BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2468—2674 (1967)

A Theory of the Electronic Structures and Spectra of Negative Ions

Hiroshi TSUBOMURA and Sigenobu SUNAKAWA*[1]

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka

(Received March 14, 1967)

Some aromatic anions in solutions show absorption spectra with many sharp bands in the visible and ultraviolet regions. It is pointed out that this is rather remarkable in view of the fact that aromatic molecules have very small electron affinities, nearly zero or even negative, in the gas phase. It is then emphasized that the potential for the electron in the negative ions is much more localized than the Coulomb potential. Accordingly, some of the features of the negative ions are deduced by the use of a simple well-type potential. The important conclusions obtained are: 1) Negative ions may have discrete electronic energy levels not only in the $E \leqq 0$ region but also in the $E > 0$ region, that is, higher than the detachment energy. 2) The larger the domain of the potential well for the electron, the discrete energy levels can exist at the higher energy. 3) These energy levels at $E > 0$ should, of course, be unstable, mostly leading rapidly to the electron detachment, but their lifetime are the longer, the larger the domain of the potential well. These consequences seem to account well for the above-mentioned spectra of aromatic anions. Other features of the negative ions and the nature of the charge-transfer states in the charge-transfer complexes are also discussed.

The study of the electronic structures and spectra of negative ions is a field relatively unexplored both theoretically and experimentally. Many negative ions are known to exist under various conditions, for example, OH^-, NO_3^-, Cl^-, Br^-, ⋯, exist in aqueous solutions or in ionic crystals. However they are under the strong influence of the solvent or the crystalline lattice. Their electronic structures must be discussed by taking account of these influences.

All the above-mentioned negative ions are formed from radicals or atoms which are unsaturated from the viewpoint of chemical valency. Negative ions formed from stable molecules are, on the other hand, much more reactive and need more laborious techniques for their preparation and maintenance. Recently, many organic molecular anions, mostly aromatic anions, are prepared in ethereal solutions in the form of alkali salts. They exist as nearly free ions, and are stable without the presence of water and oxygen. The electronic spectra and the ESR spectra have been extensively studied.[1-3] Also, some negative ions, such as O_2^-, have been claimed to exist as adsorbates on the surface of the alkali films and metal oxides.[4]

The presence of negative ions in the gas phase is studied by mass-spectrometry and other techniques. For example, H^-, O^-, C^-, O_2^-, OH^-, *etc.* are known to exist in the gaseous discharge.[5] The experimental and theoretical studies of negative ions in the gas phase is also dealt with in an illuminating book by Massey.[6] Owing to experimental limitations, however, the electronic spectra of these ions in the gaseous state have been measured only to a very limited extent.[5]

The electronic absorption spectra of halide anions in gaseous diatomic molecules of alkali halides, in aqueous solutions, and in ionic crystals of alkali halides have been known for a long time. They are named electron-transfer spectra, Charge-transfer spectra, or electron-affinity spectra.[7] The transition is characterized by the transfer of an electron from the halide core to the alkali cation or to the solvent. Similar electron-transfer spectra are found for aqueous OH^-, SH^-, CNS^-, *etc.*

---

*[1] Department of Physics, College of General Education, Osaka University, Toyonaka, Osaka.

1) (Electronic spectra of negative ions) P. Balk, G. J. Hoijtink and J. W. H. Schreurs, *Rec. Trav. Chim.*, **76**, 813, 850, 907 (1957); G. J. Hoijtink, N. H. Velthorst and P. J. Zandstra, *Mol. Phys.*, **3**, 534 (1961); A. Ishitani and S. Nagakura, This Bulletin, **38**, 367 (1965); *Theoret. Chim. Acta*, **4**, 236 (1966).

2) (ESR of negative ions) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961); A. Carrington and P. F. Todd, *Mol. Phys.*, **6**, 161 (1963); F. J. Smentowski, *J. Am. Chem. Soc.*, **85**, 3036 (1963).

