

# Line shapes of charge-transfer spectra

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The theoretical description of condensed-media line shapes of electronic transitions, as developed in earlier papers, is applied to the charge-transfer (CT) spectra of the complexes mesitylene:tetracyanoethylene (Mes:TCNE) and anthracene:chloranil (AN:CA). Results are compared with those previously published for benzene:iodine (Bz:I<sub>2</sub>), and the factors which contribute to line broadening (inhomogeneous broadening, the Franck-Condon profile, and donor-acceptor vibrational motion) are discussed. The results of an attempt to determine the contributions to the line shape made by intermolecular orbital couplings are presented. In addition, the Bz:I<sub>2</sub> CT spectrum is reinvestigated, and the question of which ionization potential of benzene is involved is addressed.

## I. INTRODUCTION

In earlier publications<sup>1-3</sup> a theoretical formalism for describing electronic absorption spectra in condensed media was developed. By taking a suitable average<sup>4</sup> (over the solvent molecules' coordinates) of the electric dipole correlation function, the intensity of absorption  $I(\omega)$  can be decomposed into zeroth-, first-, and second-order contributions, each of which contains the effects of localized intramolecular dipole transitions as well as those of intermolecular charge transfer. The first- and second-order contributions, which modify the zeroth-order dipole strength, contain the so-called "resonance" and "fluctuation" integrals, respectively, which depend upon the coupling between orbitals on neighboring molecules and fluctuations thereof. The theory has been successfully applied, in a parameterized form, to the spectra of excess electrons in ethanol glass,<sup>1</sup> anthracene anions in glassy anthracene,<sup>1</sup> styrene and cyclooctatetraene anions,<sup>3</sup> NO<sub>2</sub> in several strongly interacting solvents,<sup>5</sup> and to the benzene iodine charge-transfer spectrum.<sup>2</sup> In the charge-transfer (CT) case, the zeroth-order contribution to the line shape was shown to be given by

$$I_R^{(0)}(\omega) = \frac{N_D}{Z_v} \sum_{v_A, \bar{v}_A, v_D, \bar{v}_D} e^{-\beta E_v^{00}} \times F_{\delta-\alpha}^2(v_A, \bar{v}_A, v_D, \bar{v}_D) \tau_{0D\delta, R\alpha}^2 G[\omega, \Delta E_{\delta-\alpha}(R) + \Delta E_v, \sigma_{DA}] \quad (1)$$

for a donor (D) at the origin and an acceptor (A) at  $\mathbf{R}$ .  $F_{\delta-\alpha}(V_A, \bar{V}_A, V_D, \bar{V}_D)$  is a product of the Franck-Condon factors for the ionization of the donor molecule to give the donor cation and the addition of an electron to an acceptor molecule to give the acceptor anion.  $\tau_{0D\delta, R\alpha}$  is the transition dipole between the donor molecular orbital  $\delta$  and the acceptor molecular orbital  $\alpha$ ,  $E_v^{00}$  is the initial vibrational energy of the unionized donor and acceptor,  $\Delta E_{\delta-\alpha}(R)$  and  $\Delta E_v$  are the electronic and vibrational excitation energies, respectively, and  $G[\omega, \omega', \sigma_{DA}]$  is a Gaussian of width  $\sigma_{DA}$  centered at  $\omega'$ . The inhomogeneous broadening constant,  $\sigma_{DA}$ , can be expressed in terms of fluctuations in the energy levels of

the donor and acceptor molecular orbitals as was shown in Ref. 1.

The first- and second-order parts of  $I(\omega)$  have been found in this laboratory to make negligible or small contributions to the line shape in the cases studied previously. In order to further clarify the importance of these terms, a study of the concentration dependence of the Mes:TCNE CT spectrum was undertaken. Since the donor for this complex is totally miscible in common inert solvents, and since the existence of a ternary complex involving two donor molecules has previously been reported,<sup>6</sup> it was hoped that by increasing the mesitylene concentration, the effects of coupling between orbitals on different donor molecules could be observed. In another attempt to search for such donor-donor orbital interactions, the spectrum of AN:CA was also recorded, but in a more limited concentration range.

It is important to note that Eq. (1) gives the absorption intensity for a fixed donor-acceptor separation  $R$ . However, an important reason for the experimental fact that typical CT spectra are very broad is that, due to the Coulombic interaction term in the excited state energy, the absorption frequency is strongly dependent on the donor-acceptor intermolecular distance. It has been found in this laboratory that, while Eq. (1) alone is sufficient to explain the width of spectra which arise from localized transitions in, for example, styrene and cyclooctatetraene anions, it is unable to fully account for the width of CT spectra. In order to model the homogeneous broadening brought about by intermolecular vibrational motion, a thermal average of the above intensity expression must be performed, using a Boltzmann weighting involving the ground-state donor-acceptor potential described here in terms of the harmonic force constant,  $k$ , for donor-acceptor stretching:

$$I(\omega) \propto \int_0^\infty R^2 \exp[-(\beta k/2)(R - R_{0q})^2] I_R(\omega) dR. \quad (2)$$

$R$  in this equation is the charge separation in the excited state, which is assumed to be equal to the donor-acceptor center-of-mass distance for the  $\pi$ - $\pi^*$  complexes Mes:TCNE and AN:CA.  $R_{0q}$  is the value of  $R$  corresponding to the equilibrium geometry of the donor-acceptor ground state, and  $\beta$  is  $(k_B T)^{-1}$ . The factor  $R^2$  results from Mulliken's approximation that, neglecting overlap, the electronic transition dipole is proportional

