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Transmission of Low-energy Electrons (0—15 eV) through Thin Films of Ethers, Ketones, Alcohols, and Ice. Determination of the Quasifree Electron State Energy

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The transmission of low-energy electrons (0—15 eV) through 10—100 Å films of ethers, ketones, alcohols, and ice has been studied. Structures are indicated by electron current I_t transmitted through a thin film as a function of the incident electron energy V_i, displayed as dI_t/dV_i *vs.* V_i. With increasing the film thickness, a decrease of the height of the first peak (due to injection of electrons in the film) and an appearance of a second peak are observed for ethers and alcohols. The energies of quasifree electron state V_0 are determined by measuring the energy of the second peak from the first peak for solid diethyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-nonanol. For acetone, diethyl ketone, dimethyl sulfoxide, and ice, neither a decrease of the first peak nor an appearance of a second peak is observed, indicating that these compounds have negative V_0 values. From the energy of the onsets of broad negative peaks appeared at ≈14 eV for ethers and alcohols, the solid phase ionization energies I_s and the polarization energies of cations P^+ by the solid media are determined.

Condensed hydrocarbons are complex and electron interactions in them are the focus of much current interest. The energies of quasifree electron state V_0 have been reported for several liquid hydrocarbons.[1-5] However, attempts to measure V_0 directly in polar or nonpolar glassy matrices have failed.[5] The V_0 values in glassy matrices have been estimated by an indirect method using Eq. 1,[5-7]

$$I_l,\ I_s = I_g + P^+ + V_0 \qquad (1)$$

where I_l and I_s are the ionization potential of an impurity molecule A in a liquid and solid solution, respectively, I_g the gas phase ionization potential of A, and P^+ the polarization energy of the medium by the positive ion A^+.

Recently, Hiraoka and Hamill[8] and Sanche[9] reported a simple method for measuring the electronic levels of molecules supported as ultrathin films on a metal surface at ≈80 K. The 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 (V_i). The transmission spectra, displayed as dI_t/dV_i *vs.* V_i, were found particularly useful for detecting optically forbidden electronic transitions.[8,9] In the previous work,[10] we reported direct measurements of V_0 for solid hexane and benzene by measuring the transmission spectra dI_t/dV_i *vs.* V_i for 10—100 Å films of these compounds deposited on the metal block at ≈80 K. In this work, the interactions of injected excess electrons with solid films are studied by measuring the transmission spectra for ethers, ketones, alcohols and ice. The main objective of this work is to relate the energy dependence of the transmission features to specific interactions occurring in solid films.

Experimental

The experimental procedure has been described.[8,10] The temperature of the stainless steel metal block was ≈80 K and the pressure was $\leq 10^{-7}$ Pa. The cathode was modulated by 0.3 V at 78 Hz by the reference signal of a lock-in amplifier. The cathode voltage was swept upward with $I_t \leq 2\times10^{-9}$ A transmitted through the thin film. The transmission spectra were displayed as dI_t/dV_i *vs.* V_i, where eV_i is the energy of the incident electron. Because no established sharp transitions are available as internal standards, the zero of the electron energy scale in the present work has been chosen arbitrarily as the onset of the first peak of the spectrum dI_t/dV_i *vs.* V_i (*i.e.* for electron injection). The film thickness was changed by changing the deposition time with the constant vapor pressure of a sample at 1.3×10^{-5} Pa.

Results and Discussion

In the previous work,[10] the transmission spectra dI_t/dV_i *vs.* V_i for benzene and hexane were examined in detail. It was found that there was almost no difference in shape (height and half-width) between the first peak for the metal block and those for 2 to 10 L[†] thick benzene films. On the contrary, the first peak of transmission spectra for hexane decreased drastically and a second peak appeared and grew as the film thickness was increased. From these experimental results, it was concluded that solid films of benzene and hexane have negative and positive V_0, respectively. The energy of quasifree electron state V_0 for hexane, 0.9 eV, was determined by measuring the energy of the second peak from the first peak of the spectrum for the metal block as a reference. In the following sections, the results for ethers, ketones, dimethyl sulfoxide (DMSO), alcohols, and ice are summarized, and a discussion is made for the determination of the energy of quasifree electron state V_0, the solid phase ionization energy I_s and the cation polarization energy P^+ by the solid media.

