temperature of the catalyst reached 260 to 300°; it then dropped abruptly. Since the temperature at which this sudden drop occurs is about the same as that at which sintering starts, it appears to be related to and could be accounted for by the onset of intercrystalline diffusion of patches of aluminum into the catalyst.

If one makes the assumption that each hydrogen atom can contribute one electron and each aluminum atom can contribute 3 electrons to the d-band of the nickel atoms, the magnetic data shown in Fig. 4 seem to be explainable. For example, the W-6 catalyst on the basis of analysis and hydrogen content has about 1.8 added electrons per unit cell initially; this falls to 0.76 electron per unit cell when the hydrogen is removed. If the magnetization depends upon the number of added electrons per unit cell,[25] the value of σ would be expected to increase from 14 to 35 as the hydrogen is removed and the slope would be 0.27 per cc. of hydrogen removed. The observed values in Fig. 4 show increases from 19.5 to 35 and the slope has a value of 0.27/cc. If, as has sometimes been done,[26] one assumes that the magnetism disappears when the added electrons amount to 0.6 per gram atom, then the decrease in the number of added electrons from 0.45 to 0.22 per nickel atom as hydrogen is removed would correspond to a change in σ from 14 to 35 with a slope of 0.24 per cc. of hydrogen removed. Either of these calculations is in satisfactory agreement with the observed values and seems to suggest that each hydrogen is indeed on an average contributing one electron to the nickel.

For the D-1 catalyst similar calculations as to the total change in values of σ cannot be made because this catalyst appears to be non-homogeneous. The calculations of the slope of the magnetic susceptibility as a function of the amount of hydrogen removed might, however, be expected to be reasonable. The calculations analogous to those made for the W-6 catalyst suggest a slope of 0.28 per cc. of hydrogen removed based on the number of added electrons per unit cell and 0.16 per cc. of hydrogen based on the number of electrons per gram atom of nickel. The observed slope is 0.16 per cc. of hydrogen removed.

One final observation may be of interest. When a Raney nickel catalyst is degassed, the alloy does not wholly anneal but half of the lattice vacancies remain. It is difficult to understand why these lattice vacancies do not completely disappear when the nickel samples are heated to the 1000–1200° region. This result, however, is consistent with the observation by Littman and Dew-Hughes[7] that roughly one-half the hydrogen could be put back into a Raney nickel sample at 400° and 140 atmospheres even though the sample had first been heated to 1200°. Perhaps the small amounts of aluminum oxide tend to retard the rearrangement necessary to fill completely the vacancies in the nickel lattice.

In conclusion, it should be emphasized that the above analysis is probably over-simplified, and in fact the validity of some of the assumptions may be questionable. Nonetheless, it does give a rather detailed picture consistent with experimental data. The picture is one in which hydrogen atoms form a substitutional alloy with Raney nickel much like copper in copper–nickel alloys. This hydrogen can be removed by heating. The nickel–aluminum alloy thus created still contains a large number of lattice vacancies which can be reoccupied by hydrogen atoms by exposure to hydrogen gas at high pressures.

Acknowledgment.—The authors gratefully acknowledge the financial support of this work by the W. R. Grace Company.

BALTIMORE, MARYLAND

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[25] N. F. Mott and H. Jones, "The Theory of Metals and Alloys," Oxford University Press, New York, N. Y. 1940.

[26] W. Hume-Rothery, "Atomic Structure for Students of Metallurgy," Institute of Metals, London, England, 1946.

[CONTRIBUTION FROM THE DEPARTMENT OF THEORETICAL CHEMISTRY, UNIVERSITY CHEMICAL LABORATORY]

Molecular Complexes and their Spectra. IX. The Relationship between the Stability of a Complex and the Intensity of its Charge-transfer Bands[1]

BY J. N. MURRELL

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The matrix elements of the Hamiltonian and of the transition moment operator which occur in the theory of charge-transfer complexes are examined in more detail than has previously been attempted. The contribution to the intensity of the charge-transfer band arising from the interaction of the charge-transfer state with the ground state is compared with the contributions expected from the excited states of the donor and acceptor. It is shown that the donor-excited states will contribute the greatest intensity except when, for reasons of symmetry, they do not interact with the charge-transfer state. Contact charge-transfer absorption will be due almost entirely to the interaction of the charge-transfer and donor-excited states. It is proposed that in a series of related complexes, the relative behavior of the intensity of the charge-transfer band and the stability of the complex depends on the variation of the difference in energy between the most stable configuration and the configuration giving the greatest contribution to the intensity: these configurations are not usually identical. Examples are given to show that the intensity of the charge-transfer band may increase or decrease as the complex becomes more stable.

1. Introduction

Charge-transfer (c-t.) absorption bands have been observed for pairs of molecules which form crystalline molecular complexes (*e.g.*, the quinhydrones),[2] for molecules which appear to form a stable complex in solution but which give no crystalline complex (*e.g.*, iodine and benzene)[3] and for molecules

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[1] This work was initiated at the Department of Physics, The University of Chicago, whilst the author held a Fellowship from the Commonwealth Fund of New York.

[2] L. Michaelis and S. Granick, THIS JOURNAL, **66**, 1023 (1944).

[3] H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 2832 (1948).

which do not form a stable complex in solution (*e.g.*, iodine and *n*-heptane).[4] To cover these these three cases Orgel and Mulliken[5] have proposed the existence of both "complex" and "contact" c-t. spectra, the former being associated with a stable complex and the latter being due to absorption of light when the two molecules come together during a chance encounter. Thus the quinhydrones possess complex c-t. spectra, iodine and *n*-heptane give rise to contact spectra and the spectrum of iodine and benzene probably possesses a mixture of the two.

