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Transmission of Low-energy Electrons through Thin-films of Benzene and Hexane at 80 K

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Transmission spectra of low-energy electrons (0—15 eV) for 10—100 Å films of benzene and hexane have been measured at 80 K. Resonances are clearly indicated by electron current I_t transmitted through the dielectric as a function of the incident electron energy V_i, displayed as dI_t/dV_i *vs.* V_t. When the film thickness of hexane was increased, the height of the first peak (due to injection of electrons in the film) decreased drastically and a second peak appeared and grew strongly. From the energy of the second peak, the bulk electron affinity ($-V_0$) of thin film was estimated. The V_0 values for hexane and octane are 0.9 and 1.0 eV, respectively.

The excitation of gas-phase molecules by electron impact has often been studied by a variety of techniques ranging from low-energy threshold excitation[1,2] to energy loss spectroscopy,[3—5] using both high- and medium-energy electrons. Threshold excitation techniques of Schulz[1] and Compton *et al.*[2] are similar in that the yields of low-energy electrons produced by resonant electron impact processes are measured either by the trapped electron method or by the SF_6 scavenger technique.[2]

Applications of electron impact techniques to thin organic films have previously been restricted to the measurements of energy loss spectra of high-energy electrons transmitted through thin films of polymers.[6,7] Since the optical selection rules are relaxed for excitation by low-energy electrons,[8] it is not possible to extrapolate results from energy loss spectra involving high-energy electrons to processes involving low-energy electrons.

Recently, Hiraoka and Hamill[9—14] and Sanche[15,16] reported a simple method for measuring the electronic levels of molecules supported as ultrathin films on a metal surface at 77 K.[9—14] 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). This method was found particularly useful for detecting optically forbidden electronic transitions.

A similar apparatus was constructed. The main objective of this work is to relate the energy dependence of the transmission features to specific interactions occuring in films of benzene and hexane.

Experimental

A schematic diagram of a prototype spectrometer housed in a stainless steel high-vacuum system (ULVAC, EBD-50M) maintained at $\lesssim 2\times10^{-7}$ Pa appears in Fig. 1. An electron gun used is a commercial TV gun (The Japan Lamp Industrial Co., LTD.) consisted of an einzel lense and an indirectly heated oxide-coated cathode. The gun is mounted in a grounded stainless steel cylinder. The angle of incidence of the electron beam to a metal target is normal.

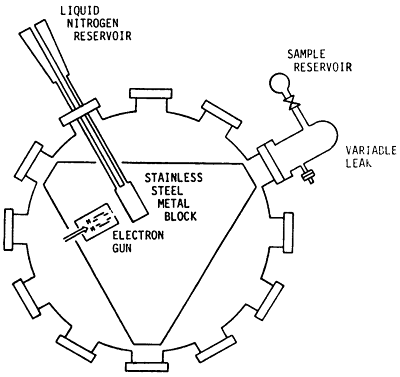

Fig. 1. Schematic diagram of the spectrometer.

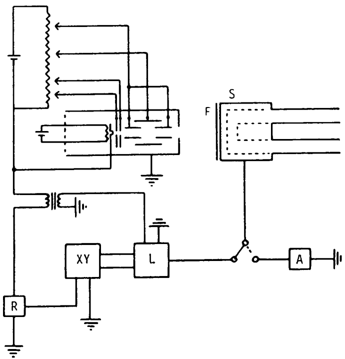

Fig. 2. Schematic arrangement of the apparatus used for measuring the electron current transmitted through the dielectric film F to the stainless steel support S at ≈80 K. Other components include a lock-in amplifier L, a ramp function generator R, a recorder XY, and an electrometer A.

A schematic diagram of the spectrometer system used for the measurement of electrons transmitted through thin solid films is shown in Fig. 2. Differentiation of the transmitted current I_t with respect to the incident electron energy V_i is accomplished electronically by superimposing a small a.c. voltage (0.3 V peak-to-peak at 78 Hz) on the base cathode voltage and synchronously detecting the resulting a.c. signal at the target with a lock-in amplifier (NF Circuit Design Block Co., LTD. model LI-573). An X-Y recorder plot of the magnitude of the a.c. signal *vs.* the the cathode potential provides the transmission spectrum, dI_t/dV_i *vs.* V_i.