3) (Electron affinities of aromatic anions) G. J. Hoijtink, E. DeEoer, P. H. van der Meij and W. P. Weijland, *Rec. Trav. Chim.*, **75**, 487 (1956); J. Jagur-Grodzinski, M. Feld, S. L. Yang and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965); D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

4) H. Imai, Y. Ono and T. Keii, *Shokubai (Catalyst)*, **7**, 332 (1965); J. H. Lunsford and J. P. Jayne, *J. Chem. Phys.*, **44**, 1487 (1966); K. M. Sancier, *J. Catalysis*, **5**, 314 (1966).

5) D. S. Burch, S. J. Smith and L. M. Branscomb, *Phys. Rev.*, **112**, 171 (1958); L. M. Branscomb, "Photodetachment," ed. by D. R. Bates, "Atomic and Molecular Processes," Academic Press, New York (1962).

6) H. S. W. Massey, "Negative Ions," Cambridge Univ. Press, Cambridge (1950).

7) E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

In all these cases, the electrons before the excitation are bound to the atom or radical fairly tightly, with electron affinities of the order of 3 eV or more. The above interpretation of the spectra is substantiated by both the spectroscopic and photo-chemical studies of the anions.

In this paper, some questions concerning phenomena involving the negative ions are raised and are clarified by a simple theoretical analysis.

Discussion

The Electron Affinities. It is unfortunate that reliable data concerning the electron affinities are at present available for only a very limited number of molecules and atoms. In principle, the photo-detachment experiment involving the anions in the gas phase is thought to give the most accurate values. However only the electron affinities for halogen, carbon, and sulfur atoms are determined by this method. The electron affinities of simple atoms and molecules like He or H_2 can also be determined by the computational method. Many attempts have been made to determine experimentally the electron affinities of molecules in solutions. In these cases, however, the results are inevitably confused by the inclusion of solvation energies, which amount to a few electron volts and are not easy to determine.8) Electron affinities determined from the charge transfer spectra of moleuclar complexes9) also contain ambiguous points. Recently, the electron affinities of gaseous molecules have been determined from their absorption coefficients for the free electrons produced in the so-called electron capture detector.10) This method seems to have a wide applicability, but its validity seems to need more examination.

To summarize the knowledge derived from all these sources, the electron affinities of aromatic hydrocarbons and other carbon compounds without specially electronegative substituents are thought to lie below 0.5 eV, many of them even below zero.8,10)

Consider an electron moving into a vacant orbital, ψ_k, of a molecule or an atom from outside. Its Hartree-Fock energy, $-E_a$, may be given by the following formula:

$$-E_a = T + V = \langle\psi_k|\Delta|\psi_k\rangle - V_{nk} + 2\sum_i J_{ik} - \sum_i K_{ik}$$

Here $-V_{nk}$ is the potential of the nucleus, while J and K are the Coulomb and exchange energies between an electron in ψ_k and that in another orbital, ψ_i. This E_a is just the electron affinity. In cases where ψ_k has an orbital with a much larger radius than the others, the absolute value of the potential energy, $|V|$, for the electron in ψ_k becomes very small, as is clear from the Gauss theorem on the electrostatic field. As ψ_k penetrates into the orbitals of the other electrons, V begins to take a large negative value.

Let us consider the fluorine atom for example. The electron coming from outside will occupy one of its 2p atomic orbitals (AO), where there are already five electrons. Hence the nucleus has a fairly large effect on the electron which has come in. The screening constant for the AO and, therfore, the average radius for the AO will be fairly small, not very different from those in the neutral F atom. This consideration accounts well for the large E_a value of fluorine (3.448 eV).11)

Next, let us consider the argon atom as another extreme case. All the sp AO's of this atom are already filled. In such a case, the screening effect on the electron from outside is very large. Consequently, it may be expected that the mean radius for the AO which will be occupied by the electron will become infinitely large; therefore, the E_a in such a case would be negative.

In many of the organic unsaturated compounds, the situation will be somewhat in between that for flourine and that for argon.

Here there arises the following question: Will negative ions really exist in cases where $E_a<0$? From the usual chemical concept, it is expected that, if negative ions are formed in such a case, they will be so unstable that the following change, called the electron detechment, will take place very rapidly:

$$A^- \rightarrow A + e$$

and that no such ions will be observable by any experimental method. What, then, is the physical meaning of the negative electron affinities, which have frequently appeared in the literature?