Mulliken's original theory of charge transfer complexes[6] brought out a general parallel between the binding energy of the complex and the intensity of the charge-transfer band. As Orgel and Mulliken[5] have pointed out, this simple theory does allow for the possibility of having charge-transfer absorption even though no stable complex is formed. However, it has still to be established that this is more than a theoretical possibility. In other words, can there be sufficient overlap of the donor and acceptor orbitals during a chance collision to give an observable charge-transfer band when this overlap is not sufficient to give a stable complex? Further, the intensity of the charge-transfer band until now has been attributed to the "mixing" of the charge-transfer state and the ground state which occurs when the two molecules are close enough for the donating and accepting orbitals to overlap. There are, however, other sources of this intensity, namely, the excited states of the donor or acceptor. There may be more mixing of the charge-transfer states with these excited states than there is with the ground state.

By examining the matrix elements of the Hamiltonian and transition moment operator between the wave functions of the separate donor–acceptor pair in more detail than has been attempted hitherto, we hope to clear up some of the questions which have been raised above.

Since, as we shall see, the matrix elements in their exact form are complicated, we shall, in the spirit of perturbation theory, evaluate them to the first order in small quantities. Unlike the more conventional perturbation theory, however, the terms contributing to the matrix elements are not simply expressible in powers of some perturbation parameter. Instead they are made up of integrals involving orbitals of the donor (D) and the acceptor (A), and although these individually go to zero as D and A are separated, they do so at different rates. To introduce some rigor into the theory, we shall define integrals which contain the overlap electron density $\phi_d\,\phi_a$ between a D orbital ϕ_d and an A orbital ϕ_a to be of first order in small quantities for the purposes of the pertubation theory. This definition will include the overlap integrals[7]

$$S_{ad} = <\phi_a(1)\phi_d(1)> \qquad (1.1)$$

nuclear attraction integrals of the type

$$H_{ad}(D) = <\phi_a(1)\phi_d(1)|Z_d/r_{1d}> \qquad (1.2)$$

where Z/r_1 is the potential field acting on electron 1 due to the nuclei of the donor (or the acceptor); the two electron integrals

$$G_{ad,a'a''} = <\phi_a(1)\phi_d(1)|1/r_{12}|\phi_{a'}(2)\phi_{a''}(2)> \qquad (1.3)$$

(and $G_{ad,d'd''}$), where $\phi_{a'}$ and $\phi_{a''}$ may, or may not, be the same as ϕ_a; and the transition moment between ϕ_a and ϕ_d

$$M_{ad} = <\phi_a(1)\phi_d(1)|r_1> \qquad (1.4)$$

However, the two electron integral

$$<\phi_a(1)\phi_d(1)|1/r_{12}|\phi_{a'}(2)\phi_{d'}(2)> \qquad (1.5)$$

will be regarded as second order since it depends on the interaction of two overlap densities.

The integrals representing the interaction of two charge densities, one on D the other on A, do not fall into the above classification; they include both one and the two electron integrals

$$H_{aa'}(D) = <\phi_a(1)\,{}_a\phi'(1)|Z_d/r_{1d}> \qquad (1.6)$$

and

$$G_{aa',dd'} = <\phi_a(1)\phi_{a'}(1)|1/r_{12}|\phi_d(2)\phi_{d'}(2)> \qquad (1.7)$$

Although these also go to zero as D and A are separated, they do so as some inverse power of the separation, whereas integrals 1.1 to 1.5 vary inverse exponentially with the separation of the donor and acceptor. It is therefore convenient to regard integrals 1.6 as zeroth order quantities.

2. Evaluation of the Matrix Elements of the Hamiltonian.—It will be assumed that we know the eigenfunctions for the donor–acceptor pair when the two molecules are far apart. They can be written as a product of eigenfunctions for the separate donor and acceptor providing that the exchange of electrons between the two molecules is allowed for. Thus we write

$$\Psi_r = \mathcal{A}\theta_{dr}(i)\theta_{ar}(j) \qquad (2.1)$$

where

$$\mathcal{H}(i,d)\theta_{dr}(i) = E_{dr}\theta_{dr}(i) \qquad (2.2)$$

and

$$\mathcal{H}(j,a)\,\theta_{ar}(j) = E_{ar}\theta_{ar}(j) \qquad (2.3)$$

$\mathcal{H}(i, d)$ contains all the terms in the Hamiltonian which depend only on the coördinates of electrons i and the nuclei of D: $\mathcal{H}(j,a)$ contains the terms which depend only on the coördinates of electrons j and the nuclei of A. $\mathcal{A}$ is the antisymmetrizing operator.

When D and A come close together the functions ψ_r will cease to be eigenfunctions of the complete Hamiltonian and, in addition, they no longer form an orthogonal set. However, we can still expand the perturbed wave functions in terms of this non-orthogonal set as

$$\Psi_{r'} = \Psi_r + \sum_{s \neq r} a_{sr}\,\Psi_s \qquad (2.4)$$

the coefficient a_{sr} being given by perturbation theory as

$$a_{sr} = \frac{\mathcal{H}_{sr} - S_{sr}\mathcal{H}_{rr}}{\mathcal{H}_{rr} - \mathcal{H}_{ss}} \equiv \frac{K_{sr}}{\Delta E_{sr}} \qquad (2.5)$$

If the complete Hamiltonian is now expanded as

$$\mathcal{H} = \mathcal{H}(i,d) + \mathcal{H}(j,a) - \sum_i Z_a/r_{ia} - \sum_j Z_d/r_{jd} + \sum_{ij} 1/r_{ij} + Z_aZ_d/r_{ad} \qquad (2.6)$$

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[4] D. F. Evans, *J. Chem. Phys.*, **23**, 1436 (1954).