Ethers. The transmission spectra, dI_t/dV_i *vs.* V_i, for diethyl ether, tetrahydrofuran (THF), and 2-methyltetrahydrofuran (2-MTHF) have been measured. The transmission spectra for diethyl ether and 2-MTHF are shown in Figs. 1 and 2. A drastic decrease of the first peak and an appearance of the

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[†] The amount of the gas admitted in the vacuum chamber is expressed in Langmuir units ($1\ \mathrm{L}=1.33\times10^{-4}$ Pa·s). When the sticking probability is unity, the surface will be covered by approximately one monolayer with 1 Langmuir gas admission.

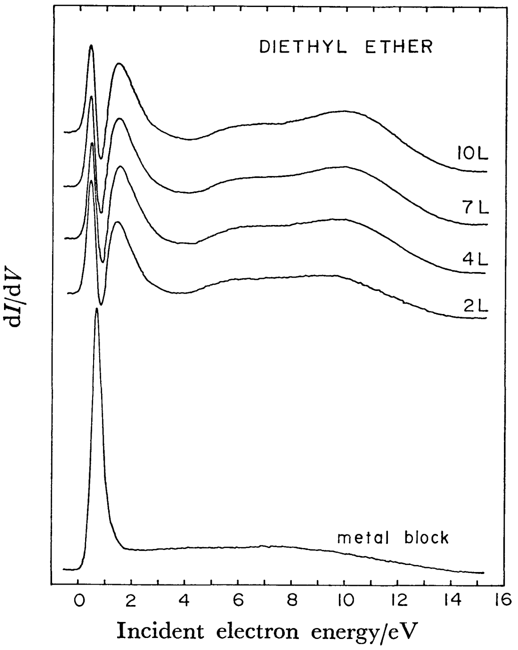

Fig. 1. The transmission spectra dI_t/dV_i *vs.* V_i for metal block and diethyl ether. The film thickness was changed from 2 to 10 L.

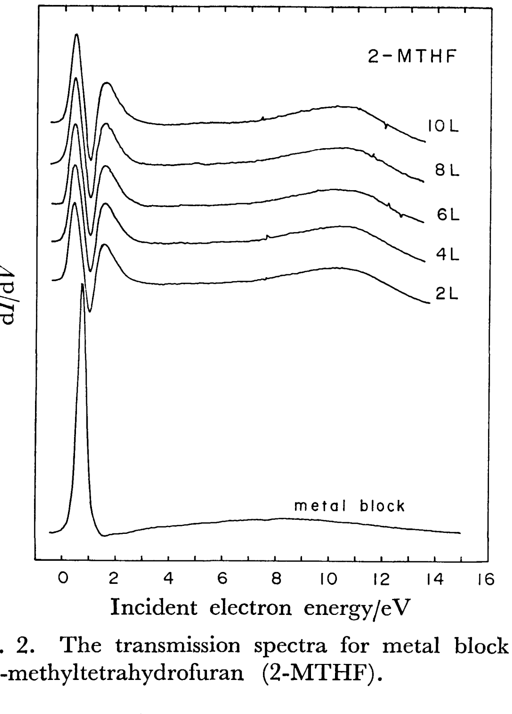

Fig. 2. The transmission spectra for metal block and 2-methyltetrahydrofuran (2-MTHF).

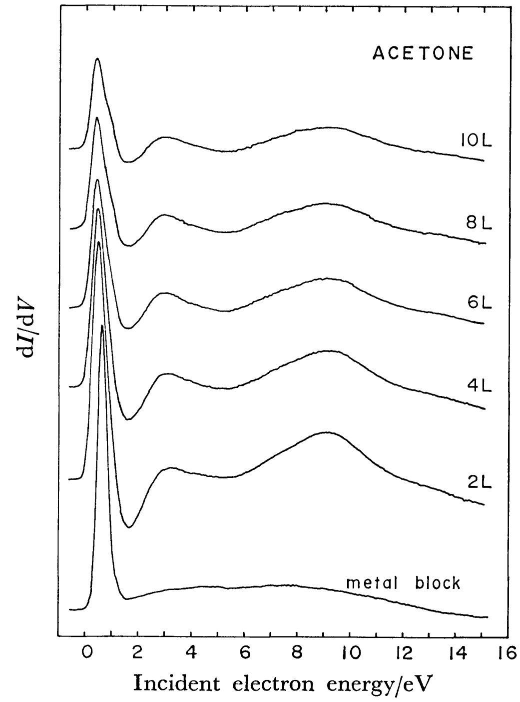

Fig. 3. The transmission spectra for metal block and acetone.

second peak and its strong growth are observed for all of these compounds, indicating that they have positive V_0.