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to the distance through which the charge is transferred.<sup>7</sup> The force constant  $k$  is related to the donor-acceptor intermolecular stretching frequency  $\nu_{DA}$  according to  $k = 4\pi^2\mu\nu_{DA}$ , where  $\mu$  is the "reduced mass" calculated as if the complex were a diatomic molecule. The dependence of the excitation energy on charge separation is modeled, following earlier work,<sup>7(b),8</sup> by a Coulombic term in the expression for electronic energy:

$$\Delta E_{\delta-\alpha}(R) = (I. P._{\delta} - E. A._{\alpha} - e^2/R) + \frac{C}{(I. P._{\delta} - E. A._{\alpha} - e^2/R)} \quad (3)$$

In the above equation  $I. P._{\delta}$  is the ionization potential of the donor orbital  $\delta$ , and  $E. A._{\alpha}$  is the electron affinity of the acceptor orbital  $\alpha$ . In the Mulliken picture, the first term in parentheses is the zeroth-order energy difference between the no-bond and dative states, while the term inversely proportional to  $I. P._{\delta} - E. A._{\alpha} - e^2/R$  results from the interaction of the zeroth-order states. The constant  $C$  is obtained from a plot of experimental CT maxima vs ionization potentials for a given acceptor complexed with a series of donors. The second term is usually of the order of a few tenths of an eV, compared to the 2-4 eV which is contributed by the zeroth-order energy difference.

In the present paper, the theory described above is applied to the spectra of a fairly strong  $\pi-\pi^*$  complex (Mes : TCNE) and a weaker  $\pi-\pi^*$  complex (AN : CA). The extent to which the intramolecular Franck-Condon profiles, inhomogeneous broadening and donor-acceptor vibration contribute to the linewidth are discussed and compared to the case of the very weak Bz : I<sub>2</sub> complex. Evidence that the first- and second-order contributions to these spectra are negligible is presented. The question of whether the first or second ionization potential of benzene is involved in the CT transition is also discussed.

## II. EXPERIMENTAL

The solvents used in our work were spectrograde and, except for anthracene (which was obtained 99.9% pure), the donors and acceptors were purified prior to use. TCNE was purified by recrystallization from chlorobenzene and repeated sublimation. Mesitylene was converted to its sulfonic acid derivative and recrystallized

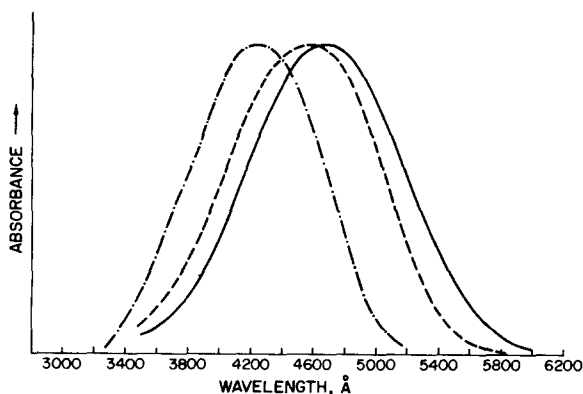


FIG. 1. - - - Gas phase Mes : TCNE (Ref. 9); - - - - -  $2.7 \times 10^{-4}$  M TCNE in mesitylene; —  $1.6 \times 10^{-2}$  M mesitylene,  $4.35 \times 10^{-3}$  M TCNE in  $\text{CH}_2\text{Cl}_2$ .

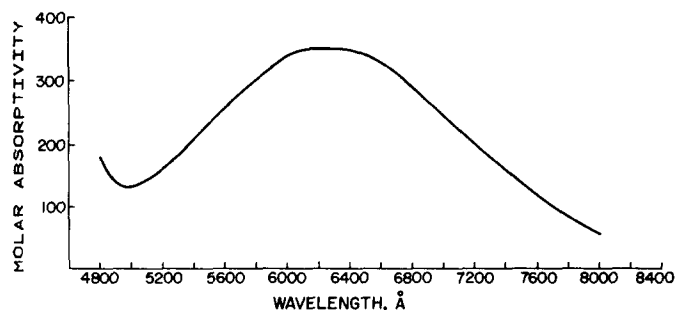


FIG. 2.  $5.6 \times 10^{-3}$  M anthracene and  $5.3 \times 10^{-3}$  M chloranil in  $\text{CH}_2\text{Cl}_2$ .

repeatedly from chloroform. Chloranil was recrystallized from chloroform and sublimed twice. The purity of the compounds was checked by taking UV and visible spectra. All spectra were recorded at room temperature on a Cary Model 14 spectrometer using 1.0 cm cells or 5.0 cm cells depending on the complex concentration. The solvent used was  $\text{CH}_2\text{Cl}_2$  for both Mes : TCNE and AN : CA.

The spectrum of Mes : TCNE in  $\text{CH}_2\text{Cl}_2$  was found to have a shape which is independent of concentration (when normalized to the same maximum absorbance) for donor concentrations in the range  $8 \times 10^{-3} - 1 \times 10^{-1}$  M and acceptor concentrations in the range  $3 \times 10^{-3} - 2 \times 10^{-2}$  M. The maxima in all the spectra occurred at 4670 Å. In neat mesitylene, the absorption maximum occurred at 4560 Å, a 0.06 eV blue shift with respect to the spectrum in  $\text{CH}_2\text{Cl}_2$ . Except for this expected solvent shift, the line shapes of the Mes : TCNE complex in  $\text{CH}_2\text{Cl}_2$  and in neat mesitylene are identical. When these spectra are plotted on an energy scale, it can also be seen that both sets of solution-phase spectra have the same line shape as the blue-shifted gas-phase spectrum.<sup>9</sup> These spectra are shown in Fig. 1. The lack of dependence of the line shape on donor concentration is taken as evidence that the coupling between the orbitals of neighboring donor molecules is negligible, in which case the zeroth-order contribution to  $I(\omega)$  should be sufficient to interpret the experimental spectrum.

