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The Electronic Structures of Condensed Materials Studied by Ultraviolet Photoelectron Spectroscopy

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The solid phase ultraviolet photoelectron spectra of water, carbon disulfide, benzene, *N*-methylaniline, and pentane condensed on a gold substrate at 77 K were measured. The features of the spectra are similar to those of the corresponding gas phase spectra. The difference between the gas and solid phase *IP*'s, the relaxation shift, is nearly constant for each compound studied except for the case of water, where the $3a_1$ molecular orbital state in solid is affected by the hydrogen bonding. The values of the relaxation shift for water, benzene and carbon disulfide are 1.1—1.3 eV, while those for *N*-methylaniline and pentane are 0.6 and 0.7 eV, respectively. The small values for the latter compounds are due to the fact that the molecules are loosely packed in the solids. The mechanisms of the band broadening for the molecular crystal are discussed in relation to the spectrum of solid carbon disulfide. For *N*-methylaniline the spectra of the gas, liquid and solid phases were compared. To our knowledge, this is the first case in which the electronic structures of all the three phases are studied by ultraviolet photoelectron spectroscopy.

The technique of photoelectron spectroscopy provides direct information about the electronic structures of materials in the gas and solid phases. Therefore, it is of considerable interest to investigate the change in the electronic structure due to the phase change by means of photoelectron spectroscopy.

In this work we measured the ultraviolet photoelectron spectra of water, benzene, carbon disulfide, *N*-methylaniline, and pentane in the solid phase and compared them with the corresponding spectra reported for the gas phase. Since all the compounds are liquids at room temperature, they are condensed easily without contamination during exposure. Water, carbon disulfide, benzene, and pentane were chosen as typical organic or inorganic compounds. *N*-methylaniline was studied, because its He I spectrum has been measured in the liquid state[1)] and we can compare the electronic structures of all the three phases of gas, liquid, and solid.

Experimental

The samples of benzene, carbon disulfide, *N*-methylaniline, and pentane were distilled twice under vacuum. For the water sample, distilled water was used.

The measurements of the spectra were carried out using an ultra-high vacuum photoelectron spectrometer, which has a preparation and an analyser chamber.[2)] The base pressure of the spectrometer was less than 3×10^{-10} Torr. The He I (21.22 eV), Ne I (16.85 and 16.67 eV) and Ar I (11.83 and 11.62 eV) resonance lines were used as the exciting sources. For the Ne or Ar doublet, the mean value of the energies was used to analyse the spectra. The resolution of the electron energy analyser was approximately 0.15 eV FWHM (full width at half maximum) in the present experiment.

In the preparation chamber the sample vapour was condensed onto a freshly deposited gold film held at 77 K. The vapour was let in the chamber at a point just above the substrate through a variable leak valve and a copper pipe. The pressure was less than 1×10^{-8} Torr during the condensation. To prevent the sample charging effect the exposure was stopped at intervals to monitor adsorbate peaks. The spectra shown in the following section are those which were measured just before the peak shift caused by the charging sets in.

Results and Discussion

Water (H_2O). Figure 1 illustrates the change in the He I spectra showing the condensation of water on a gold film at 77 K. To obtain the ionization potential (*IP*), the kinetic energy, E_K, of the electrons was determined by taking the zero of kinetic energy as the low energy cutoff of each spectrum[†] and then the relation $IP=h\nu-E_K$ was used. This method gives the work function of gold to be 4.9 eV, which is in good agreement with the value, 4.9—5.1 eV, recommended by Eastman.[3)]

In Fig. 1 the features of the spectra at about 11,

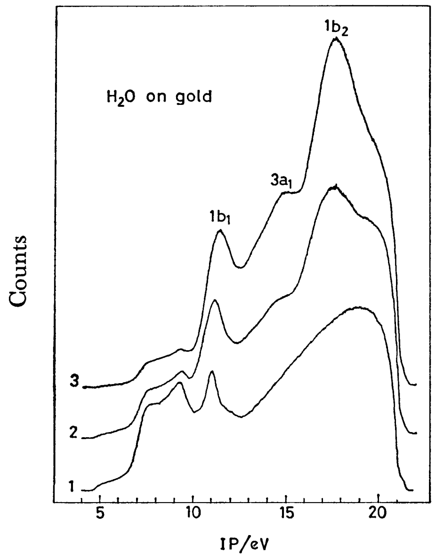

Fig. 1. He I spectra of water condensed on Au at 77 K. (1): Clean gold, (2): H_2O on gold, exposure time, 50 s at 5×10^{-9} Torr, (3): H_2O on gold, exposure time, 100 s at 5×10^{-9} Torr.