The sample was deposited as a thin film on the stainless steel block (face 3.6×2.0 cm^2) cooled by circulating liquid nitrogen. The temperature of the metal block was measured by an iron-constantan thermocouple which was spot-welded on the metal block. A sample was admitted to the vacuum chamber through a variable leak valve. The film thickness was estimated by establishing a given partial pressure of a sample vapor in the vacuum chamber for a specific time, assuming a sticking probability of unity. The pressure gauge, which reads the ion current of an ion pump, was calibrated for nitrogen. Because almost all of organic compounds have larger ionization cross sections than nitrogen, the reading of the pressure gauge must be higher than the actual pressure of an introduced organic compound at the ion pump. However, the position of the pressure gauge was far from the metal block, and the effective pressure at the metal block could be higher than the pressure at the ion pump. Thus the value of the film thickness given in this work should be considered as only a roughly estimated one. The film thickness was changed by changing the deposition time with the constant vapor pressure at 10^{-5} Pa. It has not been known whether films are crystalline or amorphous, but the randomness in the solid was suggested for benzene film at 77 K.[17)]

In the previous works,[9)–14),17)] the incident electron current of 10^{-9}—10^{-8} A with a beam spot of ≈ 1 mm in diameter was used, where it was found that the condensed films of organic compounds were very sensitive to electron bombardment. The spectrum dI_t/dV_i *vs.* V_i for the bare metal block often showed apparent difference before and after the measurement of an aromatic sample, indicating that a metal surface was contaminated by the radiolytic products. The metal block had to be cleaned every time after the measurement of an aromatic sample. Saturated molecules gave less radiolytic products than aromatic compounds under the same experimental conditions.

In this experiment, the incident electron current of $\lesssim 2\times 10^{-9}$ A with a larger beam spot was used in order to reduce the radiation damage of a film. The diameter of the aperture for electrons in the end wall of the cylinder was 5 mm. The size of the beam spot could be roughly estimated by observing weak blue luminescence from thin-film benzene bombarded by electrons with the energy of 15—20 eV. The observed faint luminous lobe was about 13 mm in diameter. Thus the current density should be at most 2×10^{-9} A/cm^2. Matsushige and Hamill measured the yields of decomposition products from multilayer films of cyclohexane and hexane caused by low-energy electron irradiation.[18)] They found the G values[†] to be ≈ 0.5 for electron energies of 10—20 eV. With decomposition yields of this magnitude, a monolayer of the hydrocarbons could be decomposed in 100 h under the conditions of our study. The spectrum for bare metal block did not change under repeated measurements for aliphatic and aromatic compounds, in agreement with the results of Matsushige and Hamill.[18)]

Results and Discussion

Benzene. The transmission spectra dI_t/dV_i *vs.* V_i for benzene are shown in Fig. 3. The film thickness was changed from 2 to 10 L.[††] The spectrum of the metal block is also shown in the Figure, which was measured before the organic sample was deposited. The temperature of the metal block was ≈ 80 K.

The spectra of benzene are in excellent agreement with the result obtained by Hiraoka and Hamill,[10)] indicating a good reproducibility of the present method. In Fig. 3 are also shown the trapped electron spectrum[19)] and the energy loss spectrum of 300 eV electrons[20)] for comparison. These spectra serve to establish the energy shift of the spectrum dI_t/dV_i *vs.* V_i. The best fit locates the zero of the incident electron energy at the onset of the first peak.