Because of solubility problems, an exhaustive concentration study of the AN : CA system was not possible. Spectra were taken in  $\text{CH}_2\text{Cl}_2$  using donor and acceptor concentrations in the range  $3 \times 10^{-3} - 7 \times 10^{-3}$  M. A typical AN : CA spectrum is shown in Fig. 2. The shorter wavelength absorption which commences at  $\sim 5000$  Å is due to an intramolecular electronic transition of chloranil. This absorption tends to obscure the high-energy portion of the CT spectrum.

A few relevant physical and spectral properties of the complexes discussed in this work are summarized in Table I. Detailed analyses of the Mes : TCNE and AN : CA spectra are given in the following sections.

## III. IMPLEMENTATION OF THE THEORY

In order to apply our model to actual CT spectra it is necessary to make use of several experimentally available quantities which relate to factors arising in Eq. (1). In addition to the adiabatic donor ionization potential

TABLE I. Physical and spectral properties of Bz: I<sub>2</sub>, AN: CA, and Mes: TCNE.

Complex	$-\Delta H_f$ Kcal/mol	$K_{\text{eq}}$ l/mol	$h\nu_{\text{max}}$ eV	$\delta_{1/2}$ (half-width) eV
Bz: I <sub>2</sub> gas	2.0 <sup>a</sup>	4.5 <sup>a</sup>	4.6 <sup>a</sup>	...
solution	1.3 <sup>c</sup>	0.17 <sup>c</sup>	4.3 <sup>b</sup>	$\sim 0.7^b$
AN: CA gas	...	...	...	...
solution	3.26 <sup>d</sup>	3.16 <sup>e</sup>	2.0 <sup>f</sup>	0.65 <sup>f</sup>
Mes: TCNE gas	9.9 <sup>g</sup>	1020 <sup>g</sup>	2.9 <sup>g</sup>	0.7 <sup>g</sup>
solution	4.5 <sup>f</sup>	17.3 <sup>h</sup>	2.6 <sup>f</sup>	0.7 <sup>f</sup>

<sup>a</sup>F. T. Lang and R. L. Strong, J. Am. Chem. Soc. 87, 2345 (1965).

<sup>b</sup>Reference 24.

<sup>c</sup>L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc. 72, 4677 (1950).

<sup>d</sup>G. Briegleb, J. Czekalla, and G. Reuss, Z. Phys. Chem. Neue Folge 30, 333 (1961).

<sup>e</sup>S. K. Chakrabarti and S. Basu, Trans. Faraday Soc. 60, 465 (1964).

<sup>f</sup>This work.

<sup>g</sup>Reference 9.

<sup>h</sup>R. E. Merrifield and W. D. Phillips, J. Am. Chem. Soc. 80, 2778 (1958).

(I. P.) and acceptor electron affinity (E. A.), the Franck-Condon factors for the relevant ionization processes are required. For each of the donors, the Franck-Condon factors are obtained from the appropriate band in the photoelectron spectrum, and are given for anthracene and mesitylene in Refs. 10 and 11, respectively.<sup>12</sup> The Franck-Condon factors for the formation of acceptor anions are not directly available from experiment. They were calculated in this work within the simple harmonic oscillator approximation, employing experimental data on the anion and neutral acceptor geometries and vibrational frequencies. Vibronic analysis of the IR and Raman spectra of TCNE and TCNE<sup>-</sup><sup>13</sup> indicates that the carbon-carbon double bond stretching frequency decreases from 1570 to 1390 cm<sup>-1</sup> upon ionization. In addition, SCF calculations<sup>14</sup> predict that the main difference in the geometries of the molecule and the anion is the longer carbon-carbon double bond in the latter. The length of this bond is 1.34 Å in neutral TCNE and 1.41 Å in TCNE<sup>-</sup>.<sup>14(a)</sup> On the basis of this evidence, only the carbon-carbon double bond stretch was considered in calculating the Franck-Condon factors for the ionization of TCNE. The force constants used were taken from Ref. 13(a). In an analogous manner, the Franck-Condon factors for chloranil were calculated for two vibrational modes, one involving primarily the carbonyl bonds ( $a_g, \nu_1$ ) and the other composed mostly of a stretching of the carbon-carbon double-bonds ( $b_{2u}, \nu_{18}$ ). Again, vibrational spectra,<sup>15</sup> as well as x-ray analysis,<sup>16</sup> of both the molecule and the anion indicate that the potential surfaces of the other modes are displaced only slightly in frequency and coordinate. Force constants for the two "active" modes were taken from Ref. 15(b).