Ketones and DMSO. The transmission spectra of acetone are shown in Fig. 3. The first peak of the transmission spectra for acetone and diethyl ketone shows only a slight decrease by the deposition of 2 L thick sample and the second peak does not show up for both of these compounds. These are characteristic features for solid films whose V_0 are negative. Thus the solid acetone and diethyl ketone are considered to have negative V_0s.

The continuous decrease of the first peak is observed for these compounds as the film thickness is increased from 2 to 10 L. This is due to the decrease of the electron emission efficiency of the cathode which is poisoned by the admission of ketone vapor in the vacuum system. The electron gun used in this experiment is a commercial TV gun (The Japan Lamp Industrial Co., Ltd) and has an indirectly heated oxide-coated cathode. This type of cathode was found to be easily poisoned by the admission of some kinds of organic vapors, especially ketones. Usually the 2 L thick film is prepared by the admission of 1.3×10^{-5} Pa vapor pressure of the sample for 20 s. In cases of acetone and diethyl ketone, 2 L thick sample was deposited by the admission of 3.3×10^{-6} Pa vapor pressure for 80 s in order to suppress the decrease of the electron emission efficiency of the cathode. This operation was successful only to some extent as shown in Fig. 3. After the samples were desorbed by increasing the temperature of the metal block, the transmission spectra were measured again. The height of the first peak for the bare metal block was found almost the same as those for 10 L thick samples at liq. N_2 temperature. If these compounds had positive V_0 values, the first peak should increase by the desorption of samples on the metal block.

In Fig. 4 are shown the transmission spectra of DMSO. The height of the first peak for 2 L thick film is even larger than that for the bare metal block and no second peak appears. There is no doubt that the solid DMSO film has a negative V_0 value.

Alcohols. The transmission spectra for methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-nonanol have been measured. The transmission spectra for methanol and 1-

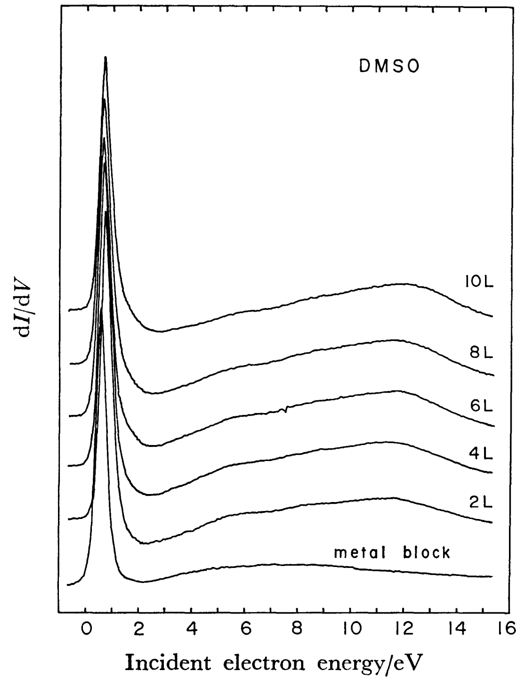

Fig. 4. The transmission spectra for metal block and dimethyl sulfoxide (DMSO).

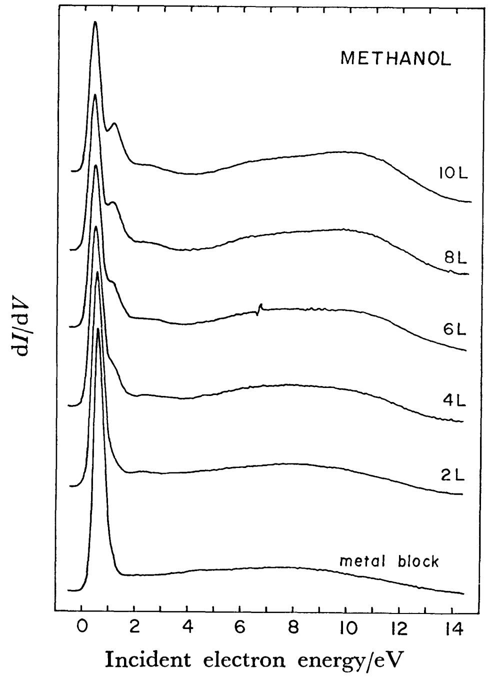

Fig. 5. The transmission spectra for metal block and methanol.