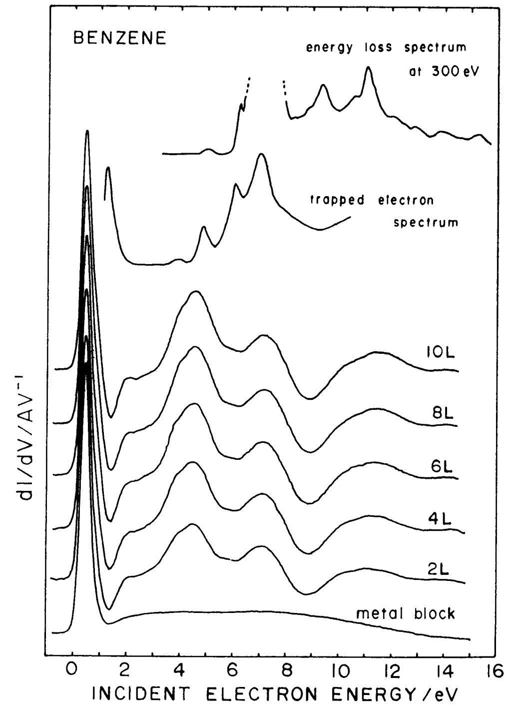

Fig. 3. The dependence of dI_t/dV_i *vs.* V_i for metal block and benzene. The film thickness was changed from 2 to 10 L. The trapped electron spectrum[19)] and the energy loss spectrum of 300 eV electrons[20)] are also shown for comparison.

The strong bands appear in the spectrum dI_t/dV_i *vs.* V_i at 3.9 and 4.6 eV in Fig. 3 which correspond to energies lost by exciting benzene to the $^3B_{1u}$ and $^1B_{2u}$ states, respectively. These optically forbidden transition bands are even larger than the optically allowed $^1E_{1u}\leftarrow{}^1A_{1g}$ transition band at 7 eV, indicating the major advantage of the electron impact over the photon spectroscopy for its ability to induce optically forbidden transitions.

Another weak events are also observed as a shoulder of the first peak and two small peaks in the range 1.5—3.0 eV. Although the shoulder peak corresponds approximately to the peak at 1 eV in the trapped electron spectrum which is due to the transient negative ion formation, the relative intensity of the shoulder peak is much smaller than the peak at 1 eV in the trapped electron spectrum, and the assignment of this peak would not be so straightforward. The origins of events in the range 1.5—3.0 eV were not well understood either. A further investigation for the detailed analysis of the spectra is now in progress.

It is evident from Fig. 3 that the 2 L film is thick enough to give a characteristic transmission spectrum of benzene and the spectra of thicker films did not show any marked dependence on the film thickness up to 10 L. This suggests that the interaction of low-energy electrons with only a few monolayers from the surface of benzene film gives the characteristic transmission spectrum. In addition, the onset of the first peak and the positions

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[†] The G value refers to the number of molecules of a product formed on irradiation per 100 eV of energy absorbed.

[††] The amount of the gas admitted in the vaccum chamber is expressed in Langmuir units (1 L$=1\times 10^{-6}$ Torr s). When the sticking probability is unity, the surface will be covered by approximately one monolayer with 1 L gas admission.

of peaks in transmission spectra appear at almost the same energies with increasing the film-thickness from 2 to 10 L. This indicates that the charging of electrons in the film is negligible for the present experimental conditions.

Since the first peak of the spectrum for the metal block describes a crude electron energy distribution function with the high-energy tail at the onset, the detailed examination of the change of the first peak after the dielectric film is deposited on the metal surface would be helpful for understanding the interaction of low-energy electrons (0—2 eV) with dielectrics. As shown in Fig. 3, there is almost no difference in shape (height and half-width) between the first peak for the metal block and those for benzene for 2—10 L. It is noteworthy that the acceptance coefficients for electrons at low energies are nearly the same for benzene and the stainless steel metal block. Only the difference is the appearance of a small shoulder peak at ≈ 1 eV and the sharp negative peak at ≈ 1.3 eV in the benzene spectra which are not observed for the stainless steel metal block.