Unfortunately, the electron affinities of the two acceptors are only known to within several tenths of an eV. In fact, one method of obtaining vertical electron affinities makes use of Eq. (3) and a series of CT spectra in-

volving the same donor and a number of different acceptors, the unknown electron affinity being obtained from a plot of  $h\nu_{\text{max}}$  vs E. A. The experimental CT absorption maximum, however, is presumably related to the vertical ionization potentials and electron affinities, and since Eq. (1) treats the electronic and vibrational energy contributions separately, the adiabatic I. P. and E. A. must be used to compute  $\Delta E_{\delta-\alpha}$ . Photodetachment studies of TCNE<sup>-</sup><sup>14(a)</sup> indicate an adiabatic electron affinity of  $2.3 \pm 0.3$  eV. Polarographic techniques and magnetron studies yield an adiabatic electron affinity of chloranil of 2.4 to 2.5 eV,<sup>17</sup> while collisional ionization experiments result in a value of  $2.76 \pm 0.2$  eV.<sup>18</sup> These uncertainties in the electron affinity will influence our approximation of the electrostatic contribution to the excitation energy, modeled by  $e^2/R$ . In the calculations reported here, the equilibrium charge separation  $R_{\text{eq}}$  was used as an adjustable parameter to obtain the correct electronic energy difference, i. e., that which predicts the absorption maximum to be at the experimentally observed frequency. Hence, certain static solvation effects are contained within our model in the cation-anion equilibrium separation  $R_{\text{eq}}$ . Since the values of  $R_{\text{eq}}$  needed to fit the theory to the experiment are quite close to the expected van der Waals separations of two pi systems and to the interplanar distance in crystalline  $\pi-\pi^*$  complexes as determined by x-ray crystallography, ( $\sim 3.4$  Å), the electron affinities chosen for use here (see Table II) are probably quite reasonable.

It is also necessary to estimate the donor-acceptor stretching frequency,  $\nu_{\text{DA}}$ , in order to use Eq. (2) in a predictive manner. In the case of Mes:TCNE an experimentally observed low frequency IR absorption at 115 cm<sup>-1</sup> has been assigned to the intermolecular vibration.<sup>19</sup> This frequency was used to calculate an intermolecular force constant for Mes:TCNE in this work. The workers of Ref. 20 have observed fine structure with a spacing of 130 to 200 cm<sup>-1</sup> in the (presumably room temperature) CT spectrum of AN:CA in various solvents, and have attributed it to donor-acceptor vibration. Since this explanation, as well as the assignment of the 115 cm<sup>-1</sup> absorption of Mes:TCNE, is subject to some doubt,<sup>21</sup> a more extensive discussion of the donor-acceptor stretching frequency is in order.

The formation of a complex involving two nonlinear molecules entails the loss of three rotational and three translational degrees of freedom from each moiety. Six of these degrees of freedom become the translational and rotational degrees of freedom of the complex as a whole, while the remaining six evolve into new vibrational modes of the complex. All of these new modes

TABLE II. Parameters used in theoretical spectra.

Complex	I. P., eV	E. A., eV	$R_{\text{eq}}$ , Å	$\sigma_{\text{DA}}$ , eV	$\nu_{\text{DA}}$ , cm <sup>-1</sup>
Bz: I <sub>2</sub> 1st I. P.	9.2	2.4	5.0	0.15	35
2nd I. P.	11.9	2.4	2.5	0.05	100
AN: CA	7.47	2.45	4.07	0.09	30
Mes: TCNE gas	8.43	2.3	3.65	0.04	115
solution	8.43	2.3	3.35	0.04	115

TABLE III. Donor-acceptor stretching frequencies.

Complex	$k$ , dyn/cm [Eq. (4)]	$\nu_{DA}$ , $\text{cm}^{-1}$ $= (2\pi)^{-1} (k/\mu)^{1/2}$	$\nu_{DA}$ , $\text{cm}^{-1}$ experiment	$\nu_{DA}$ , $\text{cm}^{-1}$ theory
Bz: I <sub>2</sub>	0.2–2.0 × 10 <sup>4</sup> <sup>a</sup>	25–75 $\text{cm}^{-1}$	80–100 <sup>b</sup>	35 (1st I. P.) 100 (2nd I. P.)
AN: CA	1.1 × 10 <sup>4</sup>	40 $\text{cm}^{-1}$	130–200 <sup>c</sup>	30
Mes: TCNE	3.5 × 10 <sup>4</sup>	95 $\text{cm}^{-1}$	115 <sup>d</sup>	115 (not varied)

<sup>a</sup>Using  $\sigma_{LJ}$  in the range 6–2 Å.<sup>b</sup>Reference 22.<sup>c</sup>Reference 20.<sup>d</sup>Reference 19.

are expected to be of low frequency (since the intermolecular potential is weak), with one of them involving a diatomiclike donor-acceptor stretch. Due to the contribution of the CT state to the ground-state dipole moment, this vibration should be infrared active. Low frequency IR absorption has been observed for strong complexes between  $n$  donors and halogen acceptors,<sup>21</sup> and has been attributed to  $\nu_{DA}$ . For some weaker complexes such as Bz: I<sub>2</sub>, low frequency IR absorption has also been observed,<sup>22</sup> but the nature of the transition responsible for the absorption is questionable since it is not certain that the vibrational motion of the more short-lived Bz: I<sub>2</sub> species could be observed on the time scale of an IR experiment. (See Refs. 21 and 2 for a discussion.) One way of obtaining an independent estimate of the order of magnitude of  $\nu_{DA}$  is to calculate the intermolecular stretching force constant  $k$  as the second derivative of the Lennard-Jones potential of the donor-acceptor pair, evaluated at the potential energy minimum,

$$k = 57.1(\epsilon/\sigma_{LJ}^2). \quad (4)$$

The well-depth  $\epsilon$  can be estimated from the heat of formation of the complex, and  $\sigma_{LJ}$  can be approximated as the intermolecular distance which minimizes the ground-state donor-acceptor potential energy,  $R_{eq}$ . (Strictly speaking,  $R_{eq} = 2^{1/6}\sigma_{LJ} \approx 1.12\sigma_{LJ}$ .) As discussed in Ref. 2, Eq. (4) has been shown to give reasonable agreement with experimentally available force constants for strong complexes, and can hopefully be used to predict  $\nu_{DA}$  when experimental information is lacking or questionable. Table III compares values of  $\nu_{DA}$  interpreted from the experimental results discussed above with those found using Eq. (4) and those used to generate an opti-

mum fit of our model to the experimental CT spectrum.