[†] To obtain the cutoff a small shoulder near 0 eV kinetic energy was taken out of consideration, because it is due to stray electrons.

15, and 17.5 eV correspond to the $1b_1$, $3a_1$, and $1b_2$ bands in the spectrum of gas phase water. The large peak between 18 and 21 eV is due to inelastically scattered electrons in the solid film.

As can be seen in Fig. 1, the structures of the spectra between 5 and 10 eV originated from the gold substrate little shift when water molecules are adsorbed. Similar results are observed for all the samples studied and are in contrast with the results observed by Yu *et al.* on a MoS_2 substrate,[4] where the MoS_2 bands gradually shift as coverage increases. They attributed the shift to a dipole between the MoS_2 substrate and the adsorbed molecules. In the case of a metal substrate, the thickness of the electron deficient layer due to the adsorbed gas is much less than the escape depth of photoelectrons. Therefore, the dipole effect may not cause the observable shift of the gold substrate peaks.

In Table 1 the gas phase vertical *IP*'s of water[5] are compared with the solid phase ones. The difference between the gas and solid *IP*'s, the relaxation shift, *R* (=*IP*(gas)−*IP*(solid)), mostly corresponds to the polarization energy due to the molecular ion left in the solid after a photoelectron is removed.

TABLE 1. THE VERTICAL IONIZATION POTENTIALS OF GAS AND SOLID WATER TOGETHER WITH THE RELAXATION SHIFTS

Orbital	*IP*(gas)[5] eV	*IP*(solid) eV	*R*[a] eV
$1b_1$	12.62	11.3	1.3
$3a_1$	14.78	15.0	−0.2
$1b_2$	18.55	17.6	1.0

a) *R*=*IP*(gas)−*IP*(solid).

Atkinson *et al.* have also measured the He I spectrum of water adsorbed on gold and found the structures at 6.3, 10.2 and 12.6 eV below the Fermi level of gold.[6] Adding 4.9 eV for the work function of gold, we have 11.2, 15.1, and 17.5 eV for the ionization potentials of solid water, which are in good agreement with the values obtained in the present experiment (Table 1).

In Table 1 the relaxation shift of the $3a_1$ state is negative. As was pointed out by Campbell *et al.*,[7] on solidification of water, the $3a_1$ molecular orbital state is predominantly affected by the hydrogen bonding because of its orbital geometry, and appears considerably perturbed in the solid state spectrum. Therefore, the negative value of the relaxation shift for the $3a_1$ state may be due to the stabilization of the $3a_1$ orbital caused by the hydrogen bonding and also to the change in the band shape.

Benzene (C_6H_6). Figure 2 shows the He I spectra of benzene condensed on the gold substrate. The characteristic features of the solid spectrum shown in the figure are summarized in Table 2 together with the corresponding features of the gas phase spectrum.[8,9] Since the e_{2g} and $a_{2u}(\pi)$ bands are not well resolved in the gas phase spectrum, they are observed as a single band at 10.7 eV in the solid phase spectrum (Fig. 2). Similarly the band at 13.1 eV is correlated to the e_{1u}, b_{2u}, and b_{1u} bands in the spectrum of the gas.

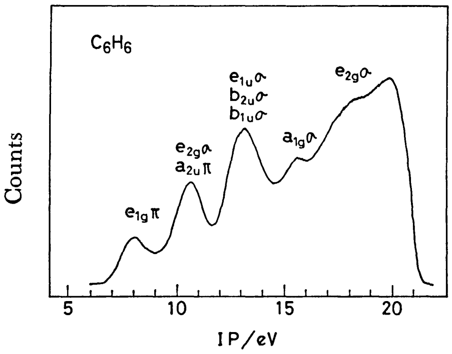

Fig. 2. He I spectrum of benzene condensed on Au at 77 K.