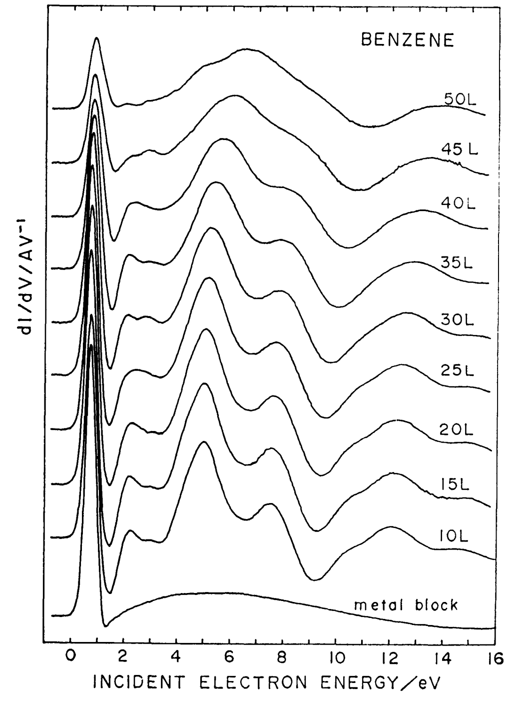

Fig. 4. The dependence of dI_t/dV_i vs. V_i for benzene. The film thickness was changed from 10 to 50 L.

In Fig. 4 is shown the change of spectra when the film thickness was increased from 10 to 50 L. The height of the first peak decreases only gradually with increasing the film thickness. The peaks of the spectra show only very small positive shifts with increasing the film thickness up to 25 L. Above 30 L, the positive shifts become more evident possibly due to the charging of the film.

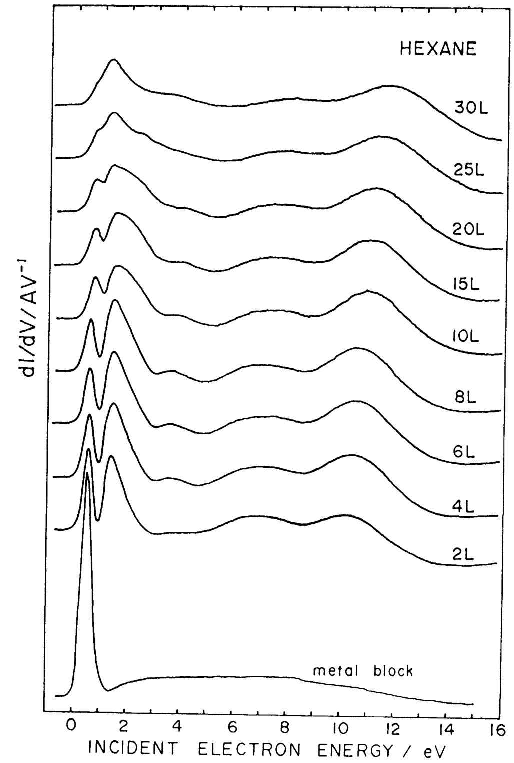

Fig. 5. The dependence of dI_t/dV_i vs. V_i for metal block and hexane. The film thickness was changed from 2 to 30 L.

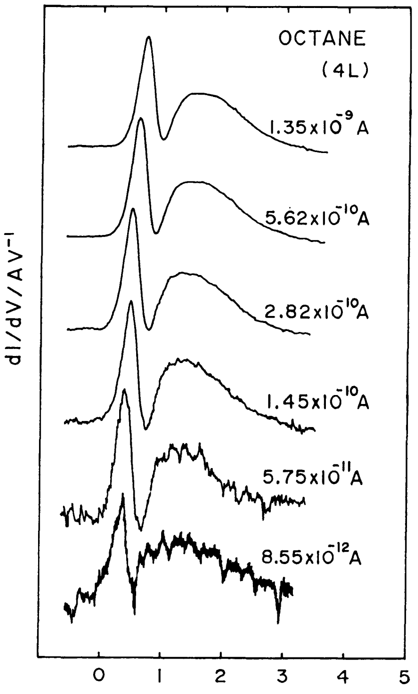

Fig. 6. Spectra of octane in the energy range 0—3 eV with the incident electron current changed from 8.55×10^{-12} to 1.33×10^{-9} A.

