THE THEORY OF CHARGE-TRANSFER SPECTRA

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WHEN solutions of chloranil (yellow) and hexamethylbenzene (colourless) are mixed together an intensely red solution is obtained. The optical density of this solution, at 5000 Å, is proportional to the product of the concentrations of the two components, and it is therefore deduced that the red colour is due to the absorption of light by a 1:1 complex.[1] In crystals of these "quinhydrone-like" complexes, the two components are stacked one upon the other in parallel planes,[2,3] and Nakamoto[3] has shown that the red colour is due primarily to the absorption of light which is polarised in a plane perpendicular to the planes of the aromatic rings. This is in contrast to the strong absorption of the separate components which takes place when the light is polarised in the plane of the aromatic rings.

Many molecular complexes of the above type can be formed between two components, one of which is an electron donor (D), and the other an electron acceptor (A). It is now generally accepted that the intense colour of these complexes is to be associated with the transfer of an electron from the donor to the acceptor. Mulliken was the first to put this idea into the language of quantum chemistry.[4] He considered the interaction of a no-bond ground state $\psi(D,A)$, and a polar excited state $\psi(D^+\text{–}A^-)$, to produce a stabilised ground state having a wave function

$$\psi_0 = \psi(D,A) + \lambda\psi(D^+\text{–}A^-),$$

and an excited state, the charge-transfer state,

$$\psi_1 = \psi(D^+\text{–}A^-) + \mu\psi(D,A).$$

λ and μ will in most cases be small compared with unity. The charge-transfer band is associated with the electronic transition $\psi_0 \rightarrow \psi_1$, and occurs at the frequency $\nu = (E_1 - E_2)/h$, where h is Planck's constant.

The term charge-transfer absorption may be used whenever there is a large electron displacement in going from the ground to the excited state. Thus, as well as for the quinhydrone complexes, charge-transfer bands have been postulated for hydrated inorganic ions, of the type

$$Cl^-(H_2O)_n \rightarrow Cl(H_2O)_n^-$$
$$Fe^{2+}(H_2O)_n \rightarrow Fe^{3+}(H_2O)_n^-$$
$$Fe^{3+}OH^- \rightarrow Fe^{2+}OH$$

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[1] Michaelis and Grannick, *J. Amer. Chem. Soc.*, 1944, **66**, 1023.

[2] Anderson, *Nature*, 1937, **140**, 583.

[3] Nakamoto, *J. Amer. Chem. Soc.*, 1952, **74**, 1739.

[4] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600; 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801.

and for the alkali halides in both the gaseous and the crystalline state, *e.g.*, $Na^+Cl^- \rightarrow NaCl$. In addition, one can observe intramolecular charge-transfer absorption in substituted organic molecules of the types (1) and (2), and in transition metal complexes.[4a]

(1)

(2)

Earlier reviews[5] have discussed charge-transfer absorption for molecular complexes and inorganic ions. It is the present purpose to expound the theoretical interpretation of charge-transfer spectra in general, both inter- and intra-molecular, including the most recent work in this field. The emphasis will be on the nature of the charge-transfer absorption rather than on the charge-transfer stabilisation of the ground state. Only the spin-allowed transitions, which give rise to the intense absorption bands, will be considered. The energy and intensity of the absorption will first be discussed separately, in general terms, and then the mathematics will be examined in detail.

The Energy of the Charge-transfer Band.—The energy of the electronic transition $(D,A) \rightarrow (D^+–A^-)$ is given to a first approximation by the expression, $I_D - E_A - C$, where I_D is the ionisation potential of the donor, E_A the electron affinity of the acceptor, and C the mutual electrostatic energy of D^+ and A^- relative to that of D and A. For example, Hassel[6] has shown that in crystals of the benzene–Br_2 complex, the Br_2 lies perpendicular to the plane of the benzene ring, the complex having C_{6v} symmetry. Benzene is the donor in this case: its vertical ionisation potential is 9·24 ev (1 ev = 8068 cm.$^{-1}$).[7] The distance from the nearest bromine atom to the centre of the benzene ring is 3·36 Å; the Br–Br bond length is 2·28 Å. Assuming that the donated electron goes into an orbital centred equally on the two bromine atoms, and that the hole it leaves behind is distributed over the six carbon atoms of the benzene ring, we calculate a coulombic energy of 3·22 ev for the complex. Unfortunately the electron affinity of Br_2 is unknown, although it is said to be positive.[8] What we require is in fact the vertical electron affinity, that is, the electron affinity calculated for the same internuclear distance as in the neutral molecule. It probably lies between 0 and 2 ev. From the formula given above, we then calculate that the charge-transfer band should occur somewhere

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[4a] Jørgensen, *Mol. Phys.*, 1959, **2**, 309.

[5] Rabinowitch, *Rev. Mod. Phys.*, 1942, **14**, 112; Andrews, *Chem. Rev.*, 1954, **54**, 713; Orgel, *Quart. Rev.*, 1954, **8**, 422; McGlynn, *Chem. Rev.*, 1958, **58**, 1113.

[6] Hassel, *Mol. Phys.*, 1958, **1**, 241.

[7] Watanabe, *J. Chem. Phys.*, 1954, **22**, 1564.