The final quantity needed to calculate the CT spectra, the inhomogeneous broadening constant  $\sigma_{DA}$ , is truly an adjustable parameter about which no independent experimental information is available. Since the experimental CT spectra are structureless,  $\sigma_{DA}$  must be at least large enough to smooth out the structure that would otherwise result from the Franck-Condon profiles. Previous studies on a variety of systems<sup>1–3</sup> have yielded  $\sigma_{DA}$  values in the range 0.02–0.09 eV, with smaller values arising for low-temperature spectra. Qualitatively, since  $\sigma_{DA}$  depends on fluctuations in the orbital energy levels caused by fluctuations in the solvent molecules' coordinates,  $\sigma_{DA}$  is expected to increase with temperature.

Having discussed the choices of the quantities needed to calculate the CT spectra, we now move on to present the results of applying our model to Mes: TCNE, AN: CA, and Bz: I<sub>2</sub>.

#### IV. RESULTS AND DISCUSSION

Figures 3–8 compare our theoretical and experimental spectra. The intramolecular Franck-Condon profiles have been included as "stick spectra" in Figs. 5–8 for comparison. The quantities used to calculate the theoretical line shapes are shown in Table II.

##### A. Mes: TCNE

Both solution-phase (Fig. 3) and gas-phase (Fig. 4) Mes: TCNE spectra were calculated and compared to the experimental spectra; the only parameter which differed in these two cases was  $R_{eq}$ , which, as mentioned earlier,

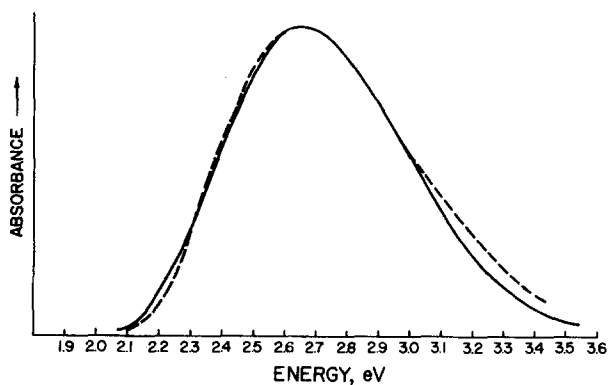


FIG. 3. Mes: TCNE, solution phase: — experimental spectrum; ---- theoretical spectrum.

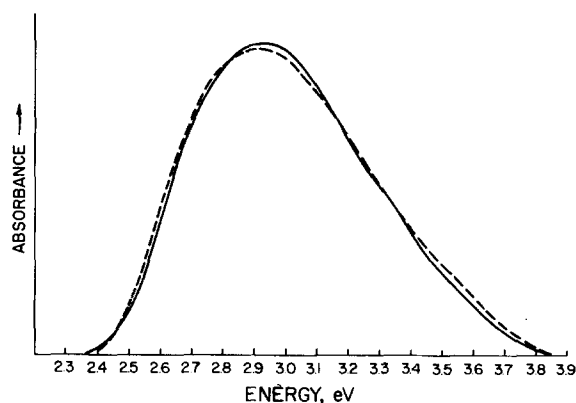


FIG. 4. Mes: TCNE, gas phase: — experimental spectrum; ---- theoretical spectrum.

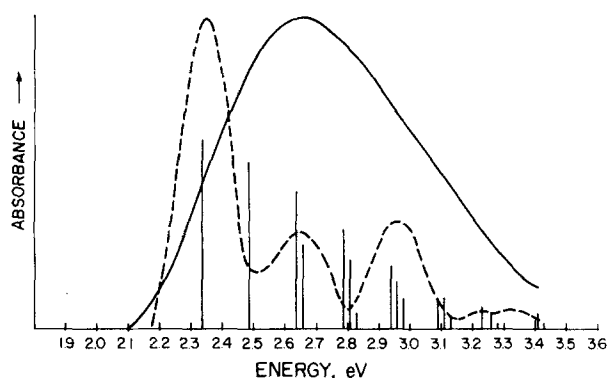


FIG. 5. Mes:TCNE, solution phase: — theoretical spectrum; ---- theoretical spectrum calculated with  $\sigma_{DA} = 0$ .

contains some static solvation effects in the ionic excited state energy. The value of  $\nu_{DA}$  was taken from the experimental IR spectrum to be  $115 \text{ cm}^{-1}$ . Since the Lennard-Jones estimate Eq. (4) was in good agreement with the experimental results, this value was not adjusted. The fact that the line shapes of the gas- and solution-phase spectra are virtually the same is reflected in the use of the same value of  $\sigma_{DA}$ . The smaller solution-phase value of  $R_{eq}$  is expected on the basis of the compressibility of the weak CT bond and is in line with the accepted explanation of solvent-vapor shifts and pressure effects of CT spectra.<sup>23</sup>

