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Conduction Band Formation through the Temporary Anion States in Organic Solids

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The transmission of low-energy electrons (0—15 eV) through thin films of benzene, toluene, pyridine, aniline, styrene, and cyclohexene was studied. The electron transmission spectra of all the aromatic compounds studied are like each other in their forms. The energies of several prominent peaks in the electron transmission spectra are in good agreement with those of temporary anion states measured in the gas phase. It is suggested that vacant orbitals of free molecules form conduction bands in molecular crystals.

Recently our group1—7) and Sanche *et al.*8—10) reported a simple method for measuring the electronic levels of molecules condensed on a metal surface at low temperature. A sample film was bombarded by a beam of low-energy electrons, and the current transmitted through the film (I_t) was measured as a function of the incident electron energy (eV_i). The electron transmission spectra, recorded as dI_t/dV_i *vs.* eV_i, were found useful for the detection of optically forbidden electronic transitions1) and the determination of energies of lowest conduction bands for many orgnic solids.2—7)

The temporary anion states of organic compounds in the gas phase have been studied by electron transmission spectroscopy.11—17) Jordan and Burrow observed the vertical temporary anion states at 1.15 and 4.85 eV for benzene, at 1.11 and 4.88 eV for toluene, and at 0.19, 0.90, 1.67, 3.37, and 4.72 eV for naphthalene.11) In the electron transmission spectra of solids, peaks at ≈1.1 and ≈4.8 eV for benzene and toluene2,4) and peaks at 1.6, 3.3 and 4.8 eV for naphthalene,4) are observed. Peak energies of the transmission spectra are in agreement with the energies of temporary anion states measured by Jordan and Burrow. This suggests that peaks observed in the transmission spectra of these solids are originated from the temporary anion states.4)

In our previous papers,5,7) the peak positions in the transmission spectra for solid normal alkanes were connected with onset energies of conduction bands with high density of states. In this work, we give a further evidence that vacant orbitals of free molecules form conduction bands in organic insulators.

Experimental

The experimental procedure has been described elsewhere.2) All samples were Tokyo Kasei extra pure products. The film thickness was controlled by the deposition time under the constant vapor pressure at 1.3×10^{-5} Pa.

Results

Transmission spectra for pyridine are shown in Fig. 1. The film thickness was changed from 2 to 16 langmuir (L).[†] The spectra for the 2 to 8 L films were almost identical. Comparing the transmission spectra of pyridine and monosubstituted benzenes with those of benzene, a marked similarity is observed, at least below 8 eV.

As described in our previous papers, 2,4) the electron energy calibration was made by comparing the transmission spectra with spectroscopic data obtained in the gas phase. Solid and gas phase data are in good agreement for benzene, toluene, pyridine, and naphthalene. Recently we measured the electron impact luminescence excitation spectra of a benzene thin film and verified that the assignment of peaks in the transmission spectrum of benzene was correct.6)

Electronic excitation of molecules takes place in 10^{-15}—10^{-16} s. An excited molecule in the solid immediately polarizes surrounding molecules. The excitation energy in the solid is generally smaller than that in the gas phase by the difference of interaction energies for the ground and excited states D. Thus peak energies of the transmission spectra calibrated