We have a second question, one which seems to be more difficult to answer. As is elucidated by quantum mechanics, a system under the Coulomb field takes continuous energy values in the region of positive energy. No discrete energy values can be formed in this region of positive energy. Thus, for atoms and molecules, absorption spectra usually become continuous in the $E>0$ range.*2

---

8) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952); R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

9) F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956); R. M. Hedges and F. A. Matsen, *ibid.*, **28**, 950 (1958); G. Briegleb, *Angew. Chem.*, **76**, 326 (1964); Ref. 11 c).

10) G. Briegleb, "Elektronene - Donator-Acceptor Komplexe," Springer, Berlin, Göttingen, Heidelberg (1961).

11) a) W. E. Wentworth and R. S. Becker, *J. Am. Chem. Soc.*, **84**, 4263 (1962); b) R. S. Becker and W. E. Wentworth, *ibid.*, **85**, 2210 (1963); c) W. E. Wentworth, E. Chen and J. E. Lovelock, *J. Phys. Chem.*, **70**, 445 (1966).

*2 It has recently been found that sharp absorption lines of atoms may exist in the range of $E>0$.12) The upper levels, however, arise from two-electron excitation. In this paper, we are dealing only with cases of one-electron excitation.

12) R. S. Berry and C. W. Reiman, *J. Chem. Phys.*, **38**, 1540 (1963).

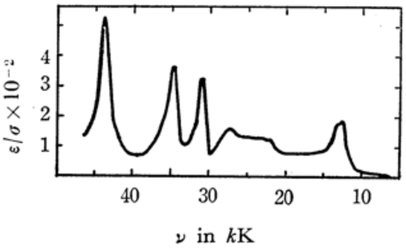

Fig. 1. Absorption spectrum of naphthalene negative ion in tetrahydrofuran (sodium ion as the counter ion). Taken by kind permission of Professor G. J. Hoijtink.

On the contrary, for some negative ions, especially for aromatic anions in solution, many sharp absorption bands are found in the visible and ultraviolet regions, although their electron affinities are definitely below 1 eV. In Fig. 1, the spectrum of the naphthalene negative ion is shown as an example. This figure shows that there are discrete energy levels up to 5 eV above the ground state of the anion; this fact seems to be difficult to explain even if the stabilization of the anion by the solvation energy is taken into account.*[3] These question will be discussed below by making use of a simple model.

The One-electron Potential for the Negative Ion. To make the problem simpler, we will, in most cases, consider negative ions as one-electron systems under a spherically symmetric potential. The potential for the outmost electron in the negative ion may be characterized by the well-type curve shown in Fig. 2-a, while those for the neutral molecules or atoms become asymptotically closer to that of the Coulomb potential at large distances (Fig. 2-b). The important difference between the two is that the coulomb potential is of a long-range nature, while the potential for the negative ion has a very limited range of action; namely, it rapidly approaches zero beyond a certain value of the radius. This latter statement has already been verified qualitatively by what has been discussed in a previous section of this paper. This characteristic of the potential for the negative ions was also pointed out by Massey, who took the hydrogen negative ion (H^-) as an example.[6] As Fig. 2-b shows, the energy levels for the electron in the Coulombic potential form the Rydberg series $E_n = R_0/(n-\sigma)^2$ as the energy approaches zero, and become continuous in the $E \geqq 0$ region. The orbital for the electron also becomes very large, with a radius larger than, say, 10 Å. In the next section we will describe what kind of a consequence these different characteristics for the potentials in the neutral molecules and negative ions have.

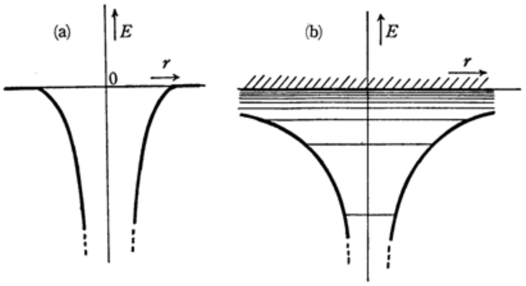

Fig. 2. The potential energy curve.
(a) For the negative ion
(b) For the neutral atoms of molecules (Coulomb potential)