[8] Massey, "Negative Ions," Cambridge Univ. Press, 1950.

between 4 and 6 ev, depending on the value for $E(Br_2)$. It is, in fact, observed[9] at 4·24 ev. This value would be obtained by using an electron affinity for Br_2 of 1·78 ev: if more direct methods fail, electron affinities can perhaps be obtained from charge-transfer spectra.

It can be seen from the above calculation that the electrostatic contribution to the charge-transfer energy is by no means unimportant. Thus an electron and a positive hole separated by 1 Å have a mutual energy of 14·4 ev. If the donor and the acceptor approach near enough to each other, then the charge-transfer state $(D^+–A^-)$ could have a lower energy than (D,A) even though $I_D - E_A$ is positive. This situation arises for the alkali halides. For the states NaCl and Na^+Cl^- in the gas phase, we have $I(Na) = 5{\cdot}14$, $E(Cl) = 3{\cdot}82$, and $C(2{\cdot}36\text{ Å}) = 6{\cdot}10$ ev. It follows that the ionic state has the lower energy, and the charge-transfer band arising from the transition to the covalent state should occur at 4·78 ev: it appears,[10] in fact, at 5·14 ev.

If only one component of the complex carries a charge, and if this charge is just redistributed in going from the ground to the excited state, then the coulombic term will be zero. This will be the case for the hydrated inorganic anions. For $Cl^-(H_2O)_n$, there will be some small contribution to the charge-transfer energy arising from the different polarisation energy of the H_2O in the field of the Cl^-, compared with that of Cl in the field of H_2O^-. This can probably be neglected.

Dainton[11] has shown that the energy of the charge-transfer band of the bivalent transition-metal ions is linearly related to the redox potential of the system, $M^{2+} \rightleftharpoons M^{3+} + e$. This suggests that the charge-transfer is to be associated with the transition, $M^{2+}(H_2O)_n \rightarrow M^{3+}(H_2O)_n^-$, rather than to $M^{2+}(H_2O)_n \rightarrow M^+(H_2O)_n^+$. Again it is probably the coulombic energy which swings the balance between these two processes, being about + 7 ev when the metal acts as donor, and — 7 ev when the water acts as donor.

For intramolecular charge-transfer, the quantities I_D and E_A of the two parts of the molecule have to be estimated from the values obtained for related molecules. For example, in aniline we might take $I(NH_2–)$ equal to the ionisation potential of ammonia[12] (10·15 ev), and $E(Ph–)$ equal to the electron affinity of benzene[13] (—1·63 ev). There will be a small error here, because the NH_2– group is more or less planar, but NH_3 is not. The coulombic energies associated with intramolecular charge transfer are often greater than those in the intermolecular case, since the donor and the acceptor are closer together, being joined by a covalent bond.

In the case of aniline there are two degenerate orbitals of the phenyl

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[9] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1950, **72**, 4677.

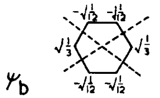
[10] Franck, Kuhn, and Rollefson, *Z. Physik*, 1927, **43**, 155; Miller and Wynne-Jones, *J.*, 1959, 1375.

[11] Dainton, *J.*, 1952, 1533.

[12] Watanabe, *J. Chem. Phys.*, 1957, **26**, 543.

[13] Hedges and Matsen, *J. Chem. Phys.* 1958, **28**, 950.

group which can accept the electron (the orbitals being taken to be the same as those of benzene). They have the symmetries shown in (3) and (4).



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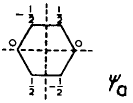
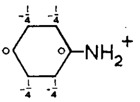
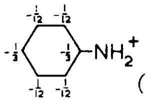


(4)

The coefficients represent the contribution of the six carbon $2p\pi$ atomic orbitals to the molecular orbital. It is now seen that taking an electron from the non-bonding π-orbital of the NH_2 group (ϕ), and putting it into the vacant benzene orbitals, gives rise to two charge-transfer states, which we might represent[14] by $\phi^{-1}\psi_a$ and $\phi^{-1}\psi_b$. However, although the orbitals ψ_a and ψ_b are degenerate, the two charge-transfer states are not. They have different coulombic energies associated with them. Thus $\phi^{-1}\psi_a$ has a charge density as in (5) (obtained by squaring the coefficients),

(5)

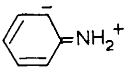




(6)

for which the attraction of the positive and negative charges gives an energy of 4·84 ev, whilst $\phi^{-1}\psi_b$ has a charge density as in (6) and an associated coulombic energy of 6·03 ev. From the formula $I - E - C$, we now calculate that $\phi^{-1}\psi_a$ has an energy 1·94, and $\phi^{-1}\psi_b$ an energy of 5·75 ev. The lowest excited state of benzene is at 4·71 ev, and we therefore expect to find this same state in aniline but somewhat perturbed by the NH_2 group: it is found at 4·31 ev. However, the second excited state of aniline should correspond to the charge-transfer state $\phi^{-1}\psi_b$: it appears at 5·27 ev. The second charge-transfer state $\phi^{-1}\psi_a$ cannot be clearly distinguished as it would appear in the same region as the higher excited states of benzene.

