequencies found are in excellent agreement with the values found from the Raman spectra. Also, the relative intensities are in good agreement with those observed in the Raman spectra as expected from the theoretical treatment. However, differences might be expected for frequencies of groups which are situated in different parts of larger molecules.

Assuming electrostatic interaction the intensity of the simultaneous transitions is determined by the presence of terms in the

TABLE I.

Substance	Simultaneous transition-spectrum with CS_2	Raman spectrum
S_2Cl_2	202	203 ^a
	~250 Shoulder	242
	447	445
PCl_3	181	190 ^a
	258	258
	505	484 {511
PBr_3	158	162 ^a
	376	380 {400
SOCl_2	201	192 ^a
	293	283
	348	343
	435 Shoulder	443
	488	488
PSCl_3	168	168 ^{a,b}
	249	244
	430	429
CCl_3SCL	217	216 ^c
	292	293
	337	336
	450	451

^a Average values according to Landolt-Börnstein, *Zahlenwerte und Funktionen, Atom- und Molekularphysik* (Springer Verlag, Berlin, 1951), Part 2.

^b The very weak band at 382 cm^{-1} is omitted; see H. Gerding and R. Westrik, *Rec. trav. chim.* 61, 842 (1942).

^c J. Duchesne, *Bull. Soc. Roy. Sci. Liège* 1, 61 (1942).