A Theory Based on a Well-type Potential. Based on the remark that the negative ion generally has a potential with a limited region of action, we approximate it by a simple well-type potential (Fig. 3) with the radius R and the depth V_0. The r coordinate is the distance from the center of the ion. The present treatment is mathematically analogous to that frequently used for the treatment of the resonance capture and the α-decay in nuclear physics.[14]

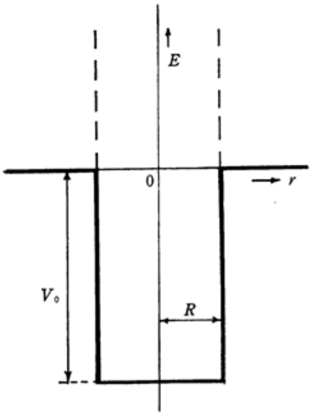

Fig 3. The well-type potential as a model for the negative ion.

The Schrödinger equation for an electron with mass m and energy E is in this case as follows:

For $r < R$ $\quad d^2u/dr^2 + K^2u = 0 \qquad (1)$

For $r > R$ $\quad d^2u/dr^2 + k^2u = 0 \qquad (2)$

where $u = r\psi(r)$, $\psi(r)$ being the wave function;

---

*[3] One might recall here the theory set forth by Plazman and Franck[13] to explain the electron transfer spectra of anions in aqueous solutions by taking account of the potential due to the solvation sphere induced by the electric charge of the anion. However, the solvents which are in question here (organic ethers) have dielectric constants (4—5) much lower than that of water (80) and so the solvation will be much weaker.

13) See, for example, H. Massey, *Endeavour*, **25**, 59 (1966).

14) R. Plazman and J. Franck, *L. Farkas Memorial Volume (Res. Council Israel)*, **1**, 21 (1952).

$E=\hbar^2k^2/2m$, and $E+V_0=\hbar^2k^2/2m$. V_0 is taken to be a positive value. These equations may be regarded as wave equations for a wave passing through two media, each having a different index of refraction. The transmission coefficient at the boundary is the same for both the in-going and out-going waves and is given by $T=4kK/(K+k)^2$. If $K\gg k$, then $T\ll 1$. This means that, once an electron with $V_0\gg E>0$ enters into the region of the well, its wave is reflected back and forth in this region with a decaying amplitude; consequently it is trapped for a while, forming a metastable state. (On the other hand, for the Colulomb potential where no boundary exists, the bound state is formed only for $E<0$, and not for $E>0$, not even momentarily.)

Thus, assuming that a metastable state is formed in the $E>0$ region, we may express the solution of Eqs. (1) and (2) as follows:

$$\text{For } r\leqq R \qquad u(r) = A\sin Kr \tag{3}$$

$$\text{For } r> R \qquad u(r) = Be^{ikr} \tag{4}$$

Equation (3) represents a stationary wave which takes the zero value at $r=0$, while Eq. (4) represents an out-going wave, which represents the decay of the metastable state. The fact that the two wave functions have the same values of u and $\mathrm{d}u/\mathrm{d}r$ at $r=R$ leads to the following equation:

$$f(E) = ikR \tag{5}$$

where

$$f(E) = KR\cot(KR) \tag{6}$$

To obtain an approximate solution of Eq. (5), we first assume the right side of (5) to be small and solve the following equation:

$$f(E_s) = 0 \tag{7}$$

to obtain the real eigenvalues,

$$E_s = (\hbar^2\pi^2/2mR^2)(n+1/2)^2 - V_0 \qquad n=1,\ 2,\ \cdots \tag{8}$$

Then, expanding $f(E)$ around E_s and taking the first non-vanishing term, we obtain

$$f(E) = (\partial f/\partial E_s)(E-E_s) = ik_sR \tag{9}$$

and:

$$E = E_s - (i/2)\Gamma_s,\ \Gamma_s = -2k_sR/(\partial f/\partial E_s) \tag{10}$$