The charge densities of the excited states of aniline which have been discussed above are those obtained by using the molecular orbitals of the benzene ring. From the valence-bond theory rather different charge-transfer states are considered, namely, those associated with the familiar "resonance" structures (7—9). If these are used we predict that the donated



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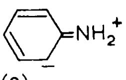

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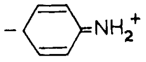

(9)

electron can appear either in the *ortho-* or the *para-* but not in the *meth-* position. This might be a good approximation to describe the electron density in the ground state, but evidence from the effect of acid on the spectra of aminoazo-compounds suggests that the electron densities in

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[14] Murrell, *Proc. Phys. Soc.*, 1955, **68**, *A*, 969.

the excited states are better represented by the molecular-orbital structures.[15]

The importance of the coulombic contribution to intramolecular charge-transfer absorption is illustrated by the aromatic nitro-amines. For these molecules the compounds in which the amino- and the nitro-groups are in *ortho*-relation absorb at considerably longer wavelengths than do the other isomers. It is tempting to attribute this to some subtle internal hydrogen-bond effect, but probably it is just that in the first excited state, where the nitro-group has gained an electron and the amino-group has lost an electron, the two charges are closer together for the *ortho*-compounds than for their isomers.

For a series of molecular complexes involving different electron donors and the same electron acceptor, it has been shown[16] that there is a reasonable linear correlation between the ionisation potential of the donor and the frequency of the charge-transfer band. This can be seen from Fig. 1, which records the charge-transfer band for a number of I_2 complexes.

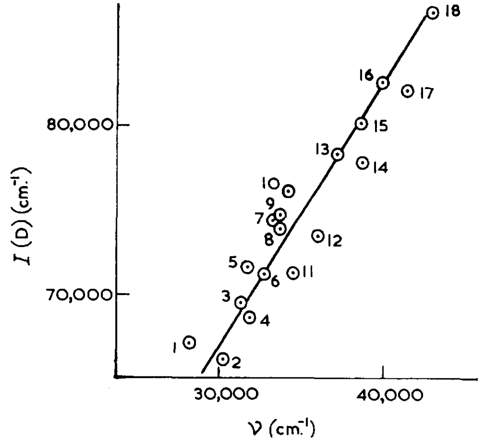

FIG. 1. *The relation between the ionisation potential of the donor and the frequency* (ν) *of the charge-transfer band for some iodine complexes.*[8]

1, Naphthalene.
2, Mesitylene.
3, *o*-Xylene.
4, *p*-Xylene.
5, 2-Methylbutadiene.
6, Toluene.
7, Cyclohexane.
8, *trans*-But-2-ene.
9, Benzene.
10, *cis*-But-2-ene.
11, Chlorobenzene.
12, Butadiene.
13, Propene.
14, *cis*-Dichloroethylene.
15, *trans*-Dichloroethylene.
16, Diethyl ether.
17, Cyclopropane.
18, t-Butyl alcohol.

The expression $I - E - C$ is only a crude approximation to the energy of the charge-transfer state, the same order of approximation as saying that ψ(D,A) and ψ(D^{+}–A^{-}) represent the wave functions of the ground and the charge-transfer state of the molecule or complex. If there is some overlap of donor and acceptor orbitals there is some "mixing" of these

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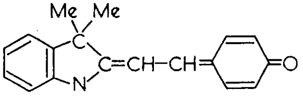
[15] Murrell, *J.*, 1959, 296.

[16] McConnell, Ham, and Platt, *J. Chem. Phys.*, 1953, **21**, 66; Hastings, Franklin, Schiller, and Matsen, *J. Amer. Chem. Soc.*, 1953, **75**, 2900.

two states, with resulting stabilisation of the ground state and destabilisation of the excited state. The energy of the charge-transfer band is increased by both effects. A necessary criterion for observing a charge-transfer band in the accessible region of the spectrum appears to be that the interaction between $\psi(\mathrm{D,A})$ and $\psi(\mathrm{D^+A^-})$ be not too large. Thus one might expect at first sight to observe a charge-transfer band for $\mathrm{BF_3{-}NH_3}$ [$I(\mathrm{NH_3}) = 10{\cdot}5$, $E(\mathrm{BF_3})$[17] $= 2$, $C(1{\cdot}6\ \text{Å}) = 9$ ev], somewhere in the visible or near infrared region of the spectrum. In fact one gets no absorption below 2300 Å, at which point the $\mathrm{NH_3}$ group itself starts to absorb. The reason would appear to be that $\psi(\mathrm{DA})$ and $\psi(\mathrm{D^+A^-})$ interact too strongly owing to the large overlap between the donor and the acceptor orbitals. The stabilisation of the complex is experimentally about 2 ev. A theoretical expression has been proposed by Hastings *et al.*[16] to cover these strongly interacting cases.

Since the ground and the charge-transfer state have very different electron distributions, it is to be expected that changing the dielectric constant or polarity of the surrounding medium should have an effect on the energy of the charge-transfer band. A polar solvent will stabilise $\mathrm{D^+{-}A^-}$ relative to DA. There appears to have been no experimental work carried out to examine this point for molecular complexes, but the effect is observed among Brooker's dyes.[18,19] The merocyanine dye shown below has two low-energy structures (10) and (11). In pure pyridine this dye has its first absorption band at $\lambda_{\max.} = 540$ mμ. When successive amounts of water are added there are shifts, first to longer wavelengths and then back to shorter wavelengths (see Table 1). The interpretation[19] of this type of behaviour is that in pyridine the quinonoid is more stable than the ionic form, but that on addition of water the ionic form is relatively more stabilised. The two structures have about the same energy with 1:1 solvent mixtures; in water-rich solvents the ionic form is the more stable.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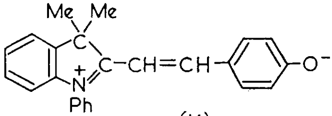
(11)

