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Discovery of a Neutral-to-Ionic Phase Transition in Organic Materials

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A systematic study of mixed stacked organic charge-transfer compounds shows that these materials are either neutral or ionic and that they range from being near the neutral-ionic boundary to being far away. Under pressure, several neutral compounds near this boundary are found to undergo a reversible phase transition to an ionic ground state. This is the first observation of a neutral-to-ionic transition in any kind of material.

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Organic charge-transfer solids are composed of planar, aromatic donor (*D*) and acceptor (*A*) molecules that tend to stack either in separate donor and acceptor stacks or in mixed stacks where donors and acceptors alternate along the stack.[1] Interest in these materials has been focused on those exhibiting high conductivity, but recently has expanded to cover other properties and aspects of this large class of materials. In this paper, we report the observation of new effects in insulating charge-transfer compounds that have mixed stacks. These materials are either neutral or ionic, but we find that under pressure certain neutral compounds become ionic. This is the first observation of a neutral-to-ionic transition in any kind of material. It is thus appropriate to begin with a discussion on what factors makes one compound neutral and another ionic.

In contrast to inorganic compounds, the overlap (transfer integral) between neighboring molecules in an organic solid is small compared with other energies involved and can be neglected. In this case, the degree of charge transfer is determined by the competition between two energies[2]: $(I-A)$, the cost of ionizing a donor-acceptor (D-A) pair (I is the ionization potential of the donor and A is the acceptor electron affinity), and $\alpha\langle e^2/a\rangle$, the electrostatic Madelung energy[3] gained if the lattice is ionic. The total energy per D-A pair is then given by[2]

$$E(\rho)=(I-A)\rho-\alpha\langle e^2/a\rangle\rho^2, \tag{1}$$

where ρ is the degree of charge transfer. For $0 \leqslant \rho \leqslant 1$, the lowest value of the energy $E(\rho)$ occurs for one of two possible values of ρ: (1) $\rho=0$ if $I-A>\alpha\langle e^2/a\rangle$ and the solid is *neutral*; or (2) $\rho=1$ if $(I-A)<\alpha\langle e^2/a\rangle$ and the solid is *ionic*. Thus, according to the simplest model, materials with small overlap are *either* neutral *or* ionic, as is observed[1] for mixed stacked organics. The effect of including the transfer integral has been studied rigorously by Soos and co-workers.[4] They find that although the overlap hybridizes the states so that ρ has values between 0 and 1, a distinct transition remains between the nominally neutral ($\rho \gtrsim 0$) and the nominally ionic ($\rho \lesssim 1$) ground states. In this paper we will refer to these states as "neutral" and "ionic," even though they are not completely neutral or completely ionic.

It is useful to calculate the energy of the electronic excitations of mixed stacks of both neutral and ionic molecules. In a neutral solid, the lowest energy excitation corresponds to exciting an electron from a donor to a neighboring acceptor along the stack. The energy of this charge-transfer (CT) transition is[2]

$$h\nu_{\mathrm{CT}}{}^{N}=(I-A)-\langle e^2/a\rangle. \tag{2}$$

For an ionic solid, the lowest excitation corresponds to transferring an electron from a charged acceptor back onto a neighboring donor[2]:

$$h\nu_{\mathrm{CT}}{}^{I}=(2\alpha-1)\langle e^2/a\rangle-(I-A). \tag{3}$$

These calculated values of $h\nu_{\mathrm{CT}}$ are plotted as the *V*-shaped straight lines in Fig. 1 versus $I-A$ (top scale). The vertical dashed line is the neutral-ionic boundary, where $I-A=\alpha\langle e^2/a\rangle$.

Experimental values of $h\nu_{\mathrm{CT}}$ are obtained by measuring the optical absorption spectrum of powdered samples dispersed in KBr. Two examples of these spectra are given in Fig. 2 (temporarily ignoring the solid-line spectrum). The strong absorption in the 3–5-eV range is characteristic of the intramolecular absorption of neutral molecules. Indeed, ionic molecules would strongly absorb in the visible region (1.5–3 eV), a fact used to determine whether these solids are neutral or ionic. The absorption band in the infrared (< 1.5 eV) is the desired charge-transfer band (arrow, Fig. 2), which shifts to lower energy as the acceptor's electron affinity increases. The energy at the absorption peak is used[5] as a measure of $h\nu_{\mathrm{CT}}$ for the series of compounds in Table I, chosen to represent a broad range of different molecules and different values of $I-A$.

In addition to values of $h\nu_{\mathrm{CT}}$, the simple theory requires values of $I-A$ and the Madelung energy.