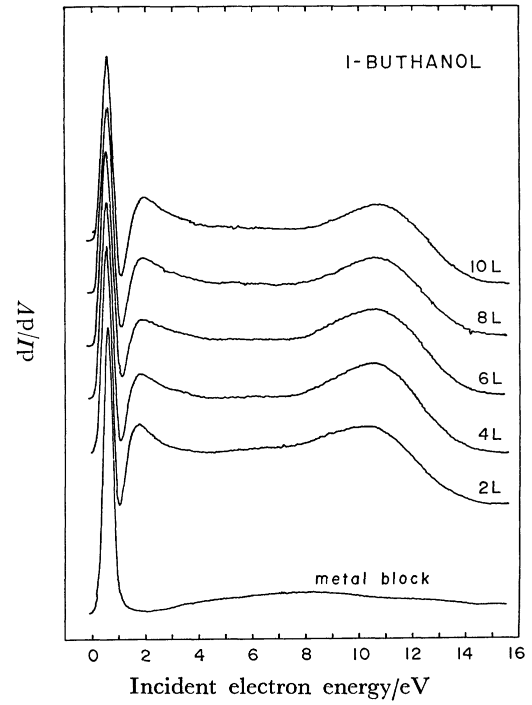

Fig. 6. The transmission spectra for metal block and 1-butanol.

butanol are shown in Figs. 5 and 6.

A decrease of the first peak and a growth of the second peak are observed for methanol with an increase of the film thickness, indicating that the solid methanol has a positive V_0.

It was found that the film thickness dependence on the transmission spectra was very similar for ethanol and higher alcohols (see Fig. 6). For these compounds, a drastic decrease of the first peak and an appearance of a sharp second peak are observed by the deposition of 2 L thick film, indicating that these compounds have positive V_0. However, the decrease of the first peak and the increase of the second peak are only very gradual for further deposition of the sample. These results strongly suggest that electrons in solid alcohols with an energy lower than V_0 have a large contribution to the transmitted electron current to the anode.

Ice. The transmission spectra of ice are shown in Fig. 7. Contrary to the spectra of alcohols, the first peak neither decreases nor a growth of the second peak is observed with an increase of the film thickness, indicating that the energy of quasifree electron state V_0 in ice is negative.

Work Function Change of the Metal Block. It is worthy to note that in the spectra of ethers and some of alcohols, the first peak shows a negative shift when samples were deposited on the metal block. If the film was charged by the electron irradiation, the first peak should show a positive shift.[10] For all compounds measured in this experiment, the peaks of the spectra do not show any shifts under repeated electron irradiation under the present experimental conditions ($I_t \leq 2 \times 10^{-9}$ A), *i.e.*, the charging of the film is negligible. Therefore, the shift of the first peak must be due to the change of the current-voltage characteristic curve determined by the contact potential difference between the cathode and the metal block. After the samples were desorbed by increasing the temperature of the metal block, the first peak shifts back to the original energy value of the first peak for the metal block. This means that the shift of the first peak is due to the work function change of the metal block by the deposition of the sample

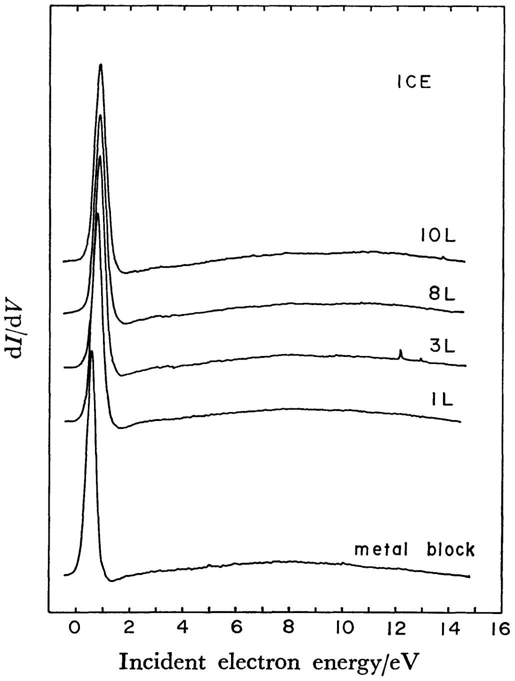

Fig. 7. The transmission spectra for metal block and ice.

on it.