Hexane. The transmission spectra are shown in Fig. 5. The film thickness was changed from 2 to 30 L. The zero of the energy scale is arbitrary. Contrary to the spectra of benzene, the first peak decreases drastically and the second peak at ≈ 1.4 eV grows strongly as the film thickness is increased. At 30 L, the first peak shows up as only a small shoulder peak of the second peak. Such a marked change of the spectra with an

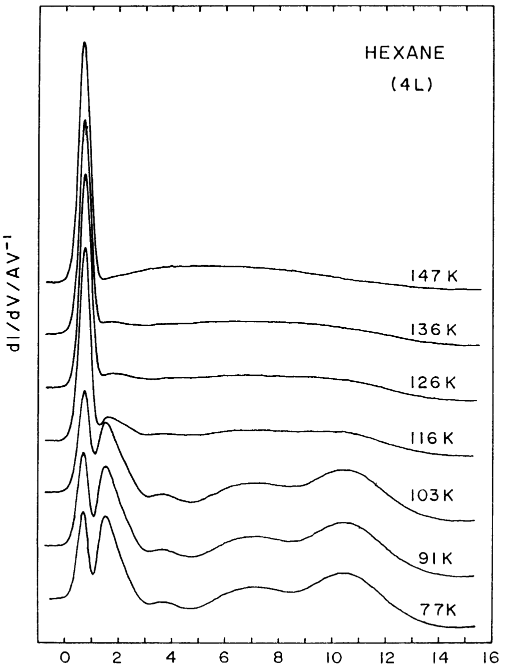

Fig. 7. Temperature programmed spectra following the adsorption of hexane on the stainless steel metal block at 77 K. The heating rate is 10 K/min.

increase of the film-thickness was also observed for octane (Fig. 6), but not for benzene and other aromatic compounds. These characteristic low-energy events of hexane may be related to the interaction of electrons with the bulk of the solid film, *i.e.*, the cluster of molecules.

Figure 7 shows spectra of the temperature dependence following the adsorption of hexane (4 L) on the metal block at 77 K. The heating rate is 10 K/min. As the temperature is increased, the intensity of first peak increases gradually with an expense of the second peak. The spectrum at 147 K coincides with that of the metal block, indicating that all samples are desorbed from the metal block at this temperature. The observed rapid desorption suggests the weak adsorption of hexane on the stainless steel substrate. Madey and Yates observed two peaks at 150—175 K and 277 K in the temperature programmed desorption spectra following the adsorption of cyclohexane on Ru(001) at 80 K.[21] They concluded that the state at 150—175 K is due to a condensed multilayer and that at 227 K is due to C_6H_{12} adsorbed in the first monolayer in contact with the Ru(001) substrate. In Fig. 7, the rapid change of spectra is observed from 77 to 126 K, but the spectra at 126 and 136 K are almost exactly the same, suggesting that these spectra are those for the monolayer of hexane on the metal substrate. The multilayer should be exhausted in this temperature range because the vapor pressure of hexane at 126 and 136 K are about 1×10^{-4} and 1×10^{-3} Pa, respectively. The second peak of spectra for 126 and 136 K is still observed but it shows the positive shift by 0.3—0.4 eV with respect to the peak of multilayer films. The coverage of hexane monolayer at these temperatures could not be estimated under the present experimental conditions.

Bulk Electron Affinity. As shown in Figs. 3 and 5, the low-energy events of benzene are very different from those of hexane in the range 0.5—2.0 eV. In the case of benzene, the first peak does not show a marked film-thickness dependence and a sharp negative peak is observed at $\approx$1.3 eV. On the contrary, a rapid decrease of the first peak accompanied by a strong growth of the second peak is observed for hexane as the film-thickness is increased. These experimental results suggest the existence of the positive energy barrier in hexane thin film and the negative one in benzene thin film for the injection of electrons from the vacuum into the film. If the positive energy barrier for hexane is due to the temporal charging of the film, the spectra should be dependent on the amount of the incident electron current at least to some extent. Figure 6 shows the spectra of octane in the energy range 0—3 eV with the incident electron current changed from 8.55×10^{-12} to 1.35×10^{-9} A. It is apparent from the Figure that the shape of the spectra does not change with an increase of the incident electron current more than two orders of magnitude. Thus the energy barrier for the incident electrons can not be attributed to the one generated by charging in the film. We would like to conclude that energy barrier is an intrinsic one for each compound, *i.e.*, the bulk electron affinity.