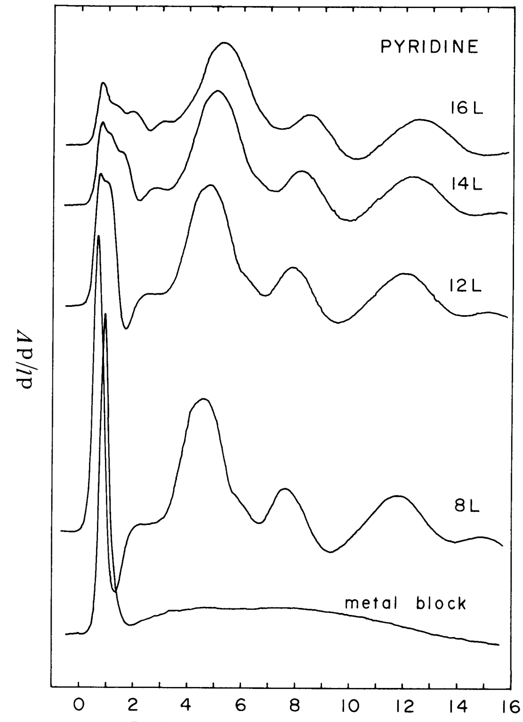

Fig. 1. The transmision spectra for pyridine. The electron energy scale was calibrated for the spectrum of an 8 L thick film. For films thicker than 8 L, all peaks including two new ones but the first peak uniformly shifted because of charging of the film. This shift was generally observed when the film was charged by electrons.

[†] The amount of the gas admitted in the vacuum chamber is expressed in langmuir units (1 L=1.33×10^{-4} Pa s).

by the gas-phase data would be overestimated by an amount of D. In molecular crystals the magnitude of D is known to be of the order of $1000\,\mathrm{cm}^{-1}$.[35]

The peak energies of the transmission spectra for pyridine are in good agreement with those of the threshold electron-impact excitation spectrum measured in the gas phase by Van Veen and Plantenga[17] (see Table 1). The assignment of peaks above ≈7 eV is difficult because the ionization of molecules in the film obscures the spectra in this energy region.

When a pyridine film thicker than 8 L suffered charging, all peaks in the spectrum except the first one uniformly shifted and the first peak decreased with the appearance of two new peaks nearby as shown in Fig. 1. The peak energies of these two were determined to be 0.7 and 1.3 eV from the spectral shift. These levels correspond to the temporary anion states (shape resonances) of pyridine at 0.62 and 1.20 eV observed in the gas phase by Nenner and Schulz.[18] For another temporary anion state at 4.58 eV observed by them, a large peak was also observed near the value in the transmission spectra.

TABLE 1. THE COMPARISON OF PEAK ENERGIES (eV) IN TRANSMISSION SPECTRA WITH ENERGY LEVELS OBTAINED WITH OTHER SPECTROSCOPIC METHODS AND THE ESTIMATED V_0 VALUES

	Electron transmission (present work)	Energy level		V_0
Benzene	1.1	1.15[b]		−0.3(−0.1[j])
	2.0			
	2.8			
	4.0		3.9[c]	
	4.8	4.85[b]	4.80[c]	
	6.1		6.16[c]	
Toluene	1.1	1.1[b]		−0.3
	2.3			
	4.0		4.1[d]	
	4.8	4.88[b]		
	5.9		5.9[e]	
Pyridine	0.7[a]	0.62[b]		−0.9
	1.3[a]	1.20[b]		
	2.4			
	4.1		4.1[f]	
	4.8	4.58[b]	4.84[f]	
	6.3		6.32[f]	
Aniline		1.13[b]		−0.9
	1.8	1.85[b]		
	3.0		3.2[g]	
	5.2	5.07[b]		
Styrene	0.7[a]	0.25[b]		−0.9
	1.3	1.05[b]		
	2.3	2.48[b]		
	3.6			
	4.7	4.67[b]		
Naphthalene	0.8[a]	0.9[b]		−1.1(−1.4[j])
	1.6	1.67[b]		
	3.3	3.37[b]		
	4.8	4.72[b]		
	5.7		5.89[h]	
Cyclohexene	2.1	2.07[b]		0.4
	4.6		4.24[j]	

a) This peak was observed when a film was charged by electrons. b) Reference 11. c) Reference 19. d) Reference 20. e) Reference 21. f) Reference 17. g) Reference 22. h) Reference 23. i) Reference 24. j) Reference 25.

Figure 2 depicts the transmission spectra of cyclohexene, benzene, toluene, aniline, pyridine, and styrene. The spectrum of cyclohexene showed a decrease of the first peak and an appearance of a second peak with increasing sample deposition. This means that the lowest conduction band energy V_0 is positive for cyclohexene and negative for other aromatic compounds.[2,4] Because the second peak approximately corresponds to the lowest conduction band energy for a compound with positive V_0,[4] the second peak of the transmission spectrum of cyclohexene can be assigned to the zero of the energy of electrons in the solid. The electron energy scale for benzene, toluene, and pyridine was calibrated using spectroscopic data.[17,19–21] The energy scale for aniline and styrene was calibrated by comparing energies of peaks indicated in the transmission spectra with those of temporary anion states measured by Jordan and Burrow.[11] They are also compared with other spectroscopic data in Table 1 and Fig. 3.

