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Synopsis

It is shown that an enhancement of infrared absorption bands observed in the molecular complex is due to change in vertical ionization energy of electron donor in the course of molecular vibrations. An enhanced infrared absorption intensity of 992 cm^{-1} of benzene in benzene-iodine complex is calculated by a semi-empirical molecular orbital theory and the charge transfer theory of Mulliken, and also using the dipole moment value of benzene-iodine complex measured by Fairbrother. The calculated intensity value agrees well with the experimental value by Ferguson and Matsen.

I. Introduction

A number of infrared absorption bands of charge transfer complexes corresponding to infrared in-active vibration of component molecules have been observed.[1-5] This was interpreted by Ferguson and Matsen[6] as that the change of vertical ionization energy or vertical electron affinity in the course of molecular vibration gave rise to a change in dipole moment of a complex which caused to enhance the infrared absorption of these vibrations. Of course, all the vibrations of a component molecule in the complex do not give rise to a change in vertical ionization energy or vertical electron affinity; in benzene complex, for example, the C-H vibrations of benzene will have no influence on vertical ionization potential. On the other hand, as a result of complex formation, one molecule will bring about shift of an absorption band of the other.

In this paper, attention will be paid to the enhancement of the infrared absorption of benzene band at 992 cm^{-1} in the complex and the intensity enhanced will be treated with a semi-empirical molecular orbital method and also the charge transfer theory of Mulliken[7].

II. Experimental values

The basic equation for the infrared intensity of i-th vibration is

$$A_i = \frac{1}{nL}\int \ln\left(\frac{I_0}{I}\right) d\nu = \frac{N\pi}{3c^2}\left|\frac{\partial \mu}{\partial Q_i}\right|^2, \qquad (1)$$

(1) J. Collin and L. D'Or, J. Chem. Phys., **23** (1957), 397.
(2) L. D'Or, R. Alewaeters and J. Collin, Rec. trav. chim., **75** (1956), 862.
(3) W. B. Person, R. E. Erickson and R. B. Buckles, J. Chem. Phys., **27** (1957), 1211.
(4) E. E. Ferguson, J. Chem. Phys., **25** (1956), 577, **26** (1957), 1357.
(5) F. Watari and S. Kinumaki, Bull. Chem. Res. Inst. Non-Aqueous Solns., **9** (1959), 1.
(6) E. E. Ferguson and F. A. Matsen, J. Chem. Phys., **29** (1958), 105.
(7) R. S. Mulliken, J. Am. Chem. Soc., **74** (1952), 811.

where n is molar concentration and L, path length. Integration is to be performed over the entire absorption band corresponding to the vibration under study. N is the number of absorbing molecules per cc. c is the light velocity and Q_i, the normal coordinate corresponding to i-th vibration. μ is the dipole moment of benzene-iodine complex which is defined by the extent of charge transfer from benzene to iodine and the distance between them. Ferguson and Matsen[6] measured the integrated intensity of the 992 cm^{-1} band of benzene in the benzene-iodine complex to be 770 ± 300 cm^{-1}/millimole/cm^2.

This intensity leads to the value $d\mu/dQ$ of 33 esu/cm-$g^{1/2}$.

III. Theoretical treatment and calculation

According to Mulliken's charge transfer theory, the extent of charge transfer is a function of the ionization potential, I, of benzene and the ionization potential of benzene may be expected, as Ferguson and Matsen did, to be a function of the normal coordinate Q of the skeletal carbons.

The variation in I with respect to the symmetrical ring stretching vibration of benzene can be estimated by molecular orbital method. The ionization potential is the electron energy of the highest occupied molecular orbital. I of benzene is given by Pople[8] with electron interaction as

$$-I = U_{11} + \frac{1}{2}(11|11) + \beta_{12} - \frac{1}{3}(11|22) - \frac{1}{6}(11|44)\,, \qquad (2)$$

where U_{11} is the core integral; β, the resonance integral; and $(pp|qq)$'s, atomic Coulomb repulsion integrals between the π-electrons located on p and q carbons. Here also the simplifying assumptions such as; 1) zero differential overlap, 2) neglect of non-neighbor core integral, $\beta_{pq}=0$, where p and q are non-neighbors, are taken into account. U_{11} and $(11|11)$ values do not vary during A_{1g} ring vibration of benzene, so the variations of the other three terms only need be considered.