[5] L. E. Orgel and R. S. Mulliken, THIS JOURNAL, **79**, 4839 (1957).

[6] R. S. Mulliken, *ibid.*, **74**, 811 (1952).

[7] The bracket (< >) notation is used in this paper to represent integration over the coördinates of all the electrons involved.

then making use of the relationships (2.1) to (2.3) we find that K_{sr} is given by

$$K_{sr} = N^{-1}<\Psi_s - S_{s1}\Psi_r| - \sum_i Z_a/r_{ia} - \sum_j Z_d/r_{jd} + \sum_{ij} 1/r_{ij}|\theta_{dr}(i)\theta_{ar}(j)> \quad (2.7)$$

N is a normalizing constant such that N^{-2} is equal to the number of ways of dividing the electrons into two groups of numbers n_i and n_j.

To continue further it is necessary to be explicit about the function ψ_s. If ψ_s differs from ψ_r in having different numbers of electrons occupying the orbitals of D and A, then an expansion of the type (2.1) will have the form

$$\Psi_s = \mathcal{A}\theta_{ds}(i')\,\theta_{as}(j') \qquad (2.8)$$

where the number of electrons i′ is not equal to the number of electrons i (and $n_j \neq n_{j'}$). Alternatively, one can use an expansion of the type

$$\Psi_s = \mathcal{A}\chi_{s\mu}(i)\,\chi_{s\nu}(j) \qquad (2.9)$$

in which the electrons i occupy the orbitals which make up the function $\chi_{s\mu}$, but these orbitals belong both to D and to A. Under these circumstances neither $\chi_{s\mu}$ nor $\chi_{s\nu}$ will in general be an eigenfunction of either $\mathcal{H}$ (i,d) or $\mathcal{H}$ (j,a). Whichever expansion is adopted the expression for K_{sr} remains complicated, involving a summation either over i′j′ or over $\mu\nu$. However, the general structure of these matrix elements can be seen by selecting a few simple examples. We shall begin by studying the matrix elements in the case when Ψ_r and Ψ_s are functions of the coördinates of just one electron. In this way we hope to obtain the leading term in the expression for K_{sr}. We shall then consider a more sophisticated example, choosing four-electron wave functions, to bring out the nature of the additional terms in K_{sr}.

The One-electron Approximation.—Suppose that in the ground state (D,A) the electron occupies an orbital ϕ_δ of D and in the charge transfer state it occupies ϕ_α of A. To determine the coefficient $a_{\delta\alpha}$ in the perturbed orbital (or state, in the one-electron approximation) $\phi_{\alpha'}$, where

$$\phi_{\alpha'} = \phi_{\delta\alpha} + a_{\delta\alpha}\phi_\delta \qquad (2.10)$$

we assume that ϕ_α is an eigenfunction for an electron moving in the electrostatic field V(A) of A and that the perturbing field is $V(\mathrm{D}^+)$ of D^+. The total Hamiltonian for the system will then be

$$H = V(\mathrm{A}) + V(\mathrm{D}^+) \qquad (2.10a)$$

Since we are using only one-electron wave functions, the matrix element of K, given by 2–7, has the form

$$K_{\delta\alpha} = <\phi_\delta - S_{\delta\alpha}\phi_\alpha|V(\mathrm{D}^+)|\phi_\alpha> \equiv V_{\delta\alpha}(\mathrm{D}^+) - S_{\delta\alpha}V_{\alpha\alpha}(\mathrm{D}^+) \quad (2.11)$$

If ϕ_δ and ϕ_α are not orthogonal, we can introduce the normalized overlap density $\phi_\delta\phi_\alpha/S_{\delta\alpha}$ and write

$$K_{\delta\alpha} = S_{\delta\alpha} <(\phi_\delta\phi_\alpha/S_{\delta\alpha}) - \phi_\alpha{}^2\,|V(\mathrm{D}^+)> \equiv S_{\delta\alpha}\mathrm{W}_{\delta\alpha}(\mathrm{D}^+) \quad (2.12)$$

$K_{\delta\alpha}$ will now depend not only on the magnitude of the overlap integral $S_{\delta\alpha}$, but also on how nearly the normalized overlap density is to being the same as $\phi_\alpha{}^2$. For example, if ϕ_δ and ϕ_α are orbitals of the same size, then the center of the overlap density lies midway between D and A. However, if one of the orbitals is much smaller than the other the overlap density will be concentrated near the smaller of the two. Figure 1, which shows the electron density $[(\phi_\delta\phi_\alpha)/S_{\delta\alpha} - \phi_\alpha{}^2]$, for two is orbitals of the type $\phi = (\zeta^3/\pi)^{1/2}e^{-\zeta r}$, plotted along the D–A axis, illustrates this point. It follows that $\mathrm{W}_{\delta\alpha}(\mathrm{D}^+)$ will be favored by having ϕ_δ small by comparison with ϕ_α. One other point of interest arising from the figure is that when ϕ_α is much smaller than ϕ_δ the electron density is localized on A and is almost independent of the D–A separation.

The integral $W_{\delta\alpha}(\mathrm{D}^+)$ will go to zero as the D–A separation goes to infinity, although this limiting value is approached more rapidly the smaller ϕ_α is in comparison with ϕ_δ. It follows that $K_{\delta\alpha}$ tends to zero more rapidly than $S_{\delta\alpha}$.

In the case that $S_{\delta\alpha} = 0$, then $K_{\delta\alpha} = V_{\delta\alpha}[\mathrm{D}^+)$, and again $K_{\delta\alpha}$ will be favored by having the donor orbital small in comparison with the acceptor.