In Fig. 6, the gradual positive shifts of the spectra are observed with the increase of the incident electron current. This is *not* due to the charging of the film. When the film thickness is $\leq$10 L, the spectra of organic compounds generally do not show any observable peak shifts under repeated and prolonged irradiation of the electron beam of $\approx10^{-9}$ A. The shifts observed in Fig. 6 is a manifestation of the positive shifts of the current-voltage characteristic curve of the electron gun. The positive shift is always observed when the voltage of the draw-out electrode in front of the cathode is increased in order to get more electron current.

For an electron of energy E in the condensed medium, the Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V\right]\Psi=E\Psi, \tag{1}$$

where V is the one-electron potential exerted by the unperturbed medium. When the potential V is periodic from one sphere to another and spherically symmetric inside the sphere, only one radial equation needs to be solved, so that the ground state eigenvalue E of Eq. 1 can be uniquely defined. Springett *et ol.*[22] calculated the energy levels of an excess electron in multiatom system by using a Wigner-Seitz model to obtain a spherically symmetric potential. In the Wigner-Seitz model each atom is replaced by a sphere of radius r_s given by

$$r_s=\left(\frac{3}{4\pi n}\right)^{1/3}, \tag{2}$$

where n is the number density. The wave function ψ is smooth inside r_s, and V is the pseudopotential approximated as ∞ for $r<\bar{a}$ and U_p for $r>\bar{a}$. This pseudopotential excludes the excess electron from the hard core radius $\bar{a}$ of the atom. U_p is the polarization potential from the atom inside and the atoms outside r_s which is approximated by

$$U_{\mathrm{p}} = \frac{-3\alpha e^2}{2r_s^4}\left[\frac{8}{7}+\left(1+\frac{8}{3}\pi\alpha n\right)^{-1}\right], \qquad (3)$$

where α is the isotropic polarizability. Then, Eq. 1 may be solved to yield

$$E = U_0 + \frac{\hbar^2 k_0}{2m} = U_0 + T_0, \qquad (4)$$

where the electron wave vector k_0 is obtained from the Wigner-Seitz boundary condition $(\mathrm{d}\psi/\mathrm{d}r)_{r=r_s}=0$, which gives the equation

$$\tan k_0 \, (r_s - \bar{a}) = k_0 r_s, \qquad (5)$$

and T_0 is the zero point energy which arises because the excess electron is excluded from the hard core region of radius in each Wigner-Seitz sphere. The lowest energy eigenvalue E of Eq. 1 is the ground state energy of an excess electron in the medium (V_0), *i.e.*, an energy required for injection of an electron from the vacuum into the medium. The bulk electron affinity of the medium corresponds to $-V_0$.

The positive bulk electron affinity may be assigned for benzene film. When the bulk electron affinity of the film is positive, the energy level of an excess electron (V_0) in the film is lower than that of the vacuum. In such a case, the electrons see the "negative" energy barrier when they enter the film from the vacuum, and the injection peak of electrons (the first peak) should not be very different from that of the bare metal block, in good agreement with the experiment. On the other hand, the excess electron in the film see the "positive" energy barrier for escaping into the vacuum. For a spherically-asymmetric distribution of elastically scattered electrons in a film, with a negative V_0, the quantum mechanical reflection coefficient at the film-vacuum interface may be given by $R=\{|V_0|/(|V_0|+E_i)\}^{1/2}$, where E_i is the energy of electrons.[16] According to this theory, the backscattered current will show an increase as the energy of incident electrons increases because it is easier for injected electrons in the film to overcome the positive energy barrier ($-V_0$) and escape the film into the vacuum at higher incident electron energy (E_i), *i.e.*, the effective reflection coefficient at the film-vacuum interface will decrease with an increase of the energy of electrons. This might explain the observed negative peak at ≈1.3 eV in the benzene spectrum.

The low-energy events observed for hexane and octane can be explained reasonably if the negative bulk electron affinity is assigned for these compounds. Figure 8 shows the schematic potential distribution along the axis of the spectrometer and the spectrum, $\mathrm{d}I_t/\mathrm{d}V_i$ *vs.* V_i, for a film whose bulk electron affinity is negative ($0<V_0$). Because of the positive energy barrier of the film for the incident electrons, the injection peak of electrons (the first peak) should be much smaller than that of the metal block, and the transmitted electron current should show a sharp increase as a second peak in the spectrum, $\mathrm{d}I_t/\mathrm{d}V_i$ *vs.* V_i, when the energy of the incident electrons exceeds the positive energy barrier, in all good agreement with the experimental results.