### B. AN:CA

The results of fitting the AN:CA spectrum tend to predict a rather small ( $\sim 30 \text{ cm}^{-1}$ ) value of  $\nu_{DA}$  for this complex, in contrast to the larger value ( $\sim 150 \text{ cm}^{-1}$ ) which derives from the structure observed in the spectra reported in Ref. 20. The smaller value, needed to fit our theory to the experiment, is more in line with the Lennard-Jones estimate (see Table III), and seems reasonable in view of the weak nature of the intermolecular attractions in this complex. Since the density of peaks in the Franck-Condon progression is small for this complex, a somewhat larger value of  $\sigma_{DA}$  (0.09 eV) was required to obtain a smooth spectrum.

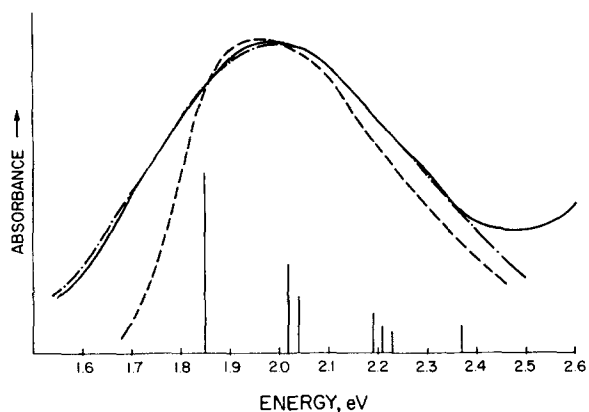


FIG. 6. AN:CA, solution phase: — experimental; - - - theoretical spectrum; ---- theoretical spectrum calculated at fixed  $R$ , using Eq. (1).

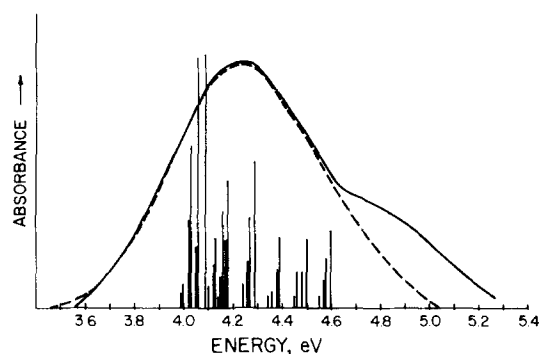


FIG. 7. Bz: $I_2$ , using first ionization potential: — experimental; ---- theoretical.

### C. Bz: $I_2$

The spectrum of the Bz: $I_2$  complex was also reinvestigated in our laboratory, and two sets of parameters, involving use of the first and second ionization potentials, respectively, are obtained. Use of the first I.P. instead of the second requires a larger value of  $R_{eq}$  (to obtain the correct value of  $h\nu_{max}$ ) and a larger  $\sigma_{DA}$  and smaller  $\nu_{DA}$  (to obtain a broad enough spectrum). Since the equilibrium geometry of the complex is unknown, it is not possible to say which of the two values of  $R_{eq}$  (2.5 or 5.0 Å) is more reasonable, especially since the charge separation here need not be nearly equal to the donor-acceptor center-of-mass distance. The value of  $\sigma_{DA}$  (0.15 eV) used to fit the spectrum assuming the first ionization potential is somewhat larger than the minimum value needed to obtain a structureless theoretical spectrum. This larger value of  $\sigma_{DA}$  (along with the smaller value of  $\nu_{DA}$ ) is required because the width of the Franck-Condon profile is much smaller for the first ionization of benzene than for the second. The value of  $\sigma_{DA}$  used to fit the spectrum using the second I.P. is 0.05 eV, which is closer to values of  $\sigma_{DA}$  used in our previous studies. The two different values of  $\nu_{DA}$  (30 and  $100 \text{ cm}^{-1}$  for the first and second I.P., respectively) are within the range of values predicted using Eq. (4) with values of  $\sigma_{LJ}$  between 2 and 6 Å. The larger value of  $R_{eq}$ , which gives rise to a smaller value of the donor-acceptor stretching force constant  $k$ , is more in line with the trends in donor-acceptor attractive forces as reflected in the  $\Delta H_f$  values of Table I. However, since the geometry of the complex is uncertain, our

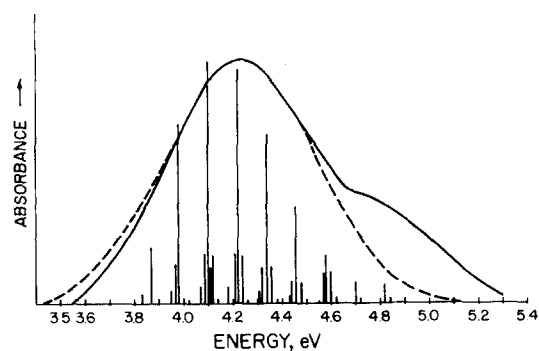


FIG. 8. Bz: $I_2$ , using second ionization potential: — experimental; ---- theoretical.

TABLE IV. Contribution of intra- and intermolecular vibrations to linewidth.