To find the coefficient $a_{\alpha\delta}$ in the perturbed donor orbital

$$\phi_{\delta'} = \phi_\delta + a_{\alpha\delta}\phi_\alpha \qquad (2.13)$$

we proceed in a similar manner to that described above, except that we emphasize ϕ_δ to be an eigenfunction of the donor and the perturbing field to be that of the acceptor, V(A). As in (2.11) and (2.12) we have

$$K_{\alpha\delta} = V_{\alpha\delta}(\mathrm{A}) - S_{\alpha\delta}V_{\delta\delta}(\mathrm{A}) \equiv S_{\alpha\delta}W_{\alpha\delta}(\mathrm{A}) \quad (2.14)$$

It is now seen that the very condition that favored $K_{\delta\alpha}$, namely, having ϕ_δ small in comparison with ϕ_α, is the one which militates against $K_{\alpha\delta}$. Moreover, if D and A are both neutral molecules, then whereas $V(\mathrm{D}^+)$ falls off as the inverse power of the distance from D, V(A) falls off as the inverse exponential of the distance from A.

Outside a sphere which contains essentially all the electrons of A we can take $V(\mathrm{A}) = 0$. It follows that the general condition that there should be no stabilization of the ground state is that the overlap density between the donating and accepting orbital should not penetrate the electron density of A in its ground state.

Instead of evaluating $K_{\alpha\delta}$ and $K_{\delta\alpha}$ separately we could have derived one from the other by making use of the orthogonality condition $<\phi_{\alpha'}\phi_{\delta'}> = 0$. If $\Delta E_{\delta\alpha}$ is the energy required to transfer an electron from ϕ_δ to ϕ_α, then to the first order in small quantities we have

$$<\phi_{\alpha'}\phi_{\delta'}> = <\phi_\alpha + (S_{\delta\alpha}W_{\delta\alpha}(\mathrm{D}^+)/\Delta E_{\delta\alpha})\phi_\delta|\phi_\delta - (S_{\delta\alpha}W_{\alpha\delta}(\mathrm{A})/\Delta E_{\alpha\delta})\phi_\alpha> = \frac{S_{\delta\alpha}}{\Delta E_{\delta\alpha}}(\Delta E_{\delta\alpha} - W_{\alpha\delta}(\mathrm{A}) + W_{\delta\alpha}(\mathrm{D}^+)) \quad (2.15)$$

It follows that if these states are orthogonal

$$W_{\alpha\delta}(\mathrm{A}) - W_{\delta\alpha}(\mathrm{D}^+) = \Delta E_{\delta\alpha} \qquad (2.16)$$

If $W_{\alpha\delta}(\mathrm{A})$ is small then $-W_{\delta\alpha}(\mathrm{D}^+) \simeq \Delta E_{\delta\alpha}$: the perturbed ground state is then $\phi_{\delta'} = \phi_\delta$, and the perturbed c-t. state is $\phi_{\alpha'} = \phi_\alpha - S_{\alpha\delta}\phi_\delta$.

The Four-electron Approximation.—We wish now to see how the matrix elements of K develop as we introduce more freedom into our wave functions. The particular freedom that is required is that of allowing the donated electron to exchange with the other electrons of the acceptor and for the hole left in the donor orbitals to exchange with any other

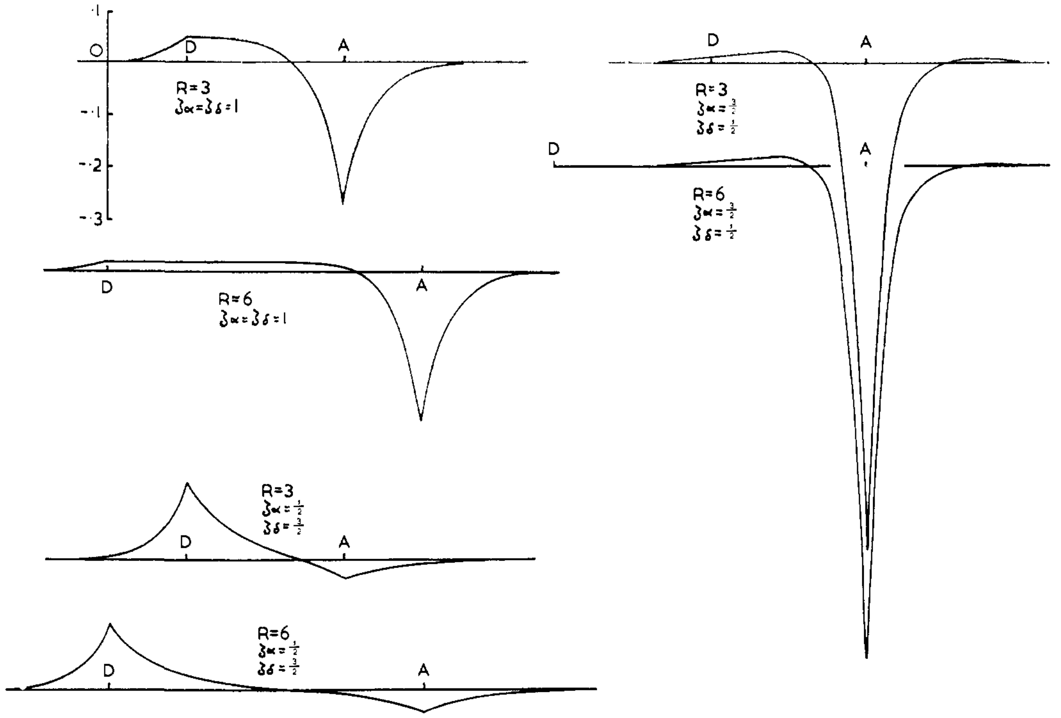

Fig. 1.

holes in the donor orbitals. The simplest wave function which will allow us to note the consequences of such exchanges and which in addition represents the interaction of closed shell molecules (the most common case of interest), will be one which is a function of the position of four electrons.