Absorption is usually associated with a variation of the work function ϕ which provides a simple procedure for monitoring the state of a surface. Moreover, the sign of the work function change $\Delta\phi$ is connected with the direction of the electron transfer between the substrate and the adsorbate, *i.e.* with the dipole moment of the adsorbate complex. Although the surface of the stainless steel metal block used in this measurements is not characterized rigorously, it would be informative to discuss the work function changes observed by the deposition of several compounds.

The observed work function changes $\Delta\phi$ are summarized in Table 1 (column 6).[††] The negative $\Delta\phi$s are observed for ethers and some of alcohols. For higher alcohols, $\Delta\phi$s are observed to become smaller. The positive $\Delta\phi$s are observed by the deposition of ice and DMSO. It has been observed that $\Delta\phi$s are nearly zero for alkanes and aromatic compounds at $\approx$80 K in the previous experiments.[10,11]

The sign and the amount of $\Delta\phi$ may give some information on the interaction of adsorbed molecules with the metal surface. The relatively large $\Delta\phi$s are observed for ethers. These compounds have large permanent dipole moments, but the positive charge is rather delocalized in molecules in comparison with the localized negative charge on oxygen atoms. Considering that the nonpolar compounds give very small $\Delta\phi$s, ethers are considered to be interacting with the metal surface directing the oxygen atoms toward the metal surface. Alcohols (protic solvents) have also negatively charged oxygen atoms but $\Delta\phi$s are generally smaller than those for ethers. This may be due to the fact that the molecules of the first monolayer on the metal surface form hydrogen bonds with molecules of the second monolayer and the dipole moments induced by the interaction between the substrate and the adsorbate are smaller than in cases for ethers. *This may explain why $\Delta\phi$ becomes smaller for higher* alcohols. The positive shifts for ice and DMSO are difficult to understand. It would only be suggested that the sign of the net dipole moments induced by the interactions between the substrate and these compounds are opposite to cases for ethers and alcohols.

It was found that $\Delta\phi$s are highly temperature-dependent and the sign of $\Delta\phi$s for some polar molecules changes as the temperature of the metal block is increased. A more detailed investigation on the work function changes in this respect is now in progress.

Table 1. V_0, I_s, I_g, P^+, and $\Delta\phi$

Compound	V_0/eV	I_s/eV	I_g/eV	P^+/eV	$\Delta\phi$/eV
Diethyl ether	1.0	8.4	9.5	−2.1	−0.2
THF	1.1	8.1	9.42	−2.4	−0.3
2-MTHF	1.1(1.15,[a] 0.98[b])	8.8			−0.3
Acetone	$\leq$0				
Diethyl ketone	$\leq$0				
DMSO	$\leq$0				+0.1
Methanol	0.7(0.13,[a] −0.01[b])	9.2	10.84	−2.3(−1.99,[a] −1.84[b])	−0.1
Ethanol	*1.1(0.34,[a] 0.24[b])*	*9.0*	*10.46*	*−2.5(−2.05,[a] −1.94[b])*	−0.2
1-Propanol	1.1(0.38,[a] 0.36[b])	9.1	10.3	−2.3(−2.04,[a] −2.01[b])	−0.1
2-Propanol	1.0	8.9	10.12	−2.2	−0.1
1-Butanol	1.3(0.47[a])	8.8	10.04	−2.5(−2.08[a])	$\approx$0
1-Pentanol	1.3	8.7			$\approx$0
1-Hexanol	1.3	8.4			$\approx$0
1-Nonanol	1.3	8.8			$\approx$0
Ice	$\leq$0(−0.36[b])				+0.2

a) Ref. 7. b) Ref. 5.

[††] For acetone and diethyl ketone, $\Delta\phi$s are not given in Table 1 because the shifts of the first peak are partly due to the work function changes of the cathode.

The Energy of Quasifree Electron State V_0. In the previous work,[10] the V_0 values are determined by measuring the energy of the second peak from the first peak of the spectrum for the metal block as a reference. In the present study, the first peak of the spectrum for the metal block can not be chosen as a reference because the first peak shows positive or negative shifts by the deposition of the sample, as was mentioned in the previous section. In this work, V_0 is estimated by measuring the energy difference between the first and second peaks of a spectrum for each compound. Here, it is assumed implicitly that the first peak represents a crude profile of the electron energy distribution function. We think that this assumption is reasonable because the half-width of the first peak remains almost the same before and after the sample deposition. The estimated V_0s are listed in Table 1 (column 2). It is evident from our experimental results that V_0s for acetone, diethyl ketone, DMSO, and ice are negative, but the estimation of their values is difficult because of the lack of sharp structures in the transmission spectra for the calibration of the electron energy scale.