Complex	Intramolecular (FC profile)	Intermolecular ( $\nu_{DA}$ )	Experimental linewidth (see text)
Bz: I <sub>2</sub> (1st I. P.)	0.6 eV	0.49 eV	~1.8 eV
(2nd I. P.)	1.0 eV	0.35 eV	
AN: CA	0.7 eV	0.47 eV	~1.1 eV
Mes: TCNE	1.1 eV	0.24 (gas) 0.23 (soln.)	1.4 eV

ability to predict  $\nu_{DA}$  here is lessened, and it is not possible to easily distinguish which fit to the Bz: I<sub>2</sub> spectrum is more reasonable on the basis of the two different values of  $\nu_{DA}$  obtained.

*Comparison of the spectra.* The relative importance of the various factors which determine the shape and width of the above CT spectra varies with each complex. The Franck-Condon (FC) profiles resulting from intramolecular vibration are included in Figs. 5–8. Two different FC profiles for Bz: I<sub>2</sub>, involving the first and second ionization potential, are shown in Figs. 7 and 8, respectively. It can be seen that the width of the spectrum of Mes: TCNE is determined primarily by the Franck-Condon envelope, whereas the breadth of the spectrum of the more loosely-bound AN: CA complex depends strongly on the effects of intermolecular vibration. This is to be expected on the basis of the fact that the force constant of the CT bond is larger (Table III) and the intermolecular bonding stronger (Table I) in Mes: TCNE than in AN: CA. In the case of Bz: I<sub>2</sub>, the importance of donor-acceptor vibration depends on which benzene orbital is assumed to be involved in the CT transition. As discussed earlier, the more narrow FC profile of the first ionization potential requires the use of a smaller value of  $\nu_{DA}$  (see Table II) in order to obtain a broad enough spectrum.

In order to make a more quantitative comparison of the contribution of intramolecular vibration vs intermolecular vibration to the spectral width, the difference in the excited state Coulombic energy at the thermally accessible turning points  $[(e^2/R_{\min}) - (e^2/R_{\max})]$  of the ground-state potential energy curves are calculated, assuming a harmonic potential,  $V = \frac{1}{2}k(R - R_{eq})^2$ , at room temperature  $k_B T = 0.025$  eV (except for gas-phase Mes: TCNE where  $k_B T \sim 0.035$  eV). This intermolecular vibrational contribution is compared to the width of the FC profile and to the experimental linewidth in Table IV. The word "linewidth" in this case is used to indicate the full energy range of absorption, and not the width at half-height as is usually implied. It is seen that the full spectral widths are accounted for rather well by the sum of the widths of the FC profile, the intermolecular contributions and twice the inhomogeneous broadening  $\sigma_{DA}$ .

In addition to spectral width, the overall shape of the calculated spectrum depends in different ways on the homogeneous as well as inhomogeneous broadening factors. Experimentally, CT spectra are often skewed

toward the high energy side. This asymmetry can arise from both the Franck-Condon profile and the factor  $R^2$  in Eq. (2). The factor  $R^2$  is only a model for the actual dependence of the CT electronic transition dipole on charge separation: A model which is based on the approximation that the overlap of the donor and acceptor molecular orbitals is zero. Since nonzero (*albeit* small) overlap is required for complex stabilization, this approximation is used for convenience sake only. It is reasonable however, to expect the CT transition moment to increase with increasing charge separation over a limited range of  $R$  values, and since increasing the charge separation destabilizes the (predominantly ionic) excited state, the result is a larger half-width on the high energy side of the absorption maximum.

The FC profile and inhomogeneous broadening also affect the calculated shape of the spectrum. For example, in the limit of zero inhomogeneous broadening ( $\sigma_{DA} = 0$ ), the Mes: TCNE spectrum has structure and peaks at too low an energy, even after the thermal averaging over  $R$  is performed (see Fig. 5). The higher density of peaks in the high energy region of the stick spectrum of the FC profile helps to shift the maximum of  $I(\omega)$  toward higher energy when a nonzero  $\sigma_{DA}$  ( $= 0.04$  eV) is included in the calculation. Thus, in analyzing the FC contribution to the line shape, one must take into consideration not just the amplitudes of the individual FC "sticks," but also, the density of sticks in a given energy range.

In the case of AN: CA, the FC profile has a lower density of peaks, and a large value of  $\sigma_{DA}$  ( $= 0.09$  eV) is therefore required to obtain a structureless spectrum. The effect of intermolecular vibration for this more weakly bound complex provides the dominant factor in determining the spectra symmetry, as well as sufficient width. Inspection of the FC profiles in Figs. 7 and 8 reveals why different parameters must be used for Bz: I<sub>2</sub>, depending on which ionization potential is assumed to be involved in the CT absorption. In both cases the stick spectrum alone peaks at too low an energy. The value of  $\sigma_{DA}$  (0.15 eV) used to fit the spectrum when the first ionization potential is used is larger than the minimum value needed to obtain a structureless spectrum. This larger value of the inhomogeneous broadening constant is needed to compensate for the more narrow FC envelope without using a value of  $\nu_{DA}$  smaller than the lower bound to the Lennard-Jones estimate (see Table III). In the absence of any other information, a value of  $\sigma_{DA} = 0.15$  eV seems somewhat large, but it may be that this large value is required in order to compensate for a poor model of the intermolecular motion. For example, the Bz: I<sub>2</sub> complex may have many possible orientations in solution, and a simple one-dimensional model for intermolecular stretching would ignore other degrees of freedom which could contribute to line broadening. The unusually large value of  $\sigma_{DA}$  may, therefore, contain the effects of these other degrees of freedom. In support of this assignment, we point out that this value of  $\sigma_{DA}$  gives a quite consistent total linewidth when combined with FC and intermolecular motion factors. Assuming that the second ionization potential is involved, the shape and width of the FC profile do a better job of accounting

for the observed spectrum; hence a smaller value of  $\sigma_{DA}$  and larger value of  $\nu_{DA}$  are required to obtain an optimum description of the experimental line shape. The shoulder in the high energy region is not accounted for in either case, and remains an unsolved problem.