TABLE 1. *The effect of polarity of the solvent on the wavelength of a typical merocyanine dye.*

Pyridine (vol. %)	100	95	90	80	70	60
$\lambda_{\max.}$(mμ)	540	548	552	554	554	556
Pyridine (vol. %)	50	40	30	20	10	5
$\lambda_{\max.}$(mμ)	554	554	553	552	548	545

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[17] Savard and Simons, *J. Chem. Phys.*, 1939, **7**, 2.
[18] Brooker and Keyes, *J. Amer. Chem. Soc.*, 1951, **73**, 5356.
[19] Platt, *J. Chem. Phys.*, 1956, **25**, 80.

The interaction between the ionic and the quinonoid forms prevents the frequency of the charge-transfer band from becoming zero at the crossing point.

The Intensity of Charge-transfer Bands.—The integrated intensity of an absorption band, the oscillator strength, is given theoretically by

$$f = (1{\cdot}085 \times 10^{11})\, M_{01}{}^2 \nu_{01},$$

where ν_{01} is the frequency in cm.$^{-1}$, and M_{01} the transition moment, is given by

$$M_{01} = \mathrm{e} \int \ldots \int \psi_0 (\sum_{i=1}^{n} \boldsymbol{r}_i) \psi_1 \, \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_n .$$

where e is the electron charge and $\boldsymbol{r}_i$ is the position vector of the ith electron. If ψ_0 and ψ_i are one electron functions, M_{01} is just the dipole moment of the charge density $\psi_0\ \psi_i$.

Since ψ_0 and ψ_1 must both be eigenfunctions of the donor–acceptor pair, they must be orthogonal. That is,

$$\int \ldots \int \psi_0 \psi_1 \, \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_n = 0.$$

Now, if D and A are so far apart that none of the donor orbitals has any region of overlap with any of the acceptor orbitals, then the ground and the excited state of (D,A) are orthogonal to all the charge-transfer states (D^+–A^-), and transitions from the ground state to any of the charge-transfer states are forbidden. In order to observe charge-transfer bands it is necessary that there must be some region of overlap between the orbitals of D and those of A.

Let us consider for simplicity a one-electron system, such that the ground state has an electron in a donor orbital ϕ_d and in the charge-transfer state this has been transferred to an acceptor orbital ϕ_a. That is $\psi(D,A) = \phi_d$, and $\psi(D^+–A^-) = \phi_a$. Under the influence of the Hamiltonian these interact to give a new ground stated ϕ'_d and a new excited state ϕ'_a, and the intensity of the charge-transfer band is proportional to the square of the dipole moment of the electron density $\phi'_d \phi'_a$. Fig. 2 shows this type of behaviour for two 1s-orbitals. The wave functions and density are plotted along the line joining the two nuclei. The dipole moment of the electron density $\phi'_d \phi'_a$ is directed along the internuclear axis, so that it is the component of the light whose electric vector is parallel to this axis that is absorbed. The charge-transfer band is said to be polarised along the internuclear axis.

Nakamoto's observation that the first absorption band of the "quinhydrones" is polarised in a plane perpendicular to the planes of the two components is evidence that these bands have charge-transfer character. However, to find that a band was polarised in a plane parallel to the aroma-

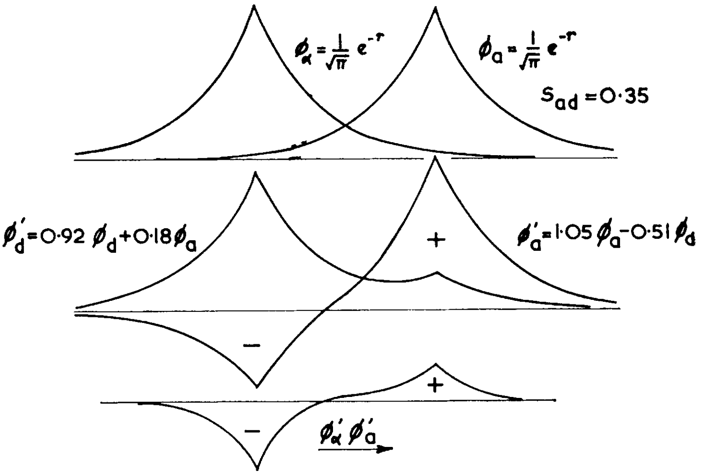

FIG. 2. *Charge-transfer between orbitals of the same symmetry.*

tic rings would not mean that it was not a charge-transfer band. The transfer of charge between D and A is *not* always associated with a transition polarised in the direction of charge transfer. For example, in Fig. 3

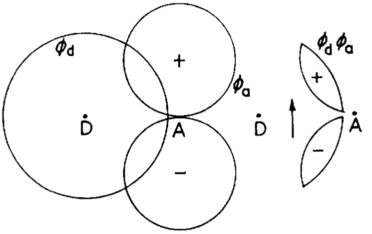

FIG. 3. *Charge-transfer between orbitals of different symmetry.*

we see that if ϕ_d is an *s*-orbital, and ϕ_a a *p*-orbital the charge-transfer band will be polarised at right angles to the internuclear axis. One can observe a charge-transfer band of this type even though the charge-transfer state cannot, by symmetry, lead to any stabilisation of the ground state.