Let us write the ground state wave function as

$$\Psi_0(\mathrm{D,A}) = |\phi_d(1)\bar{\phi}_d(2)\phi_a(3)\bar{\phi}_a(4)| \quad (2.17)$$

this being a normalized Slater determinant represented for brevity by its principal diagonal. An unbarred orbital will be taken to contain an electron of α-spin, a barred orbital one of β-spin. If $\phi_{d'}$ is a vacant oribtal of D and $\phi_{a'}$ a vacant orbital of A, then we can represent typical singlet excited states of the D–A pair by the wave functions

$$\Psi_1(\mathrm{D^*,A}) = \sqrt{\frac{1}{2}}\{|\phi_d(1)\bar{\phi}_{d'}(2)\phi_a(3)\bar{\phi}_a(4)| - |\bar{\phi}_d(1)\phi_{d'}(2)\phi_a(3)\bar{\phi}_a(4)|\} \quad (2.18)$$

$$\Psi_2(\mathrm{D,A^*}) = \sqrt{\frac{1}{2}}\{|\phi_d(1)\bar{\phi}_d(2)\phi_a(3)\bar{\phi}_{a'}(4)| - |\phi_d(1)\bar{\phi}_d(2)\bar{\phi}_a(3)\phi_{a'}(4)|\} \quad (2.19)$$

A typical c-t. state will then be

$$\Psi_3(\mathrm{D^+A^-}) = \sqrt{\frac{1}{2}}\{|\phi_d(1)\bar{\phi}_{a'}(2)\phi_a(3)\bar{\phi}_a(4)| - |\bar{\phi}_d(1)\phi_{a'}(2)\phi_a(3)\bar{\phi}_a(4)|\} \quad (2.20)$$

We shall be interested in comparing the amounts of ground state Ψ_0, donor excited state Ψ_1 and acceptor excited state Ψ_2, which are introduced into the c-t. state Ψ_3 when the two molecules come close together

If Ψ_3 is expanded in the form of (2.1) in which we write

$$\theta_{d3}(i)\theta_{a3}(j) = \sqrt{\frac{1}{2}}\{\phi_d(1)|\bar{\phi}_{a'}(2)\phi_a(3)\bar{\phi}_a(4)| - \bar{\phi}_d(1)|\phi_a(2)\phi_a(3)\bar{\phi}_a(4)|\} \quad (2.21)$$

(the requirement that this function be an eigenfunction of the total spin operator S^2 necessitates the use of two terms), then the perturbation term in the Hamiltonian will be

$$-Z_a/r_{1a} - \sum_{j=2,3,4}(Z_d/r_{jd} - 1/r_{1j}) + Z_aZ_d/r_{ad} \quad (2.22)$$

Z_a represents the effective nuclear charge of A stripped of its two electrons in ϕ_a, and Z_d is the effective nuclear charge of D stripped of its two ϕ_d electrons. Evaluating the matrix elements of K from (2.7), we have

$$K_{03} = \sqrt{2}\,\{{}_dH_{a'}(\mathrm{D}) + G_{da',dd} - S_{da'}[H_{a'a'}(\mathrm{D}) + G_{a'a',dd}] - S_{da}[H_{aa'}(\mathrm{D}) + G_{aa',dd}]\} \quad (2.23)$$

$$K_{13} = H_{d'a'}(\mathrm{D}) + G_{d'a',dd} - S_{d'a'}(H_{a'a'}(\mathrm{D}) + G_{a'a',dd}) - S_{d'a}(H_{aa'}(\mathrm{D}) + G_{aa',dd}) + S_{da'}(H_{dd'}(\mathrm{A}) + 2G_{dd',aa}) - S_{da}G_{dd'aa'} + G_{da',dd'} \quad (2.24)$$

$$-K_{23} = H_{da}(\mathrm{D}) + G_{da,dd} - S_{da}(H_{aa}(\mathrm{D}) + G_{dd,aa}) - 2S_{da'}(H_{aa'}(\mathrm{D}) + G_{dd,aa'}) \quad (2.25)$$

The field acting on electron i due to the nuclei and electrons of D is

$$-Z_d/r_{ia} + 2\phi_{da}(1)/r_{i1} \quad (2.26)$$

It follows that we can replace $H_{da'}(\mathrm{D}) + G_{da',dd}$ by $V_{da'}(\mathrm{D^+})$. Similarly $H_{dd'}(\mathrm{A}) + 2G_{dd',aa}$ can be replaced by $V_{dd'}(\mathrm{A})$. The matrix elements then take the form

$$K_{03} = \sqrt{2}\{V_{da'}(\mathrm{D^+}) - S_{da'}V_{a'a'}(\mathrm{D^+}) - S_{da}V_{aa'}(\mathrm{D^+})\} \quad (2.27)$$

$$K_{13} = V_{d'a'}(\mathrm{D^+}) - S_{d'a'}V_{a'a'}(\mathrm{D^+}) - S_{d'a}V_{aa'}(\mathrm{D^+}) + S_{da'}V_{dd'}(\mathrm{A}) + G_{da',dd'} - S_{da}G_{dd'aa'} \quad (2.28)$$

$$-K_{23} = V_{da}(\mathrm{D^+}) - S_{da}V_{aa}(\mathrm{D^+}) - 2S_{da'}V_{aa'}(\mathrm{D^+}) \quad (2.29)$$

If we now look at the c-t. state from the point of view of Ψ_0, ϕ_d is the donating and $\phi_{a'}$ the accepting orbital: from the point of view of Ψ_1, however, it is $\phi_{d'}$ that is the donating orbital, whilst from the point of view of Ψ_2 it is ϕ_a which is the accepting orbital. We notice the appearance of the terms $V_{\delta\alpha}(D^+) - S_{\delta\alpha}V_{\alpha\alpha}(D^+)$ in all three matrix elements, where ϕ_δ is the donating and ϕ_α is the accepting orbital. These are just the terms that we obtained in the one-electron approximation.