This solution for E, being of the complex number, represents a quasi-stationary state with energy centered at E_s and decaying according to the formula $\exp(-\Gamma_s t/\hbar)$. According to the uncertainty principle, this means that the E_s level has a width of Γ_s. From (9) and (10) we obtain:

$$\Gamma_s = 2k_s\hbar^2/mR \tag{11}$$

Let us first see how these results agree numerically with the experimental results. First, one may see that the energy levels, E_s, given by (8) are the same as for the equation frequently used to represent the stationary energy levels of a particle with $E<0$ in the well-type potential. The formula also agrees (with a minor difference) with that derived from the so-called free electron theory. In our treatment, therefore, the energy levels for the true stationary states ($E<0$) and those for the metastable states ($E>0$) are expressed by one formula.[*4]

It is well known that this formula gives a good semi-quantitative representation of the electronic spectra of conjugated molecules. For example, taking R to be 3 Å, the transition energy from the nth to the $(n+1)$th level becomes *ca.* 2.0 $(n+2)$ eV. By using the same R value, the width is calculated as follows from (11):

$$\Gamma_s = \sqrt{E}\,\hbar/\pi\sqrt{2m}\,R = 1.4(n+1/2)\ \text{eV}$$

These values seem to accord fairly well with the observed spacings and widths of the electronic bands of aromatic negative ions in spite of the crude model we have adopted here.

To make a more detailed comparison between these results and the experimental data, we must define the quantum numbers for each anion. The anions actually contain many electrons; hence, reasonable values of the quantum numbers for the electron in the question might be obtained by distributing all the electrons in the anion in accordance with the Pauli principle, with, that is, electrons filling each of the energy levels defined by (8) and shown in Fig. 4. Whether a molecule (or an atom) has a positive or negative electron affinity depends on whether there is a vacant level in that molecule or atom with $E<0$. Actually, however, the determination of quantum numbers

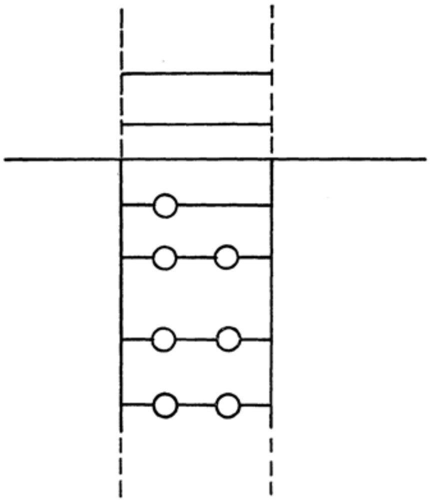

Fig. 4. Electronic configuration of the negative ion, an example.

[*4] This might suggest that it is a fairly good approximation to use the usual LCAO-MO-type wave functions not only for the true stationary states ($E<0$), but also for the metastable states ($E>0$).

for each molecule or atom is not a simple matter, for, first, the potential used here is too simple for a treatment of molecules or even complex atoms, and second, the angular part of the wave-functions must be taken into account. Hence, we must be satisfied at the moment to see that the results for E_s and Γ_s give fairly reasonable values for the spacing of the energy levels and their width.

The main conclusions obtained from the foregoing treatment may be summarized as follows:

1) For the negative ions, the potential for the outmost electron has a much more limited range of action and may, in this respect, be approximated by the well-type potential.

2) For the well-type potential, or, more generally for a potential with a limited range of action, the electrons may have metastable, discrete energy levels, even in the $E>0$ range.*5

3) The width of the metastable level and, hence, the decay rate become larger, the higher the energy level and the smaller the range of action, R. In other words, the larger the size*5 of the negative ion, the higher the energy range becomes where discrete energy levels are found.

Aromatic Negative Ions and Their Electronic Spectra. The conclusions given above seem to be in good accord with the presence of many sharp absorption bands in the spectra of the solutions containing aromatic anions. Namely, the large size of these anions is considered to be favorable for the formation of discrete electronic energy levels up to a considerably high level of energy. It has been pointed out by Hoijtink and his group that the absorption spectra of aromatic anions are very similar to those of the cations; this can be explained by the theory of the molecular orbitals of the alternant hydrocarbons.1) However, no argument has been made for the validity of applying the MO theory to such systems as the negative ions, where a part of the energy levels are thought to be much higher than the detachment energies. The present treatment has made it clear that negative ions can have discrete energy levels in a region higher in energies than that for the detachment energies. In such cases, the factors which determine the energy levels are mainly the shape and spatial extent of the potential well and not the electron affinities.