In aniline, the charge-transfer state $\phi^{-1}\psi_b$ will give rise to a band polarised along the two-fold axis, and this state can stabilise the ground state and give rise to the band at 5·27 ev; on the other hand, $\phi^{-1}\psi_a$ does not stabilise the ground state, and transition to this state would be polarised at right angles to the two-fold axis.

As stated earlier, there must be some region of overlap between the donor and the acceptor orbitals for a charge-transfer band to appear, and the more the overlap the stronger the bands. It follows that the intensity of charge-transfer bands is sensitive to steric effects which inhibit this overlap. For example, *ortho*-substituents in *NN*-dimethylaniline or nitrobenzene turn the dimethylamino- or the nitro-group out of the plane of the aromatic ring, reducing the overlap between the donor and the acceptor orbitals Wepster and his co-workers[20] have estimated the angle by which the substituent groups are turned out of the plane, from the reduction in intensity of the intramolecular charge-transfer band. Some of their results are given in Table 2.

TABLE 2. *The angle* (θ) *by which the substituent group is twisted out of the aromatic plane by* ortho-*substituents.*[20]

	λ	ϵ	θ
Nitrobenzene	251	8900	0
o-Nitrotoluene	251	6070	34°
2-Nitro-*m*-xylene	250	1500	66°
NN-Dimethylaniline	251	15500	0
NN-Dimethyl-*o*-toluidine	248	6360	50°
N,*N*,2,6-Tetramethylaniline	262*	2240	68°

* This maximum is almost certainly not associated with the charge-transfer band, but belongs to the band which in dimethylaniline occurs at 2950 Å and is shifted to the blue region by *ortho*-substituents.

Further discussion of the intensity of charge-transfer bands will follow the more detailed investigation in the next section.

Mathematics of Charge-transfer Spectra.—In this section we consider the details of the interaction between the ground state and the charge-transfer state, and its effect on the intensity of the charge-transfer band. We again consider just a one-electron system, in which we write the ground and the charge-transfer state wave functions as:

$$\psi(\mathrm{D,A}) = \phi_\mathrm{d} \qquad (1)$$
$$\psi(\mathrm{D^+{-}A^-}) = \phi_\mathrm{a}.$$

We now specify that ϕ_d shall be an eigenfunction of the neutral donor, and ϕ_a an eigenfunction of the acceptor negative ion. If we write the total Hamiltonian for the complex as:

$$H = V(\mathrm{D^+}) + V(\mathrm{A}) + T, \qquad (2)$$

where $V(\mathrm{D^+})$ is the electrostatic field of $\mathrm{D^+}$, $V(\mathrm{A})$ the field of A, and T the kinetic energy operator, then from our definition, it follows that

$$[V(\mathrm{D^+}) + T]\phi_\mathrm{d} = E_\mathrm{d}\phi_\mathrm{d},$$

and

$$[V(\mathrm{A}) + T]\phi_\mathrm{a} = E_\mathrm{a}\phi_\mathrm{a}, \qquad (3)$$

Now if the perturbed ground and the charge-transfer state which result from the interaction of the donor and acceptor are written

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[20] Burgers, Hoefnagel, Verkade, Visser, and Wepster, *Rec. Trav. chim.*, 1958, 77, 491.

$$\phi'_d = \phi_d + \lambda_{ad}\phi_a,$$

and

$$\phi'_a = \phi_a + \lambda_{da}\phi_d, \qquad (4)$$

then by perturbation theory we have:

$$\lambda_{ad} = \frac{H_{ad} - S_{ad}H_{dd}}{E_d - E_a}; \qquad \lambda_{da} = \frac{H_{ad} - S_{ad}H_{aa}}{E_a - E_d}, \qquad (5)$$

where $H_{ad} = \int\phi_a H \phi_d \mathrm{d}\tau$ and $S_{ad} = \int\phi_a\phi_d \mathrm{d}\tau$.

By substituting for H, as given by eqn. (2), and making use of the expressions (3), we obtain coefficients:

$$\lambda_{ad}(E_d - E_a) = V_{ad}(\mathrm{A}) - S_{ad}V_{dd}(\mathrm{A}),$$

and

$$\lambda_{da}(E_a - E_d) = V_{ad}(\mathrm{D}^+) - S_{ad}V_{aa}(\mathrm{D}^+). \qquad (6)$$

Introducing the normalised charge density $\phi_d\phi_a/S_{ad}$, we have

$$\lambda_{ad}(E_d - E_a) = S_{ad}\int\left[\frac{\phi_a\phi_d}{S_{ad}} - \phi_d^2\right]V(\mathrm{A})\mathrm{d}\tau \equiv S_{ad}W_{ad}(\mathrm{A})$$

$$\lambda_{da}(E_a - E_d) = S_{ad}\int\left[\frac{\phi_a\phi_d}{S_{ad}} - \phi_a^2\right]V(\mathrm{D}^+)\mathrm{d}\tau \equiv S_{ad}W_{da}(\mathrm{D}^+) \qquad (7)$$