Other terms in the matrix elements arise from our allowing the donated electron to exchange with the other electrons of the donor or acceptor. For example, we can construct Ψ_3 from Ψ_0 by the electron transfer $\phi_d \rightarrow \phi_{a'}$ followed by the exchange $\phi_a \leftrightarrow \phi_{a'}$. This gives rise to the contribution $-S_{da}V_{aa'}(D^+)$ in K_{03}. Similarly we construct Ψ_3 from Ψ_1 by $\phi_d \leftrightarrow \phi_{d'}$ followed by $\phi_{d'} \rightarrow \phi_{a'}$. This gives rise to contribution $S_{da'}V_{dd'}(A) + G_{da'dd'}$ in K_{13}. The other terms can be associated with similar combinations of transfer and exchange. It is noticed that all the terms over and above those of the one-electron approximation involve the product of an overlap integral, or overlap density, and the transition density between two orthogonal orbitals. Thus whereas the integral $V_{a'a'}(D^+)$ will vary as the inverse first power of the D–A separation (if D is a neutral molecule), $V_{aa'}(D^+)$ will vary as the inverse second power or higher power of this separation, depending on whether the transition density $\phi_a\phi_{a'}$ can be approximated by a dipole or a higher multipole. For this reason it is to be hoped that the matrix elements evaluated for the one-electron approximation (with suitable spin factors: $\sqrt{2}$ for K_{03}, 1 for K_{13} and -1 for K_{23}) will give the most important contribution to the matrix elements.

3. The Intensity of the C-T. Band and the Binding Energy of the Complex.—We are now in a position to examine the questions posed in the introduction, namely, what is the most likely source of the intensity of the c-t. band, and can one observe c-t. absorption if no stable complex is formed?

Returning to the example of section 2 in which four-electron wave functions were used, we can write the perturbed ground state function

$$\Psi_0' = \Psi_0(DA) + a_{30}\Psi_3(D^+A^-) \qquad (3.1)$$

and the perturbed c-t. state

$$\Psi_3' = \Psi_3(D^+A^-) + a_{03}\Psi(DA) + a_{03}\Psi(D^*A) + a_{23}\Psi_2(DA^*) \qquad (3.2)$$

Since Ψ_0' and Ψ_3' must be orthogonal, we have, to the first order

$$a_{30} + a_{03} = -S_{03} \qquad (3.3)$$

and using this relationship the transition moment between these two states is then found to be

$$\mathbf{M}'_{03} = (\mathbf{M}_{03} - S_{03}\mathbf{M}_{00}) + a_{30}(\mathbf{M}_{33} - \mathbf{M}_{00}) + a_{13}\mathbf{M}_{01} + a_{23}\mathbf{M}_{02} \qquad (3.4)$$

The first two terms correspond to the expression for the c-t. transition moment given by Mulliken,[6] and discussed again in reference 5. Since the coefficient a_{30} is a measure of the c-t. stabilization of the ground state, the second term in (3.4) has been taken to represent the "complex" c-t. transition moment whilst the first term represents the contact c-t. transition moment.

Using the wave functions (2.17) and (2.20) it easily can be shown that

$$\mathbf{M}_{03} - S_{03}\mathbf{M}_{33} = \sqrt{2}\{\mathbf{M}_{da'} - S_{da'}\mathbf{M}_{dd} - S_{da}\mathbf{M}_{aa'}\} \qquad (3.5)$$

The first two terms in (3.5) are those given by the one-electron approximation; after normalizing the electron density $\phi_d\phi_{a'}$ it can be seen that they are equal to the overlap integral $S_{da'}$, multiplied by the dipole moment of the electron density $[(\phi_d\phi_{a'}/S_{da'})\cdot\phi_d^2]$. Following the same reasoning as in section 2, the largest values of this moment will be obtained when $\phi_{a'}$ is small compared with ϕ_d. However, since the reverse situation is more likely to be realized in practice, we can conclude that this dipole moment usually will be rather small.

The relative magnitude of the terms in (3.4) can best be seen by inserting the expressions for the coefficients a_{30}, a_{13} and a_{23} which are derived in section 2. Using the one-electron approximation with the correct spin factors, we have

$$M_{03}' = \sqrt{2}S_{da'}\{<(\phi_d\phi_{a'}/S_{da'}) - \phi_d^2|r> - <\phi_{a'}^2 - \phi_d^2|r> (\Delta E_{03})^{-1}W_{a'd}(A)\} + M_{01}S_{d'a'}(\Delta E_{13})^{-1}W_{d'a'}(D^+) - M_{02}S_{da}(\Delta E_{23})^{-1}W_{da}(D^+) \qquad (3.6)$$

The condition for a_{30} to be zero and hence no stabilization of the ground state, is that the overlap density $\phi_d\phi_{a'}$ shall not penetrate the electron cloud of A. This condition is most likely to be satisfied if $\phi_{a'}$ is a diffuse orbital and ϕ_d is a compact orbital. However these are just the conditions which lead to small values for the "contact" c-t. transition moment as defined by Mulliken and Orgel. We conclude therefore that both contributions to the c-t. intensity which have been considered in previous papers in this series will be appreciably smaller for contact DA pairs than they will be for true complexes.