When  $\nu_{DA}$  is not known with certainty and both  $\nu_{DA}$  and  $\sigma_{DA}$  must be adjusted to fit the spectrum, the question of whether the final values for the two parameters are unique should be addressed. Of course, a lower bound to  $\sigma_{DA}$  is the value which is required to calculate a smooth, structureless spectrum, and  $\nu_{DA}$  can be estimated as discussed in Sec. III. In addition, one can compare the values of  $\sigma_{DA}$  used in this work with those previously obtained for spectra of *localized* transitions,<sup>1,3,5</sup> where intermolecular vibration is not considered. Since the values of  $\sigma_{DA}$  used in this work are comparable to those of earlier calculations (0.02–0.09 eV), the final values of  $\sigma_{DA}$  and  $\nu_{DA}$  are probably reasonable.

A source of inaccuracy that must be considered is the calculation of the Franck–Condon factors for the ionization of the acceptors. For TCNE/TCNE<sup>-</sup> and CA/CA<sup>-</sup>, the simple harmonic oscillator approximation is probably reasonable, since the frequency and coordinate changes upon ionization are such that only the low-lying vibrational states ( $v=0, 1$ ) of the active modes of the anion contribute significantly to the Franck–Condon profile. For  $I_2/I_2^-$ , however, the changes in bond length and in frequency are more drastic (see Ref. 2), and much higher vibrational states of the anion are excited. In this case the anharmonicity is sure to cause the simple harmonic oscillator approximation to fail. As discussed above, the height as well as density of peaks in the stick spectrum can influence the final shape of the spectrum. Anharmonicity in the  $I_2^-$  potential would give rise to a higher density of FC peaks at higher frequencies, and could contribute to at least part of the high energy shoulder observed in the Bz : I<sub>2</sub> CT spectrum.

The inability of the model presented here to distinguish which benzene ionization is involved in the CT transition would seem to indicate some inadequacy of the model. It should be pointed out, however, that the Mes : TCNE and an AN : CA spectra can be interpreted quite easily using the available experimental data and reasonable values of  $\sigma_{DA}$  and  $\nu_{DA}$ .

It is our feeling that the model presented here is likely to be most successful for stronger complexes. For those weak complexes in which the intermolecular motion ( $\nu_{DA}$ ) dominates the determination of the line shape, our model cannot be used to determine anything about the FC profile of the participating ionization process.

As mentioned earlier, one difficulty with our fit to the Bz : I<sub>2</sub> spectrum is our inability to account for the shoulder in the high-energy region. This shoulder has been observed by the workers in Ref. 24, who subtracted out the absorption due to free benzene, and in our laboratory, where a reference cell with two compartments was used to automatically subtract the free benzene and iodine absorptions. It is not known whether this shoulder absorption is an electronic transition of the complex, or an intramolecular benzene transition which is normally

forbidden under the higher symmetry of the free molecule. It is also possible that the anharmonicity of the  $I_2^-$  potential surface could give rise to a higher density of sticks in the Franck–Condon profile at higher energy, due to the excitation of closely-spaced vibrational levels of  $I_2^-$ . Such an effect could conceivably give rise to the observed shoulder in the high frequency wing of the CT spectrum.

In summary, it has been found that the theoretical formalism exploited here is probably most useful for interpreting the spectra of strong complexes. The Bz : I<sub>2</sub> complex may in fact be so loosely bound that it is not possible to account for the homogeneous broadening in terms of a simple one-dimensional stretching motion ( $\nu_{DA}$ ). A variety of different intermolecular geometries are probably sampled, and the resulting potential surface would necessarily be more complicated. As a result, the broadening attributed to the intermolecular vibration is probably underestimated by such a one-dimensional harmonic oscillator model. For this reason it is likely that the unusually large value of  $\sigma_{DA}$  arising in the fitting of the Bz : I<sub>2</sub> spectrum also contains the effect of other unaccounted for intermolecular motions. The one-dimensional model is more appropriate to the treatment of the spectra of the more tightly bound  $\pi$ – $\pi^*$  complexes, AN : CA and Mes : TCNE. Since the most favorable geometry of a  $\pi$ – $\pi^*$  complex predicts that the plane of the donor molecule be parallel to that of the acceptor, it is likely that the other low frequency modes of these complexes (e.g., ring twisting and bending) do not perturb the charge separation as greatly as the donor–acceptor stretch. Hence our description of the homogeneous broadening in terms of one-dimensional intermolecular motion is more likely a good one for these complexes. The most favorable example of the adequacy of the model arises in the case of Mes : TCNE, where a good fit to experiment was obtained with a minimum number of adjustable parameters. The AN : CA spectrum is slightly more uncertain, due to lack of knowledge concerning  $\nu_{DA}$ . In spite of the fact that the Bz : I<sub>2</sub> complex has been extensively studied, there is not enough experimental data to say whether or not the theoretical formalism presented here is appropriate to the interpretation of the spectrum of this complex. The fact that equally good “fits” of the observed experimental spectrum can be obtained by using either the first or second ionization potentials of benzene indicates that our model is not ideally suited to such weak complexes.

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