We notice the lack of symmetry in these expressions: $\lambda_{ad} \neq -\lambda_{da}$. The integrals W involve the interaction of the electrostatic field of the acceptor or the donor positive ion with a charge density which integrates to zero. The overlap density $\phi_d\phi_a$ is concentrated in the region between D and A if the orbitals ϕ_d and ϕ_a are about the same size. However, if one of these orbitals is much smaller than the other then the overlap density will be concentrated near the smaller of the two. If ϕ_d is small compared with ϕ_a, then $\phi_d\phi_a$ is centred on D, and it follows that $W_{da}(\mathrm{D}^+)$ will be large, but $W_{ad}(\mathrm{A})$ small. On the other hand, if ϕ_d is large compared with ϕ_a then $\phi_d\phi_a$ is centred on A, $W_{ad}(\mathrm{A})$ will be large and $W_{da}(\mathrm{D}^+)$ small. This can be seen from Fig. 4 which shows the electron density $[(\phi_d\phi_a)/S_{da} - \phi_a^2]$

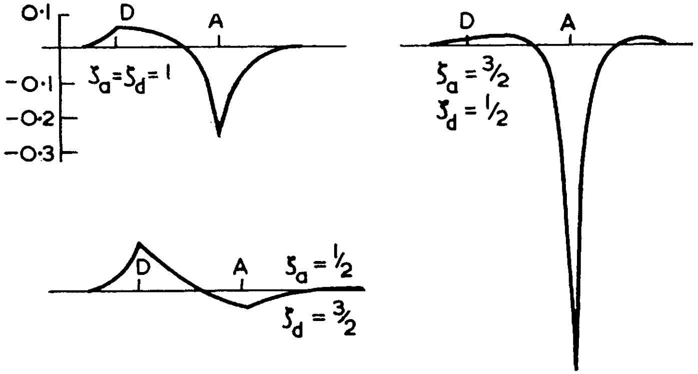

FIG. 4. *The overlap density between* 1*s-orbitals of different size.*

for two 1*s*-orbitals of the type $\phi = (\zeta^3/\pi)^{\frac{1}{2}}e^{\zeta r}$ plotted for various values of ζ_a and ζ_d along the internuclear axis.[21] (The larger ζ, the smaller is the orbital.)

In general, we expect ϕ_a to be larger than ϕ_d since it is an eigenfunction of a negative ion. We therefore predict that

$$W_{da}(D^+) \gg W_{ad}(A). \tag{8}$$

This prediction is supported, not only by an examination of the overlap density, but also by the fact that $V(D^+)$ falls off much more slowly than $V(A)$, the latter being zero outside the electron cloud of A.

From expression (8) it follows that

$$|\lambda_{da}| \gg |\lambda_{ad}|. \tag{9}$$

This result can also be seen from the condition of orthogonality between ϕ_d' and ϕ_a': one deduces

$$\lambda_{da} + \lambda_{ad} + S_{ad} = 0. \tag{10}$$

If S_{ad} is positive and $E_a > E_d$, then λ_{ad} will be positive, and it again follows that $|\lambda_{da}| > |\lambda_{ad}|$. In other words, there is more ground state introduced into the charge-transfer state than *vice versa*. If $W_{ad}(A)$ is approximately zero, then the ground state is

$$\phi_d' = \phi_d, \tag{11}$$

and the charge-transfer state

$$\phi_a' = \phi_a - S_{ad}\phi_d. \tag{12}$$

The stabilisation of the ground state is given by

$$-\Delta E_d = \lambda_{ad}^2(E_a - E_d), \tag{13}$$

and the elevation of the charge-transfer state by

$$\Delta E_a = \lambda_{da}^2(E_a - E_d). \tag{14}$$

Again it follows that the excited state is generally destabilised more than the ground state is stabilised.

So much for the energy of the charge-transfer band. Its intensity is determined by the transition moment between ϕ_d' and ϕ_a':

$$M_{da}' = \int\phi_d'M\phi_a'd\tau = M_{da} + \lambda_{da}M_{dd} + \lambda_{ad}M_{aa} + \text{a term in } \lambda^2 \tag{15}$$

Use of the orthogonality relationship (10) converts this into

$$M_{da}' = \lambda_{ad}(M_{aa} - M_{dd}) + (M_{da} - S_{ad}M_{dd}). \tag{16}$$

This type of expression was first obtained by Mulliken.[4] It shows that there are two contributions to the transition moment. The first is proportional to the dipole moment of the transferred electron and the hole

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[21] Murrell, *J. Amer. Chem. Soc.*, 1958, **81**, 5037.

it leaves behind (this is itself proportional to the distance through which the charge is carried) and is related to the stabilisation of the ground state through the coefficient λ_{ad}. We have shown that in general λ_{ad} is small, so that the first term in eqn. (16) may perhaps be neglected. However, Mulliken has pointed out that, even if λ_{ad} is zero and there is no stabilisation of the ground state, one could still observe a charge-transfer band through the influence of the second term in eqn. (16). Orgel and Mulliken[22] attribute the intensity of contact charge-transfer absorption to just such a term: the expression "contact charge-transfer absorption" is used to describe the absorption which appears, for example, in I_2–heptane mixtures around 2600 Å, although there appears to be no stable complex formed.[23] It is now necessary to consider if this interpretation of contact charge-transfer absorption is reasonable.