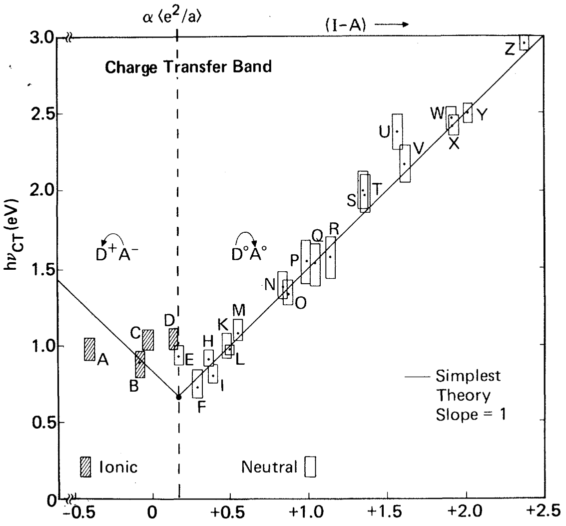

FIG. 1. Comparison of simplest model with $h\nu_{\mathrm{CT}}$ for the compounds in Table I. Vertical dashed line is neutral-ionic boundary.

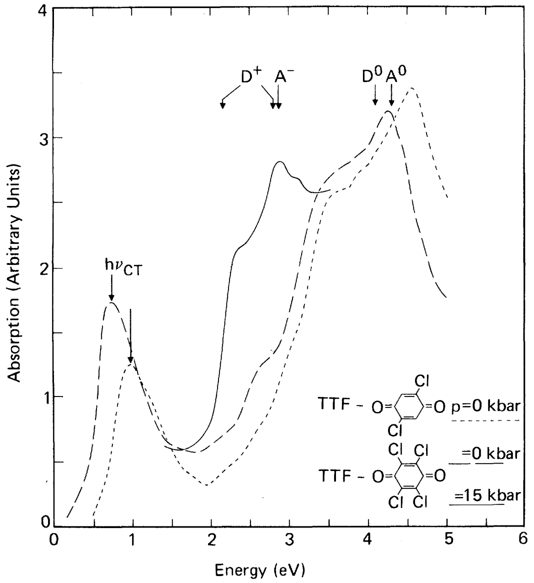

FIG. 2. Absorption spectra of compounds *K* and ***F*** as powders dispersed in KBr and that of a sublimed film of ***F*** at 15 kbar (solid).

TABLE I. Compounds in Fig. 1. TMPD stands for tetramethylphenylenediamine; TCNQ, tetracyanoquinodimethane; TMDAP, tetramethyldiaminopyrene; TTF, tetrathiafulvalene; DEDMTSeF, diethyldimethyltetraselenafulvalene; DDQ, dichlorodicyano-*p*-benzoquinone; TCNE, tetracyanoethylene; PMDA, pyromelliticdianhydride.

Symbol	Compound	*N*/*I*
A	TMPD-tetrafluoroTCNQ	*I*
B	dimethylphenazine-TCNQ	*I*
C	TMPD-TCNQ	*I*
D	TMPD-chloranil	*I*
E	TMDAP-TCNQ	*N*
F	TTF-chloranil	*N*
G	TTF-fluoranil	*N*
H	DibenzeneTTF-TCNQ	*N*
I	DEDMTSeF-diethylTCNQ	*N*
J	TMDAP-fluoranil	*N*
K	TTF-dichlorobenzoquinone	*N*
L	perylene-tetrafluoroTCNQ	*N*
M	perylene-DDQ	*N*
N	perylene-TCNE	*N*
O	perylene-TCNQ	*N*
P	TTF-dinitrobenzene	*N*
Q	perylene-chloranil	*N*
R	pyrene-TCNE	*N*
S	pyrene-chloranil	*N*
T	anthracene-chloranil	*N*
U	hexamethylbenezene-chloranil	*N*
V	naphthalene-TCNE	*N*
X	anthracene-PMDA	*N*
Y	anthracene-tetracyanobenzene	*N*
Z	phenanthrene-PMDA	*N*

Since the gas phase values of I and A are difficult to obtain for all the molecules in Table I, we utilize the well-established relationship[6] between the solution electrochemical oxidation (reduction) potential and the ionization potential (electron affinity). Thus, we approximate $I - A = \Delta E_{\mathrm{red/ox}} + \Delta G$, where $\Delta E_{\mathrm{red/ox}}$ is the difference between the oxidation potential of the donor and the reduction potential of the acceptor, and ΔG is a constant representing the solvation energy. Madelung-energy calculations have been performed[7] on only four of the compounds in Table I, but this energy differs by only a few tenths of an electron volt for these four different compounds. Since these differences are much smaller than the large differences in $\Delta E_{\mathrm{red/ox}}$, the latter must dominate the differences between compounds. Thus, we can assume for our purposes that the Madelung energy is approximately the same for all the compounds in Table I.