By the calibration of electron-energy scale for the electron transmission spectra described above, the lowest conduction band energies V_0 can be estimated from the amounts of positive shifts of the transmission spectra.[4] The estimated V_0 values are listed in

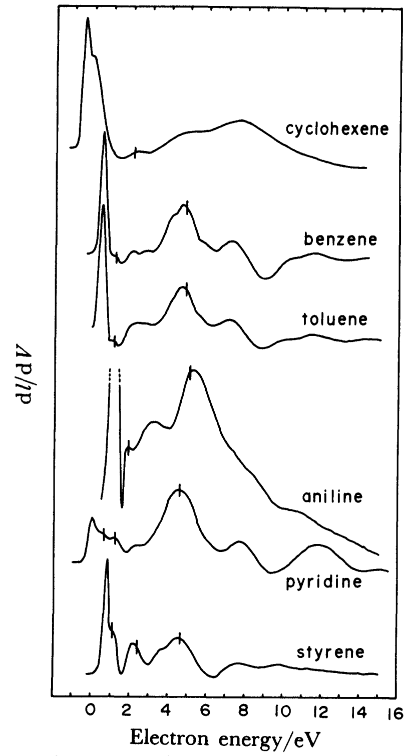

Fig. 2. The transmission spectra for cyclohexene, benzene, toluene, aniline, pyridine, and styrene. The film thickness is 16 L for pyridine and 10 L for the other compounds. The zero of the electron energy scale corresponds to the lowest conduction band energy except for pyridine. Positions of temporary anion states messured in the gas phase were indicated.[11]

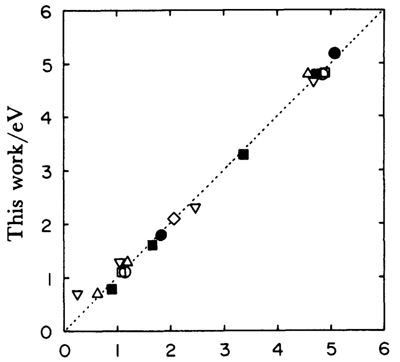

Fig. 3. The comparison of peak energies in the electron transmission spectra with temporary anion states measured in the gas phase.[11]. ○; benzene, □; toluene, △; pyridine, ●; aniline, ▽; styrene, ■; naphthalene, ◇; cyclohexene.

the last column of Table 1. The experimental error was estimated to be around ±0.3 eV. Riga *et al.*[25] compared the ESCA valence band spectra of solid polyacenes with gas phase UPS results, and obtained the V_0 values for solid benzene and naphthalene as -0.1 ± 0.2 and -1.4 ± 0.2 eV, respectively, which are fairly in good agreement with our values.

Discussion

Despite a good agreement of peak energies, there is a marked difference in their relative intensity between the transmission spectra and the threshold electron impact excitation spectra of aromatic compounds in the gas phase.[2-4,17] In the transmission spectra, peaks at about the same energies of temporary anion states are generally larger than those assigned for the exciton formation.[2,4,6,26-28] For example, excitonic peaks of pyridine observed at 4.1 ($^3A_1$) and 6.3 eV ($^1A_1$) are weaker than peaks at 0.7, 1.3, and 4.8 eV which are assigned to the temporary anion states. A large peak in the transmission spectra is due to sharp increase in the transmitted electron current at its energy. In our previous papers,[4-7] it was suggested that the transmission spectra reflect the profile of conduction bands and their peaks might correspond to the onsets of conduction bands with high density of states. Large peaks in the transmission spectra at the energies of temporary anion states suggest that the vacant orbitals of free molecules form unoccupied conduction bands when molecules are condensed.