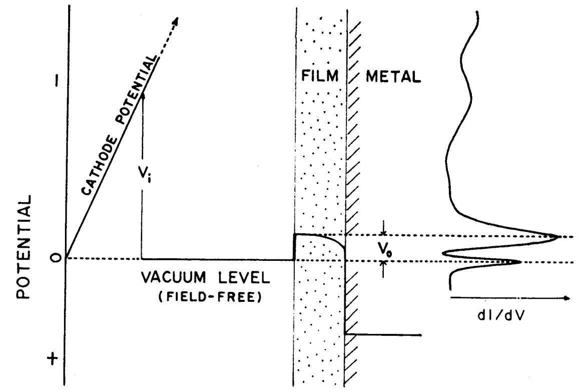

Fig. 8. The schematic diagram of the potential distribution along the axis of the spectrometer. The space between the electron gun and the metal block is field-free. The bulk electron affinity of the film shown in the figure is negative. The spectrum of hexane, $\mathrm{d}I_t/\mathrm{d}V_i$ *vs.* V_i, is shown along the potential axis in the right part of the figure. V_i is the accelerating voltage. V_0 represents the ground state energy of excess-electrons in the film. The value of the bulk electron affinity corresponds to $-V_0$.

If the observed low-energy events are manifested by the bulk electron affinity of the films, it might be possible to estimate the bulk electron affinities from the spectra $\mathrm{d}I_t/\mathrm{d}V_i$ *vs.* V_i. The spectrum is a convolution of the current-voltage characteristics of an electron gun $I(V)$, and the energy dependent acceptance coefficient of electrons for the film $F(V)$. $F(V)$ may be affected by many factors such as the bulk electron affinity, the density and the structure of the film, density of trapping sites and the distribution of the well-depth of trapping sites, *etc.* Because so many factors are involved in the low-energy events of the spectra, it would be difficult to determine the bulk electron affinity unequivocally. Here the bulk electron affinity ($-V_0$) is tentatively estimated by the energy difference of the first peak for the metal block and the second peak of the spectra for hexane and octane, which are -0.9 and -1.0 eV, respectively.

The positive bulk electron affinity could be estimated by the amount of the positive shift of the spectrum if the reference peak is available for the determination of the energy scale. For benzene, the horizontal axis of Fig. 3 is the energy for the trapped electron spectrum[19] and the energy loss spectrum of 300 eV electrons.[20] With this scale, the energy of the transmission spectrum is increased by 0.3 eV to establish a coincidence between structures present in these spectra. Thus the bulk electron affinity of benzene film could be estimated as about 0.3 eV (V_0 is -0.3 eV).

For solid hydrocarbons, no direct experimental V_0 determinations have been reported so far. Jortner's calculations[22,23] give nearly equivalent V_0 values for solid and liquid argon. On the other hand, recent experiments by Noda *et al.* have shown that V_0 increases with decreasing temperature in liquid ethane.[24] Recently Grand and Bernas[25,26] measured V_0 for solid hydrocarbons indirectly by measuring the ionization potential of a solute in various polar and nonpolar rigid solvents. Their indirectly measured V_0 for rigid hexane is 0.98 eV, in good agreement with our value (0.9 eV).

The Springett, Jortner and Cohen model for calculating V_0 (Eq. 4) was originally developed for rare gas liquids[22] but has been applied to hydrocarbons.[24,27] For liquid hexane, U_0 and T_0 can be calculated as -2.4 and 1.77 eV, respectively, and thus V_0 is -0.63 eV. The experimental value of V_0 in liquid hexane by photoelectric work function measurements is 0.04 eV,[28] which is much smaller than the value in rigid hexane. Grand and Bernas[26] also found that the 77 K V_0 values appear significantly greater than the ones measured at 298 K (liquid) by 0.7—1.0 eV.

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