Hence, for the compounds in Table I, we plot in Fig. 1 the measured $h\nu_{\mathrm{CT}}$ vs $\Delta E_{\mathrm{red/ox}}$, the electrochemical measure[8] of $I - A$. The data for neutral compounds are shown as open boxes, while those for compounds showing ionic absorption are hatched. Shifting the V-shaped prediction of the simplest theory, there is a relatively unique fit to the data (Fig. 1), that is remarkably good considering the simplicity of the theory and the approximations used. In addition, the neutral-ionic boundary (dashed vertical line in Fig. 1) actually tends to separate the neutral from the ionic compounds. The poor agreement for the ionic compounds is presumably because their frequency [Eq. (3)] is more sensitive to the Madelung factors. A separate test of the fit evident in Fig. 1 is to compare the magnitudes of the resulting parameters. Using the value[6] of $\Delta G = 3.9$ eV and the fits to Eqs. (2) and (3) shown in the figure, we obtain $\langle e^2/a\rangle = 3.4$ eV and $\alpha\langle e^2/a\rangle = 4.1$ eV, compared with the average calculated values[7] of 3.4 and 4.4 eV, respectively. This agreement demonstrates the validity of using Fig. 1 as a rough guide for comparing, correlating, and obtaining an overview of these materials. We can also conclude that mixed stack compounds in Table I form *a class of materials which are either neutral or ionic, but which range from being near the neutral-ionic boundary to being far away.* Either $h\nu_{\mathrm{CT}}$ or $\Delta E_{\mathrm{red/ox}}$ in conjunction with Fig. 1 can be used as a measure of how far the compounds are from this boundary. Since $h\nu_{\mathrm{CT}}$ is a solid-state measurement and since it includes a measurement of $\langle e^2/a\rangle$ [Eq. (2)], it is a more accurate measure than $\Delta E_{\mathrm{red/ox}}$ which is a solution measurement.

The potentially interesting compounds in Fig. 1 are those near the boundary between neutral and ionic. The idea occurred to us to take some of the neutral compounds nearest the boundary, and to apply pressure, thus favoring the ionic state. In these easily compressible solids, the pressure would decrease the spacing between molecules, increase the Madelung energy, and hence shift the boundary in Fig. 1 toward the right. If the boundary shifts far enough, the neutral compound would become ionic. This change would be readily detectable by the appearance of absorption in the visible region; that is, neutral compounds near the boundary are generally yellow or light green in color because the neutral molecules absorb only in the ultraviolet, while ionic compounds are highly colored due to the intramolecular transition of the ions. Thus, the experiment consists of taking several very thin, yellow single crystals of one of the neutral compounds near the boundary and placing them into a diamond anvil pressure cell. As the pressure is increased, the color of the sample is monitored visually. If there is a distinct change in color to red or brown, the pressure of this onset is measured using the R lines of ruby chips placed in the cell.

Such transitions were observed in ten of the compounds in Table I. The pressure at the onset[9] of the distinct color change is plotted in Fig. 3 versus[10] $h\nu_{CT}$ (a better experimental measure of proximity to boundary than $\Delta E_{red/ox}$). The experimental errors are apparent, as well as some breakdown in our approximations, including the assumption that the Madelung energy and its pressure dependence are the same for all materials. Nevertheless, the general trend of the data in Fig. 3 is as expected: Materials farther from the neutral-ionic boundary (higher $h\nu_{CT}$) require higher pressures for the transition.

In order to examine more quantitatively this pressure-induced color change, we have measured the absorption spectrum of TTF-chloranil (compound F) at 15 kbar. The spectrum obtained by transmission through a film sublimed onto one of the diamond anvils is shown as the solid line in Fig. 2, for comparison with the atmospheric pressure spectrum (dotted line). (Films and pellets give the same spectrum.) The change in color at the transition from yellow to red is clearly caused by the appearance of the intense absorption peak in the visible near 2.9 eV. The energy at this peak may be compared with the energies at the intense peaks in the solution spectra[11,12] of ionic $(TTF)^+Br^-$ and $K^+(chloranil)^-$ at 2.85 and 2.9 eV, respectively. In contrast, the solution absorption peak of the neutral molecules $(TTF)^0$ and $chloranil^0$ are in the ultraviolet at 4.1 and 4.3 eV, respectively, compared with the peak at 4.2 eV for TTF-chloranil at atmospheric pressure and 300 K (Fig. 2). This correlation between solid-state and molecular spectra provides strong evidence that the transition at 8 kbar in TTF-chloranil is from neutral to ionic.