Figure 4 shows the transmission spectra of benzene and styrene measured in the gas[11] and solid phases. The π_1* and π_2* states in the gas phase spectra have vibrational structures, unlike π_3* and π_4* states, their lifetimes ($\geq 10^{-14}$ s) being longer than those of the latter (10^{-14}—10^{-15} s)[11]. It is notable that the short-lived temporary anion states (π_3* and π_4*) give the larger and broader peaks in the transmission spectra than long lived-states (π_1* and π_2*). This may be understood as follows. When an electron is taken in a resonant state of antibonding nature in a molecule, the nuclei will oscillate along a potential well with a large equilibrium internuclear distance. Thus, the molecule suffers vibrational excitation due to the resonance. The degree of excitation is a function of spatial displacement of the nuclei in the temporary anion, hence it depends upon a lifetime of the intermediate state. Through the formation of long-lived π_1* and π_2* states for solid benzene and toluene, a primary electron would have much chance to suffer inelastic scattering. On the contrary, short-lived π_3* and π_4* states are less involved in the vibrational excitation. Besides, an electron with an excess energy of a few eV may have a mean free path $l\leq 37$ nm[29,30] in the solids. Under the circumstances, an electron generated by autoionization of a short-lived temporary anion may be delocalized in the initial phase and characterized by a wave vector k. In this case, an electron would propagate coherently in the solid and contribute to the increase of the transmitted electron current.

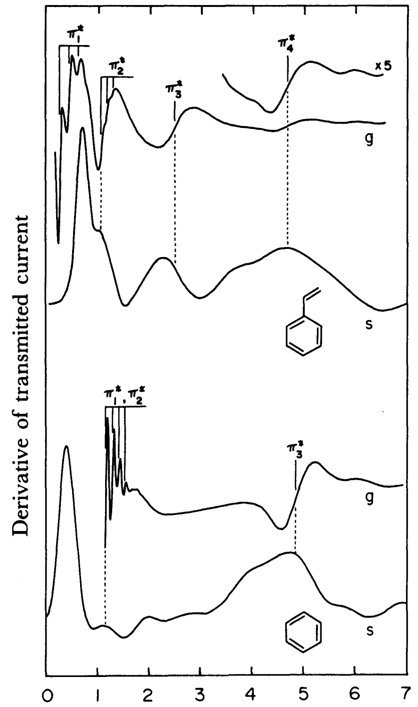

Fig. 4. The comparison of transmission spectra measured in the gas (g)[11] and solid (s) phases for benzene and styrene.

In principle, no level below the vacuum level is observed with the electron transmission experiment. For instance, the band originated from the π_1* state of styrene cannot be detected in the transmission spectrum (Fig. 4). However, this band could be observed when the film suffered charging by electrons. Two new peaks were also observed for a charged pyridine film as described before. For compounds with negative V_0 values, one might examine some levels below the vacuum level by charging the films as much as $|V_0|$.

The energy of the lowest conduction band V_0 listed in Table 1 corresponds to the ground state energy of quasi-free electrons in the condensed phase. The theoretical model for the estimation of V_0 was given by Springett *et al.*[31] The second lowest conduction bands for benzene and toluene, for instance, are observed at 1.1 eV with respect to the lowest conduction band. These bands were generated from the lowest vacant molecular orbitals of free molecules as already described.

For benzene, two peaks at 2.0 and 2.8 eV remain to be explained. In this energy region, unresolved peaks are also observed for toluene, aniline, octylbenzene,[4] biphenyl,[32] and pyridine. Because energies of these peaks are lower than the first excitonic levels, these peaks may also be due to the conduction bands. Since any kind of vacant molecular orbitals can contribute to the formation of conduction bands,[33] the origin of these bands could be the vacant molecular orbitals. Possible candidates for the formation of these bands are vacant C–C, C–H, and Rydberg orbitals. Although Jordan and Burrow could observe the transient anions associated with C–Cl* orbitals,[34] those associated with vacant C–C, C–H, and Rydberg orbitals have never been observed due to their very short lifetimes, and no comparison with the transmission spectra can be made at the present stage.

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