The second term in expression (16) can be written in a different form if we again introduce the normalised overlap density:

$$M_{da} - S_{ad}M_{dd} = S_{ad}e\int[(\phi_d\phi_a)/S_{ad} - \phi_d^2]\, r\,d\tau \qquad (17)$$

By comparing expressions (7) and (17), we see that the reason for expecting that λ_{ad} will be small, namely, that ϕ_d is small compared with ϕ_a, will here make the second term in (16) small also. It is not possible to say definitely that the second term in expression (16) will be zero if the first is zero, but we can say that factors which make one large or small make the other large or small at the same time. For Orgel and Mulliken's interpretation of contact charge-transfer absorption to be correct, it is necessary that the overlap density $\phi_d\phi_a$ lies so far away from A that $W_{ad}(A)$ is zero, but not so close to D such that the dipole moment of $[(\phi_d\phi_a)/S_{ad} - \phi_d^2]$ is zero.

There is one special case when contact charge-transfer absorption as interpreted above can certainly be observed. If ϕ_a and ϕ_d have different symmetries, as in Fig. 3, then S_{ad} and λ_{ad} will be zero but M_{ad} need not be zero. A charge-transfer band polarised in a plane perpendicular to the direction of charge transfer can be observed without any stabilisation of the ground state.

There are other sources of charge-transfer intensity which were not considered in the early work on charge-transfer complexes, but have been taken to be important in the field of intramolecular charge-transfer spectra: these sources are the excited states of the donor and acceptor. If the donor has a transition $\phi_d \rightarrow \phi_{d^*}$ which gives rise to an intense absorption band, and if the charge-transfer state ϕ_a interacts with the donor excited state to give:

$$\phi_a' = \phi_a + \lambda_{d^*a}\phi_{d^*},$$

the effect will be that the charge-transfer band arising from the transition

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[22] Orgel and Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4839.
[23] Evans, *J. Chem. Phys.*, 1954, **23**, 1436.

$\phi_d \rightarrow \phi_a'$ will now have borrowed some intensity from the donor absorption band. The amount borrowed will be proportional to $(\lambda_{d^*a})^2$ and to the intensity of the donor band. The coefficient λ_{d^*a} is given by an expression similar to that for λ_{da}, namely:

$$\lambda_{d^*a}(E_a - E_{d^*}) = S_{ad^*}W_{d^*a}(D^+). \tag{18}$$

Since ϕ_{d^*} is an excited-state orbital, we expect that it will be "blown up" relative to ϕ_d. In general then we expect S_{ad^*} to be greater than S_{ad}. Even if the donor and the acceptor do not approach close enough for ϕ_d and ϕ_a to overlap there may still be some overlapping of ϕ_{d^*} and ϕ_a. This mechanism therefore provides another interpretation of contact charge-transfer absorption.

The borrowing of charge-transfer intensity from excited states of the acceptor can be shown to involve the overlap of the ground-state donor orbital ϕ_d, and a ground-state orbital of the *neutral* acceptor (ϕ_a is an orbital of A^-). This will probably be unimportant in the case of intermolecular charge-transfer spectra since exchange repulsion will tend to prevent ground-state orbitals of D and A from overlapping to any large extent. It may, however, be important for intramolecular charge-transfer absorption, as in aniline, where the donor and acceptor are held rather closely together by direct covalent bonding.

Although we have reason to believe that it is, in general, the excited states of the donor that contribute the largest part of the charge-transfer intensity, there may be particular cases where for reasons of symmetry this is not so. For example, if in the quinhydrone complex the quinone and the quinol sit symmetrically one upon the other in parallel planes, then the charge-transfer bands which are polarised perpendicular to the aromatic rings cannot, by symmetry, have picked up any intensity from the low-lying excited states of the quinone or quinol since these bands are polarised in the planes of the aromatic rings. It is probably true to say that in general these rigid symmetrical structures are the exception rather than the rule in solution. In solution we may expect to find a large number of different configurations of the complex in which the least symmetrical, although it is the least stable, may give rise to the largest charge-transfer intensity.

In the series of complexes between iodine and the methylbenzenes, we find that as the complex becomes more stable the charge-transfer intensity falls.[24] However, for the chloranil–methylbenzene complexes the reverse situation arises, an increase in stability being accompanied by an increase in intensity of the charge-transfer band (see Table 3).[25]

Theoretically we expect that in such a series the relative behaviour of stability and charge-transfer intensity should depend on the variation of the difference in energy between the most stable configuration and the configuration giving the largest charge-transfer intensity. These are not

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[24] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1952, **74**, 4500.

[25] N. Smith, Ph.D. Thesis, University of Chicago, Ill.

necessarily the same. For instance, Orgel and Mulliken interpret the behaviour of the iodine–benzene series as being due to the chance contacts giving rise to the greatest charge-transfer intensity, the relative number of these contacts being reduced as the complex becomes more stable. The chloranil–benzene complexes are more stable, and by reason of their geometry it is difficult to obtain much overlap of the donating and the accepting orbitals except when they lie one upon the other in parallel planes. The charge-transfer intensity will, therefore, arise mainly from the interaction between the ground and the charge-transfer state, and we get the expected increase of intensity with an increase of stability. It is interesting that the charge-transfer intensity of the chloranil–benzene complexes is much less than for the iodine complexes. This is in agreement with our proposal that much greater intensity can be obtained when the charge-transfer state can borrow from the donor excited states.