The third and fourth terms in (3.4) can also be considered as contributing to the contact c-t. transition moment. The magnitudes of $\mathbf{M}_{01}$ and $\mathbf{M}_{02}$ depend on the intensity of the transitions D → D* and A → A* of the donor and acceptor, respectively. For an intense absorption band ($f \sim 1$) occurring with an energy of 50,000 cm.$^{-1}$, the transition moment is about equal to that associated with the displacement of a unit charge through 6 Å. We see that for intense absorption bands $\mathbf{M}_{01}$ and $\mathbf{M}_{02}$ can be as large as the expected values for $\mathbf{M}_{33}$ - $\mathbf{M}_{00}$. The coefficients a_{13} and a_{23} depend primarily on the magnitude of the overlap integrals $S_{d'a'}$ and S_{da}, respectively. As a result of the more diffuse nature of excited state orbitals we can assume

$$S_{d'a'} > S_{da'} > S_{da}$$

For example, with Slater 1s orbitals having exponents $\zeta_d = \zeta_a = {}^3/_2$ and $\zeta_{d'} = \zeta_{a'} = {}^1/_2$, then at a D–A separation of 6 a.u. we have[8]

$$S_{d'a'} = 0.349;\ S_{da'} = 0.081;\ S_{da} = 0.005$$

It is clear that there may be appreciable interaction of the c-t. state with the donor-excited states even when there is no stabilization of the ground state. The interaction of the c-t. state with the acceptor-excited state is likely to be unimportant except when a very stable complex is formed, since the two molecules have to approach close enough for the ground state orbitals to overlap, and this will generally be opposed by the exchange repulsive forces.

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(8) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

There is some experimental evidence for the small part played by the acceptor-excited states. In the strong complexes between iodine and pyridine[9] or trimethylamine,[10] the visible band of iodine lies on the long wave length side of the c-t. band and has been shifted to the blue by an amount which is a little greater than the stabilization of the ground state. Any appreciable interaction between the iodine excited state and the c-t. state would have tended to give a red shift to this band.

In addition to the above arguments based on the magnitude of the overlap integrals, it is seen that a_{13} (and a_{23}) depend on the energy of an overlap density in the electrostatic field of the donor positive ion, whereas a_{30} depends on the energy of an overlap density in the field of a neutral molecule A. Moroever, the c-t. states and donor-excited states are likely to be closer in energy than are the c-t. and ground state. Everything points to the fact that it is the interaction of the c-t. state with the donor-excited states which gives the most important contribution to the c-t. intensity, and this can certainly operate under conditions in which no stable complex is formed.

In the discussion so far, no mention has been made of any restrictions to the matrix elements imposed by the symmetry of the complex. If the direction of polarization of the c-t. state is perpendicular to the direction of polarization of some donor-excited state, then there will be no mixing of the two. To illustrate the importance of symmetry in determining the intensity of a c-t. band, we will consider the example of the benzene–iodine complex.

The X-ray studies of Hassel[11] on crystals of the Br_2:Benzene complex suggest that the most stable configuration for such molecules is one in which the halogen molecule points down toward the center of the benzene ring, the whole molecule having axial symmetry. For such a geometry the c-t. states are polarized at right angles to the direction of polarization of any $\pi \rightarrow \pi^*$ transition of the benzene molecule, hence the excited states of the donor will not contribute to the intensity of the c-t. band. However, in solution there will no doubt exist other configurations for the complex with slightly higher energy which no longer have such a high symmetry. The halogen molecule may for example lie over one of the C–C bonds, it may be tilted away from the perpendicular to the benzene ring, or it may even lie in the same plane as the benzene ring. For these configurations of lower symmetry there is now the possibility that the direction of charge transfer is no longer orthogonal to the direction of the $\pi \rightarrow \pi^*$ transitions of the donor, hence the donor excited states can now contribute to the intensity of the c-t. band. We therefore have good reason to believe that in the benzene–iodine complex it is those configurations which have rather high energy which contribute the greatest intensity to the c-t. band: some of the higher energy configurations may only exist during an accidental contact of the donor and acceptor.

In the series of complexes between iodine and the methylated benzenes the intensity of the c-t. band decreases as the complex becomes more stable (see Table I). Orgel and Mulliken[5] ascribed this behavior to the existence of contact c-t. absorption: as the complex becomes more stable the number of contact configurations will decrease. In this paper I have put forward an explanation, based on the important influence of donor-excited states, of why the contact absorption may well be more intense than the absorption of the stable complexes.

TABLE I

THE CHARGE-TRANSFER BANDS OF IODINE AND CHLORANIL WITH THE METHYLATED BENZENES

The iodine complexes were examined in CCl_4: those of chloranil were examined in butyl ether, except that the first five hydrocarbons in the table were studied in the presence of the competing complex of chloranil and N,N-dimethylaniline.

	Complexes with iodine[12]			Complexes with chloranil[13]		
	λ_{max}	ϵ_{max}	K_{eq}	λ_{max}	ϵ_{max}	K_{eq}
Benzene	292	16400	0.15	340	2180	0.30
Toluene	302	16700	.16	365	1920	0.50
o-Xylene	316	12500	.27	385	2090	1.05
m-Xylene	318	12500	.31	390	2000	0.84
p-Xylene	304	10100	.31	410	1960	0.89
1,2,4-Trimethylbenzene	..	...	..	420	1985	1.02
1,3,5-Trimethylbenzene	332	8850	0.82	410	2250	1,17
1,2,3,4-Tetramethylbenzene	..	...	..	445	2585	2.65
1,2,3,5-Tetramethylbenzene	..	...	..	450	2495	2.47
1,2,4,5-Tetramethylbenzene	332	9000	0.63	470	2320	3.02
Pentamethylbenzene	357	9260	0.88	480	2680	5.32
Hexamethylbenzene	375	8200	1.35	505	2880	9.08

In a series of related complexes, the relative behavior of the c-t. intensity and the stability of the complexes will depend roughly on the variation of the energy difference between the most stable configuration and the configuration giving the greatest c-t. intensity. To show that the behavior of the I_2–Benzene complexes is not always followed, although there are many examples which behave in the same way (for references see the review by McGlynn),[14] Table I also records the pertinent data for the chloranil–benzene complexes. For this series the c-t. intensity increases as the complex becomes more stable. It may well be that for these complexes, the donating and accepting orbitals, both being π molecular orbitals, can only overlap to an appreciable extent when the two molecules lie one on the other in parallel planes. In this configuration the direction of charge transfer is perpendicular to the benzene ring. It is to be noted that the intensity of the c-t. band is much less than for the iodine complexes.