In Table 1, the values of V_0 in some solid alcohols and 2-MTHF measured by an indirect method[5,7] are also shown in parentheses of column 2. The agreement between these values and our directly measured values is good for 2-MTHF but poor for alcohols. The observed disagreement seems to be larger than the experimental errors in our measurements and it likely comes from the completely different experimental approaches for the determination of V_0. It is worthy to note that for almost all of solid alkanes,[5-7,10,11] a good agreement is observed between V_0 values determined by these two different methods. As shown in Table 1, V_0 values for alcohols obtained by an indirect method[5-7] are 0.6—0.8 eV lower than those obtained in this experiment. As is pointed out in the previous section, the contribution of electrons in solid alcohols with an energy lower than V_0 to the transmitted electron current is much larger than that in other solid samples whose V_0 are positive. This suggests the existence of dense trapping sites in solid alcohols for the efficient transport of nearly zero-energy electrons. In the indirect method, if the impurity molecules could be photoionized by ejecting electrons to the energy levels of pre-existing dense trapping sites, the onset of the recombination luminescence or of the appearance of the absorption of ionized impurity molecules would extend to lower photon energy and the rigorous determination of V_0 would be intrinsically difficult. This might explain the observed discrepancy. Although the Springett-Jortner-Cohen model[12] gives the rigorous theoretical definition for V_0, the experimentally determined V_0 represents the macroscopic "bulk" properties of the solid and the experimental V_0 could be highly dependent on each experimental method.

Cation Polarization Energy P^+ by the Medium. It has long been known that the ionization potential of a molecule in a condensed phase is lowered relative to the value measured in the gas phase. Lyons and his coworkers[13,14] emphasized the importance of the polarization of the medium P^+ around the cation and the ejected electron. Since I_g is known, the V_0 value may be derived by Eq. 1[5,7] if the cation polarization energy P^+ can be evaluated. So far, P^+ has been calculated by Eq. 2,

$$P^+ = -\frac{e^2}{2r_0}\left(1-\frac{1}{\varepsilon}\right) \tag{2}$$

where ε is the optical dielectric constant and r_0 the cation radius.

Since the V_0 values are directly measured in this experiment, P^+ may be derived by Eq. 1 if I_s can be measured experimentally. When a molecule in a solid film is ionized by an incident electron, the incident and ejected electrons in the film will have energies nearly equal to or larger than V_0 with respect to the vacuum. Because the produced hole (cation) in the film will be ultimately annihilated by a recombination or diffusion to the anode by tunneling or hopping mechanisms, the ionization of a molecule in a film by an incident electron must contribute to the "decrease" of the transmitted current. When the film has a positive V_0 value, the reflection coefficient for an electron at the film-vacuum interface is considered to be small enough that a discernable negative peak is expected to appear in the transmission spectrum. All transmission spectra for compounds whose V_0 are positive have broad negative peaks with onsets at around 9—10 eV. We think that these broad negative peaks observed at $\approx$14 eV are due to the ionization of molecules in a film.

For a film with a positive V_0, the threshold ionization energy I_s may be obtained by measuring the energy of the onset of a negative peak from the "second" peak as a reference. The measured I_s values are listed in Table 1 (column 3) with the reported I_g values (column 4). By knowing the values I_s, I_g, and V_0, the P^+ values can be derived by Eq. 1 which are shown in Table 1 (column 5), with the calculated P^+ by Eq. 2 in parentheses.[5,7] The error for values of I_s and thus P^+ which arises from the uncertainty for the determination of the onsets of the broad negative peaks may be estimated as ±0.4 eV. The experimentally determined P^+ are a few tenths of an eV higher than the calculated P^+.

For a compound with $V_0<0$, the onset of a negative peak would not correspond to that for the ionization of a molecule in the film because the ejected electron with an energy $\approx V_0$ with respect to the vacuum can not escape to the vacuum due to the positive energy barrier ($-V_0$). Thus the I_s values for compounds with $V_0<0$ are difficult to estimate by the present method.

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