It is known that discrete energy levels exist for some atoms and molecules in the region higher than their ionization potentials. They are thought to arise from the excitation from inner cores, or from the two-electron excitation. The present treatment does not logically exclude the possibility that the sharp absorption bands found for the negative ions are partly due to these types of excitation. The present treatment of the negative ions may logically explain why these ions do not necessarily show continuous absorption in the region higher than their detachment energies.

It must be pointed out that the energy of solvation may stabilize the electronic energy levels of the negative ions considerably, making a few levels true stationary states. The characteristics of the spacing and width of the levels will, however, be determined mainly by the potential for the electron in the molecule itself, and not much by the solvent.

For electrons under the influence of the Coulomb potential, the radius of the orbital whose energy is near the ionization limit is very large. For the negative ions, however, the radii for the orbitals with energies near the detachment energy or higher will probably be about the same as that for the molecule. This accounts well for the fact that the electronic spectra of negative ions are little influenced by the solvent effect, in spite of the large electrostatic forces between the solvent molecule and the negative ion. Marchetti and Kearns reported that no photo-current was detected for solutions containing aromatic negative ions when they were excited in the range of their first absorption bands, but one was detected by light in the region of the second absorption bands.15) This observation seems to be explainable by assuming that the excited state corresponding to the first absorption band is below the detechment energy, while that for the second absorption band is above it.

For an understanding of the actual spectra of aromatic anions, the configuration interactions between configurations arising from various types of one-electron excitation must be taken into account.

As has already been mentioned, the fact that many sharp bands have been observed in the electronic spectra of aromatic anions can probably be explained by taking account of the large size of these anions. For the simpler anions, halides, OH^-, *etc.*, the range of the potential well must be much smaller. This may account for the fact that each of these anions has only one broad absorption peak in the ultraviolet region.*6

The Effect of the Centrifugal Barrier. In the foregoing discussions, no account has been taken of the angular momentum of the outmost electron in the negative ion. In other words, it has been tacitly assumed that we are dealing with s-electrons ($l=0$). For the electron whose angular momentum

---

[*5] Although the present treatment is based on the well-type potential, we feel that the main conclusions described in this paper can probably be drawn from a more general type of potentials with a more limited range of action than that for the Coulomb potential. More precisely speaking, the size of the orbital for the outmost electron.

15) J. M. Blatt and V. F. Weisskopf, "Theoretical Nuclear Physics," John Wiley, New York (1952). Esp. Chapter VIII.

[*6] Some halide anions show two peaks by the *L-S* coupling in the upper states.

is given by the quantum number $l(\neq 0)$, there is a potential called the centrifugal barrier and given by:

$$\hbar^2 l(l+1)/2mr^2 = 3.8\, l(l+1)/r^2 \quad (\text{eV}, r \text{ in Å}) \qquad (12)$$

In Fig. 5, this potential is drawn in the cases when $l=1$, 2, and 3.

Let us, for example, take a negative ion whose potential due to the nuclei and other electrons is given by V in Fig. 5, and whose outmost electron has $l=3$. Then, the total potential, that is, the sum of the two, is shown by the broken line. The angular momentum thus produces a barrier potential for the electrons trapped in the molecule. As may be seen from the figure, the effect of the centrifugal barrier on the shape of the potential seems to be rather small and it may be expected that not much change in the general pattern of the spacings and width of the excited states of the anions will be produced by the centrifugal barrier. Some of the metastable energy levels near $E=0$ may, however, become lower than this barrier. Consequently, they become more stable, and the absorption spectra corresponding to these states of the anion may become sharper as a result. Owing to the tunnelling of the electron through this barrier, however, these levels are still not true stationary states.[*7]

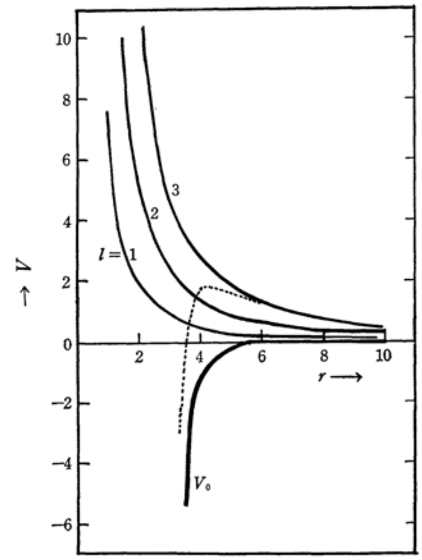

Fig. 5. Potentials arising from centrifugal force.