In conclusion, a reversible electronic phase transition has been discovered at which a number of organic charge-transfer solids are transformed from neutral to ionic under pressure. This is the first observation of such a neutral-to-ionic phase transition in any type of material. The transition in SmS, for example, is very different, involving a transition between different states of Sm, but not involving the S atoms. In our case the transition involves both molecules: $D^0+A^0 \rightleftharpoons D^++A^-$.

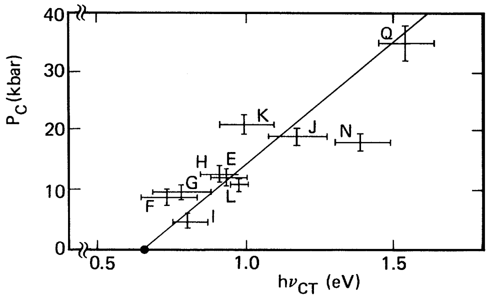

FIG. 3. Pressure at onset of distinct color change, indicating neutral-to-ionic transition. Line is drawn to guide eye.

This discovery represents the observation of a new, general, and fundamental phenomenon and reflects an increased understanding of organic materials.

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Adsorption and Dissociation of H_2 on Mg Surfaces

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A self-consistent calculation of the potential-energy surface for a molecule (H_2) on a metal surface [Mg(0001)] is presented. The following experimentally observable adsorption features are identified and interpreted: (i) an activation barrier for molecular adsorption, (ii) a mobile molecularly chemisorbed state ("precursor state"), (iii) an activation barrier for dissociation ($E_a{}^d$), and (iv) a strong dependence of $E_a{}^d$ on the adsorption-site geometry.

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For surface physics the understanding of the role of surfaces in chemical reactions, in particular the adsorption of a gas molecule, is imperative. Kinetic experiments have revealed various forms of adsorption: associative, dissociative, activated, nonactivated, or proceeding via precursor states, e.g., molecularly adsorbed states, in which the molecule is trapped on approaching the surface and is then free to move along the surface in order to seek out the preferred site of adsorption or dissociation.[1]

So far, theoretical descriptions of molecular adsorption processes on an atomic scale are scarce. Aspects of relative stabilities[2] and activation energies[3] have been deduced from calculations of one-electron energy distributions. Total energies, giving adiabatic potential-energy curves, have only crudely been obtained in semiempirical schemes.[4] The nature of the precursor state has been even less investigated, most authors describing it as a molecule weakly bound to the surface by van der Waals forces, as suggested by Lennard-Jones.[1]

This Letter presents results from detailed calculations of the potential-energy surface for H_2 on the Mg(0001) surface. These lead to a picture of the adsorption process for H_2 on Mg(0001) (Fig. 1) that can be summarized as follows: (i) As the molecule approaches the surface, it meets a barrier. It is directed towards the atop position (Fig. 1), where the barrier is lowest [the point denoted *X* in Fig. 1(a)]. Behind this barrier there is a molecularly chemisorbed state [denoted *M* in Fig. 1(b)], with a bond length only slightly larger than that of free H_2. (ii) A molecule accomodated into this state is almost free to move along the surface, i.e., it has a negligible activation energy for migration [well *M* of Fig. 1(a)]. (iii) The dissociation of the molecule above the atop site into two separate H atoms in the energetically more favorable bridge [*B* in Fig. 1(b)] or center sites is hindered by a second activation barrier [at *D* in Fig. 1(b)]. (iv) For the dissociation over the bridge site into the adjacent center sites we find that the activation energy is much lower (0.1 eV as compared to 0.5 eV in Fig. 1). Therefore, when the molecule has reached the molecularly adsorbed state *M*, it migrates around until it finds a bridge site, where it can easily dissociate. The chemisorption state *M* is consequently a good candidate for a *precursor state*.[1]

These results have been obtained with a method earlier applied to *atomic* potential-energy curves for H adsorbed on Al, Mg, and Na (Ref. 5) and Si, O, Cl, and Na on Al.[6] The calculations are self-consistent solutions of the Kohn-Sham equations with exchange and correlation effects described in the local-density approximation with