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(9) C. Reid and R. S. Mulliken, THIS JOURNAL, **76**, 3869 (1954).

(10) S. Nagakura, *ibid.*, **80**, 520 (1958).

(11) O. Hassel, *J. Mol. Phys.*, **1**, 241 (1958).

(12) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **74**, 4500 (1952).

(13) N. Smith, Ph.D. Thesis, University of Chicago, Chicago, Illinois.

(14) S. P. McGlynn, *Chem. Revs.*, **58**, 1113 (1958).

The series of complexes between *s*-trinitrobenzene and substituted anilines[15] occupy a position intermediate between the iodine–benzene and chloranil-benzene complexes. The intensity of the c-t. band is almost constant throughout the series, and what little variation there is, does not appear to be related to the variation in the equilibrium constant.

If we have a series of complexes in which the most stable configuration is one which allows the donor-excited states to contribute to the c-t. intensity, then we should also expect the intensity to increase as the complexes become more stable. Unfortunately there appear to be few examples in the literature which could be expected to satisfy these conditions (there is some evidence that the I_2–alcohol complexes may provide one example).[16] Most complexes which have been studied involve an aromatic molecule as a donor, and in these cases the direction of charge transfer in the most stable configuration is always roughly perpendicular to the plane of the aromatic molecule.

In the discussion so far we have considered the form of the interaction between the ground state and a typical c-t. state. However, it must be remembered that all c-t. states, and not only the one of lowest energy, can contribute to the stabilization of the ground state. In the complexes between iodine and a condensed aromatic hydrocarbon, we can expect that as the size of the hydrocarbon is increased, the overlap of the donating and accepting orbital will generally decrease, since the donor orbital is presumably spread over the whole molecule. The intensity of the c-t. band will therefore decrease and the stabilization of the ground state due to the lowest c-t. state probably will decrease also. However, as the hydrocarbon increases in size the number of c-t. states which can interact with the ground state is increased, and although their accompanying c-t. bands may be hidden beneath the absorption bands of the two components, they can all contribute to the stabilization of the complex. The net result of increasing the size of the aromatic molecule may therefore be to give more stable complexes which have weaker c-t. bands. This behavior is observed both for iodine and chloranil complexes (see Table II).

TABLE II

THE COMPLEXES OF IODINE AND CHLORANIL WITH SOME CONDENSED AROMATIC HYDROCARBONS

	Complexes with iodine[17]			Complexes with chloranil[13]		
	λ_{max}	ϵ_{max}	K_{eq}	λ_{max}	ϵ_{max}	K_{eq}
Benzene	292	16400	0.15	340	2180	0.30
Naphthalene	360	2395	0.62	460	820	1.17
Phenanthrene	378	1492	1.06	..	..	..
Anthracene	430	112	52.35	610	325	7.60

In conclusion therefore we can say that c-t. absorption can be observed even if no stable complex is formed but that the intensity of this absorption comes not from the ground state but from the donor-excited states. The relative behavior of the intensity of a c-t. band and the stability of the complex for a series of similar donors depends on the variation of the difference in energy between the most stable configuration and the configuration which gives the most intense c-t. band.

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(15) A. Bier, *Rec. trav. chim.*, **75**, 866 (1956).

(16) P. A. D. deMaine, *J. Chem. Phys.*, **26**, 1192 (1957).

(17) R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958).

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Proton Spin Relaxation in Aqueous Solutions of Paramagnetic Ions. III. Copper(II)-Diamine Complexes[1-3]

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Proton spin relaxation times, T_1 and T_2, in copper(II) nitrate solutions are strongly dependent upon concentration of added ethylenediamine and 2,2'-bipyridine. Relaxation in ethylenediamine solutions is attributable to magnetic proton–electron dipole–dipole interaction and, at higher ethylenediamine concentrations, in part to isotropic proton–electron spin exchange in the complex species. In solutions having an excess of ethylenediamine beyond that required for formation of diaquobisethylenediaminecopper(II) ions, transverse relaxation (T_2) depends largely upon the rate of proton exchange between ligand molecules and solvent water molecules, permitting evaluation of the first-order proton exchange rate constants. The proton exchange rate R obeys a bimolecular rate law: $R = k'[\mathrm{Cu(en)_2(H_2O)_2}^{++}][\mathrm{en}]$, in which $k' = 2.4 \times 10^7 M^{-1}$ sec.$^{-1}$ at 27°. In copper(II)–2,2'-bipyridine solutions relaxation is by dipole–dipole interaction alone.

Introduction

The influence of dissolved paramagnetic species on proton spin relaxation times in aqueous solutions has been discussed extensively in previous papers[3,5] and in references cited there. Of particular interest in connection with the work to be reported in this paper are the data on proton thermal (T_1) and phase memory, or transverse, (T_2) relaxation times in copper(II) salt solutions over a wide range of frequencies[3,6,7] and at a number of different temperatures.[7] The present consensus is

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(3) Paper II: *J. Chem. Phys.*, **31**, 365 (1959).

(4) Magnolia Petroleum Company Fellow, 1958–1959.

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