The Problem of Weak Charge-transfer Complexes. The theory of charge-transfer (CT) interactions and charge-transfer spectra is so well known that it is not necessary to give a detailed description here. We need only describe what is necessary for our present discussion. The ground state of the donor-acceptor pair is given by the wave function:

$$\Psi_{\mathrm{G}} = a\Psi(\mathrm{A}\cdots\mathrm{D}) + b\Psi(\mathrm{A}^-\!-\!\mathrm{D}^+) \qquad (13)$$

There is the excited state:

$$\Psi_{\mathrm{E}} = -b^*\Psi(\mathrm{A}\cdots\mathrm{D}) + a^*\Psi(\mathrm{A}^-\!-\!\mathrm{D}^+) \qquad (14)$$

The CT spectrum is thought to arise from the transition from G to E. The transition energy for weak complexes is often given by the following equation:

$$\begin{aligned} \boldsymbol{h}\nu &= \mathrm{W_E} - \mathrm{W_G} \approx \mathrm{W}(\mathrm{A}^-\!-\!\mathrm{D}^+) - \mathrm{W}(\mathrm{A}\cdots\mathrm{D}) \\ &= I(\mathrm{D}) - E_a(\mathrm{A}) - e^2/R + \Delta \end{aligned} \qquad (15)$$

where $I(\mathrm{D})$ is the ionization potential of the donor; $E_a(\mathrm{A})$, the electron affinity of the acceptor; $-e^2/R$, the Coulomb energy between D^+ and A^-; and Δ, other minor interaction energy terms. The binding energy between $\Psi(\mathrm{A}\cdots\mathrm{D})$ and A and D in the CT complex is explained as arising from the configurational interaction between $\Psi(\mathrm{A}\cdots\mathrm{D})$ and $\Psi(\mathrm{A}^-\!-\!\mathrm{D}^+)$. This is an outline of the theory, developed mainly by R. S. Mulliken, that has turned out to account well for quite many experimental results.

It might be clarifying to build a potential energy curve for the electron transferring from D to A. Without the presence of A, the curve is evidently that for an ionization curve, which tends to take the shape of the Coulomb potential curve over a long distance. With the presence of A, which causes van der Waals contact with D, the total potential will be as given in Fig. 6. Here ϕ_i and ϕ_j show the orbital energies of the highest filled MO and the lowest vacant MO, respectively. With the one-electron approximation used here, these correspond to the energy of the molecule in the ground and the lowest excited state, respectively. CT shows the energy of the CT configuration, usually given by Eq. (15). This setting of the CT level implies that an electron originally in ϕ_i is elevated to the lowest vacant MO of A under the influence of D^+ (mostly Coulombic energy).

When the distance between D^+ and A^- is very large, the CT level defined above has a clear physical meaning. As D^+ and A^- approach each other, however, the CT level as defined does not necessarily have a definite physical meaning. For strong acceptors with E_a's of a few electron volts,

---

[*7] If one assumes the aromatic hydrocarbons, benzene, napthalene, *etc.*, to have approximately the shape of a circular disk, then the quantum number, q, for the Hückel-type π-electron MO's $(0, \pm 1, \pm 2, \cdots)$ defines the angular momentum of the electronic motion around the principal symmetry axis of the molecule.[16] In benzene, the highest filled orbital has $q=1$, so that the electron coming from outside will occupy the orbital with $q=2$. For the naphthalene anion, the electron from outside will occupy the orbital with $n=3$. In Fig. 5, the broken curve for the synthetized potential is drawn with naphthalene in mind. For the actual molecules, the situation is, of course, much more complex. However it might still be possible to take these quantum numbers as representing the approximate angular momentum of the levels.