TABLE 3. *Charge-transfer bands: the variation of the extinction coefficient with the equilibrium constant of the complex.*

	Complexes[20] with I_2			Complexes[21] with chloranil		
Benzene or deriv.	λ	ϵ	κ	λ	ϵ	κ
Benzene	292	16,400	0·15	340	2180	0·30
Toluene	302	16,700	0·16	365	1920	0·50
o-Xylene	316	12,500	0·27	385	2090	1·05
m-Xylene	318	12,500	0·31	390	2000	0·84
p-Xylene	304	10,100	0·31	410	1960	0·89
1,2,4-Trimethyl	—	—	—	420	1985	1·02
1,3,5-Trimethyl	332	8850	0·82	410	2250	1·17
1,2,3,4-Tetramethyl	—	—	—	445	2585	2·65
1,2,3,5-Tetramethyl	—	—	—	450	2495	2·47
1,2,4,5-Tetramethyl	332	9000	0·63	470	2320	3·02
Pentamethyl	357	9260	0·88	480	2680	5·32
Hexamethyl	375	8200	1·35	505	2880	9·08

If our proposal for the benzene–iodine complexes is correct, that is, that some of the least stable structures contribute most to the charge-transfer intensity, then as the temperature is raised the measured extinction coefficient of the charge-transfer band should increase, even though the net absorption decreases, as less molecules are involved in complex-formation. This prediction has not been tested for the I_2–benzene complex, but Ross has observed this type of behaviour for the trinitrobenzene–aniline and –naphthalene complexes (reported in ref. 22).

We have only used one-electron wave functions to describe the electronic states involved in the charge-transfer absorption. If many-electron wave functions are used the matrix elements become more complicated, but the most important terms have the form given above.[21] We have also based our arguments for the magnitude of the charge-transfer interactions on the assumption that D and A are both neutral molecules. If one or both is an ion, then some of the statements made above will not be applicable.

Conclusion.—By my original definition of charge-transfer absorption as one involving a large charge displacement, I have excluded the possibility of charge-transfer absorption when the donor and acceptor are identical, as in the *N*-ethylphenazyl dimer[26] or biphenyl.[27] In fact it has been found convenient to interpret the electronic states of such systems by using as a basic set the wave functions AA, A^+A^-, A^-A^+, etc. However, any state of the system must contain an equal contribution from A^+A^- and A^-A^+, so there cannot be any actual charge displacement associated with a transition. A state of the type $A^+A^- \pm A^-A^+$ could perhaps be called a charge-resonance state, and a transition from the ground state AA to such a state could be called a charge-resonance transition. The term two-way charge transfer has also been used for this type of molecule, and also, for example, in molecules such as the Ag^+–benzene complex, where the structures $AgC_6H_6^+$ and $Ag^{2+}C_6H_6^-$ are probably both important in stabilising the ground state.

My definition of a charge-transfer transition also excludes cases when both the ground and the excited state are equal mixtures of DA and D^+A^- since again there is no net charge transferred from one part of the molecule to the other in the excitation. This situation may occur in the molecules of the type BF_3–NH_3 and amongst Brooker's dyes. However, an exactly equal mixture will occur so infrequently that it is not worth making it a special case.

In this Review I have restricted my attention to the case in which both D and A have closed-shell electronic structures. Other cases are, however, important, a notable example being the charge-transfer bands associated with complexes between oxygen and aromatic molecules.[28,29] It has recently been shown that these charge-transfer states play an important role in the intensification of the singlet–triplet absorption bands of aromatic molecules induced by oxygen and nitric oxide.[29,30]

In complexes involving heavy atoms, one expects the spin-selection rules to be broken down by spin–orbit coupling. This must certainly occur in the I_2–benzene complex since spin–orbit coupling is known to be important for the iodine molecule (I_2) itself. Platt[31] has pointed out that the charge-transfer state of this complex lies very close to one of the expected triplet states of benzene, and there must be considerable interaction between the two. Charge-transfer states, together with spin–orbit interaction, provide a mechanism for the intensification of the singlet

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[26] Hausser and Murrell, *J. Chem. Phys.*, 1957, **27**, 500.
[27] Longuet-Higgins and Murrell, *Proc. Phys. Soc.*, 1955, **68**, *A*, 601.
[28] Evans, *J.*, 1953, 345.
[29] Mulliken and Tsubomura, *J. Amer. Chem. Soc.*, in the press.
[30] Murrell, *Mol. Phys.*, 1960, **3**, 319.
[31] Platt, personal communication.

triplet absorption bands of aromatic molecules dissolved in methyl iodide.[32]

In conclusion, I must emphasise that in general it will not be possible to separate the electronic states of the system into those which are purely charge-transfer and those which have no charge-transfer character. This will be particularly true for intramolecular absorption. For example, it has been calculated[14] that the first excited state of aniline has 17% of charge-transfer character and the second excited state 68%. As has been pointed out above, the second state has sufficient charge-transfer character to show the expected dependence of its intensity on steric effects: the first state has not. In a similar vein, the charge-transfer states of $Cl^-(H_2O)_n$ will resemble highly excited or Rydberg states of Cl^-, so that the distinction between charge-transfer states and excited states of the donor becomes meaningless.

[32] Kasha, *J. Chem. Phys.*, 1952, **20**, 71.