β is expressed by Pariser and Parr[9] in a suitable extrapolation fitted the ethylene and benzene resonance integrals which have been determined already from the first transition energy and their bond lengths, as

$$\beta(r) = -6442\exp(-5.686r)\ \text{eV} \quad (r \text{ in Å})\,. \qquad (3)$$

The two center electronic repulsion integrals $(pp|qq)$ are determined also by Pariser and Parr[9] for $r\leq 2.80$Å by the use of the following equation:

$$ar + br^2 = \frac{1}{2}[(pp|pp) + (qq|qq)] - (pp|qq)\,, \qquad (4)$$

in which a and b are determined by fitting values calculated from an equation of the following form for $r=2.80$Å and $r=3.70$ Å:

$$(pp|qq) = \frac{7.1975}{r}\left\{\left[1+\left(\frac{1}{2r}\right)^2(R_p-R_q)^2\right]\right.^{-1/2}$$

(8) J. A. Pople, Trans. Faraday Soc., **49** (1953), 1375.
(9) R. Pariser and R. G. Parr, J. Chem. Phys., **21** (1953), 767.

$$+\left[1+\left(\frac{1}{2r}\right)^2(R_p+R_q)^2\right]^{-1/2}\Big\}\ \mathrm{eV}, \tag{5}$$

in which

$$R_p=\frac{4.597}{Z_p}\times 10^{-8}\ \mathrm{cm}, \tag{6}$$

where Z_p is Slater's effective nuclear charge. It should be noted here that on this treatment, $(pp|pp)$ and $(qq|qq)$ values are not necessary to be determined, whereas their values are the necessary ones in the molecular orbital theory.

$(pp|qq)$ is expressed numerically as

$$(pp|qq)=\frac{1}{2}\{(pp|pp)+(qq|qq)\}-6.386r+0.8273r^2\ \mathrm{eV}. \tag{7}$$

Then, (11|22) and (11|44) are obtained as follows:

$$(11|22)=\frac{1}{2}\{(11|11)+(22|22)\}-6.386r+0.8273r^2\ \mathrm{eV}, \tag{8}$$

$$(11|44)=\frac{1}{2}\{(11|11)+(44|44)\}-12.772r+3.309r^2\ \mathrm{eV}, \tag{9}$$

where r is the C-C bond length of benzene in Å.

Since the vibration of iodine molecule does not essentially mix with the ring stretching of benzene owing to its large mass and the weak force acting between them, it is considered substantially that the vibration band at 992 cm^{-1} under study is due to benzene only.

There are two A_{1g} vibrations in benzene ; one is the ring stretching mode and the other the C-H stretching. The C-H stretching has so much higher frequency that there is essentially no mixing with the ring carbon stretching. The symmetry coordinate for A_{1g} ring stretching is:

$$S=\left(\frac{1}{6}\right)^{1/2}\sum_{i=1}^{6}\Delta r_i, \tag{10}$$

where Δr_i is a change in length of the i-th C-C bond.

From the above reason, the normal coordinate of the ring stretching is then effectively

$$Q\approx\left(\frac{m}{6}\right)^{1/2}\sum_{i=1}^{6}\Delta r_i, \tag{11}$$

where m is the mass of carbon atom.

The relation between the symmetry coordinate and the normal one is obtained in the following form:

$$Q=m^{1/2}S\ . \tag{12}$$

From the equations (2), (3), (8), (9) and (10), we have the change of the ionization potential with respect to the normal coordinate at the equilibrium C-C bond length (r=1.39Å)

$$\frac{\partial I}{\partial S}=-6.319\ \mathrm{eV}. \tag{13}$$

For a donor-acceptor resonance complex the ground state and the excited state wave functions may be written as

$$\Psi_N = a\psi_0 + b\psi_1, \quad \Psi_E = a^*\psi_1 - b^*\psi_0, \tag{14}$$

where ψ_0 is the no-bond structure wave function and ψ_1 the dative state one. One should notice that a' s used here are different from a and b in eq. (4). Second-order perturbation theory gives following approximate relation between coefficients a and b:

$$\frac{b}{a} = -\frac{\beta_0}{W_1 - W_0}, \tag{15}$$

where the quantities of the right hand side in equation (15) are the following integrals:

$$\begin{aligned} \beta_0 &= H_{01} - SW_0 \approx H_{01}, \\ H_{01} &= \int \psi_0 H \psi_1 d\tau, \\ S &= \int \psi_0 \psi_1 d\tau, \\ W_0 &= \int \psi_0 H \psi_0 d\tau, \\ W_1 &= \int \psi_1 H \psi_1 d\tau, \end{aligned} \tag{16}$$

and H is the exact Hamiltonian operator for nuclei and electrons. W_1 is the potential function of excited state without resonance and is equal to $I_D - E_A - \Delta H$, where I_D is the ionization potential of a donor, E_A the electron affinity of acceptor and ΔH the binding energy in polarized state.

Mulliken estimated values of a, b, a^* and b^* using the dipole moment μ of the benzene-iodine complex by Fairbrother as

$$a = 0.97, \quad b = 0.17, \quad a^* = 0.99, \quad b^* = 0.27. \tag{17}$$

The value of $W_1 - W_0$ can be estimated to be 3.8 eV from the charge transfer energy $h\nu_{max}$[10].

Then, with equation (13) we obtain

$$\frac{db}{dS} = -\frac{a^2 b}{W_1 - W_0}\frac{dI}{dS} = 0.265. \tag{18}$$

The dipole moment of the complex is given by

$$\mu = b^2 \mu_D, \tag{19}$$

where μ_D is the dipole moment of the dative state and is qual to $e \cdot r_{AD}$, in which e is the charge of electron and r_{AD}, the equilibrium distance between a donor D and an acceptor A in units of Å. r_{AD} was estimated as 3.4Å[11] and it leads to 16.33 D for μ_D.

(10) G. Briegleb and J. Czekalla, Z. Elektrochem., **59** (1955), 184.

(11) R. S. Mulliken, J. Am. Chem. Soc., **49** (1952), 811. E. E. Ferguson and F. A. Matsen, J. Chem. Phys., **29** (1958), 105.

From the equations (18) and (19), we obtain

$$\frac{d\mu}{dS} = 2\,b\,\mu_D \frac{db}{dS}$$

$$= 1.471 \quad \text{(Debye/Å)}, \tag{20}$$

$$\frac{d\mu}{dQ} = 33 \quad \text{esu/cm-g}^{1/2}\,. \tag{21}$$

The above value for the change of the dipole moment of the complex with respect to the normal coordinate corresponding to the 992 cm^{-1} band of benzene agrees well with that calculated from the measured infrared intensity. The forbidden benzene band at 992 cm^{-1} in the benzene-iodine complex can be enhanced by complex formation with the electron acceptor in which the A_{1g} vibration causes the dipole moment of the complex to change.

IV. Discussion

In the molecular orbital expression of ionization potential of π-electron system, several assumptions are made usually and the terms neglected have minor influence on the molecular orbital energy. Here the numerical value of each term in the expression is not necessary, but we need only their derivatives. There may be a case that though the numerical value of the term itself is small, as compared with the other, its derivative is large and takes important part in the derivative of the ionization potential. Overlap integral varies in large extent as the corresponding interatomic distance changes. Nevertheless, the measured intensity is satisfactorily in agreement with the value calculated using simplified expression of I and the dipole moment of the complex measured by Fairbrother. Another value of the dipole moment of benzene-iodine complex has been reported by Kortuem and Walz[12], and its value is 2.5 times as large as that of Fairbrother. And this leads to 98 esu/cm-$g^{1/2}$ of $\partial\mu/\partial Q$ that is 3 times as large.

Recently Ferguson and Matsen[13] reported the net value of the enhanced infrared intensity of benzene 992 cm^{-1} in benzene-iodine complex to be 220 cm^{-1}/millimole/cm^2. When this is the case, the intensity which is calculated using the dipole moment 1.80 D of benzene-iodine complex measured by Kortuem and Walz is too large, as compared with this measured intensity. Here, of course, it should be noticed that one can not make any comment about measured dipole moment values of the complex, because of assumption made above in the expression of ionization potential.

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(12) G. Kortuem and H. Walz, Z. Elektrochem., **57** (1953), 73.
(13) E. E. Ferguson and F. A. Matsen, J. Am. Chem. Soc., **82** (1960), 3268.