16) A. Marchetti and D. R. Kearns, *J. Chem. Phys.*, **44**, 1301 (1966).

the CT level is well below the top of the barrier, P. In such a situation, the modification of the configuration due to the influence of the potential of D^+ will be small, and it seems reasonable to take the CT configuration as a first approximation to the real state.

For many organic molecules known to act as acceptors, however, the E_a's are about zero; the CT level thus defined may be above P, as is shown in Fig. 6. On account of this conditions, the situation drastically changes. If we do not make use of the concept developed in the early part of this paper, the CT configuration seems to become inadequate as a first approximation to the real state, because, according to the usual concept, a CT configuration higher than the point P may be very unstable; the CT level width becomes very broad, and its energy has no definite value. Therefore, the question arises why the CT configuration yields results which agree with the experimental data.

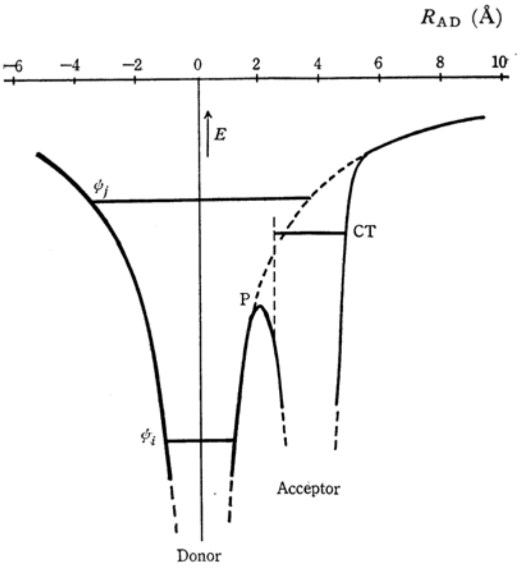

Fig. 6. Potential for an electron in the charge-transfer complex.

This question may be much clarified by introducing the theoretical consequences of the present paper. Namely, in the CT complex the potential for the electron appears to have a rather sharp edge at the turning point, P; the discrete energy level may, therefore, exist in the region above P as a metastable state, and the wave function may be relatively localized within the acceptor molecule. Therefore, even in such a case it is reasonable to take the CT configuration as a first approximation. The potential due to D^+ changes only slowly in the region of the acceptor; hence it will cause only a small change in the nature and energy of the acceptor level. It will just depress the latter by a constant amount whose average value will probably be given by $-e^2/R$ fairly accurately. Thus, the validity of Eq. (15) seems to be proved.

It should be added that some of the excited configurations of the donor arising from such transitions as $\psi_i \rightarrow \psi_j$ may interact with the CT configuration. It is very probable that there are always one or two locally-excited configurations of the donor or the acceptor which may interact rather strongly with the CT configurations. This has already been suggested in Mulliken's original paper.[17]

The above statement will be true for extremely weak CT interactions in such systems as named "contact CT pairs" by Mulliken.[18] For example, the spectra arising from the interaction between an oxygen molecule and various organic molecules can be explained as due to a kind of CT interaction.[19] The electron affinity of the oxygen molecule is experimentally found to be 0.15 or 0.46 eV[20] In spite of this small electron affinity, it seems probable that O_2^- has discrete upper energy levels with relatively localized orbitals.

Recently, Ferguson and Broida proposed a CT interaction between nitiric oxide as a donor and krypton as an acceptor.[21] This interpretation appears to be going too far, for rare gases such as krypton are conceivably atoms that act as acceptors only with difficulty. However, from what has been described in this paper, there are no definite theoretical grounds for refuting the idea. Hence, this assumption is open to future scrutiny and criticism.

The authors' thanks are due to Sachiko Ozaki for her help in preparing the manuscript.

---

[17] J. R. Platt, *ibid.*, **17**, 484 (1949).

[18] R. S. Mulliken, *Rec. Trav. Chim.*, **75**, 845 (1956).

[19] H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960).

[20] 0.15—0.46 eV, See Ref. 5.

[21] E. E. Ferguson and H. P. Broida, *J. Chem. Phys.*, **40**, 3715 (1964).