TABLE 2. THE VERTICAL IONIZATION POTENTIALS OF GAS AND SOLID BENZENE TOGETHER WITH THE RELAXATION SHIFTS

Orbital	*IP*(gas)[8,9] eV		*IP*(solid) eV	*R*[a] eV
$1e_{1g}\pi$	9.24		8.1	1.1
$3e_{2g}$	11.49	11.8[b]	10.7	1.1
$1a_{2u}\pi$	12.3			
$3e_{1u}$	13.8	14.3[b]	13.1	1.2
$1b_{2u}$	14.7			
$2b_{1u}$	15.4			
$3a_{1g}$	16.85		15.5	1.3_5
$2e_{2g}$	19.2		—	—

a) *R*=*IP*(gas)−*IP*(solid). b) Centre of the bands.

As shown in Table 2, the relaxation shift of solid benzene is 1.1—1.3 eV, which is in good agreement with the corresponding values obtained by Yu *et al.* (1.0 eV)[4] and Grobman and Koch (1.15 eV).[10]

The observed relaxation energies for naphthalene,[10] anthracene[10] and naphthacene[11] are 1.1, 1.2, and 1.0—1.3 eV, respectively. Thus the relaxation energy is essentially constant for the aromatic molecules, benzene to naphthacene. This means that the value of the relaxation energy for polycyclic aromatic crystals depends on the molecular packing, irrespective of the size of the molecules.

Carbon Disulfide (CS_2). Figure 3 shows the He I, Ne I and Ar I spectra of carbon disulfide condensed on the gold substrate. The peak positions in the spectra are the same for the three different excitation sources.

In Table 3 the vertical *IP*'s of solid carbon disulfide obtained from Fig. 3 are compared with those of the gas.[8] The relaxation shift for each band is 1.2—1.3 eV, being nearly constant as in the case of benzene.

It is worthwhile to note that the width of each band in the solid spectra is fairly constant and also does not depend on the excitation energy (Fig. 3). Subtracting the background emission due to the secondary electrons, we obtained the FWHM's (full width at half maximum) of the π_g, π_u, σ_u, and σ_g bands to be 0.8_5, 0.9_5, 0.8_0, and 0.9_0 eV, respectively. On the other hand, the corresponding FWHM's estimated

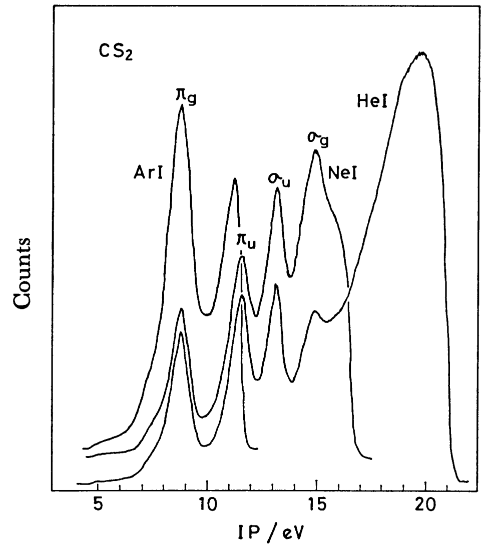

Fig. 3. He I, Ne I, and Ar I spectra of carbon disulfide condensed on Au at 77 K.

Table 3. The vertical ionization potentials of gas and solid carbon disulfide together with the relaxation shifts

Orbital	IP(gas)[8] eV	IP(solid) eV	R[a)] eV
π_g	10.10	8.8	1.3
π_u	12.84	11.6	1.2
σ_u	14.48	13.2	1.3
σ_g	16.20	14.9	1.3

a) $R = IP(\text{gas}) - IP(\text{solid})$.

from the envelope of the vibrational structure of the gas phase spectrum are very different and are 0.10, 0.27, 0.03, and 0.03 eV, respectively.[8] The small FWHM values for the σ_u and σ_g bands in the gas spectrum are due to the fact that each of these bands consists of the strong 0-0 peak with the very weak vibrational progression.

In order to interpret the difference in the bandwidth between the solid and gas phase spectra, it is necessary to know the mechanisms of broadening of the solid state bands. Since, as described above, the bandwidth in the solid spectra little depends on the excitation energy, the width of the upper state in solid (conduction bandwidth) is considered not to make large contribution to the broadening of the bands in contrast to the cases of metals or ordinary semiconductors. For the molecular crystal such as solid carbon disulfide, possible dominant mechanisms of the broadening are:[12] (a) the polarization energy dispersion due to the lattice vibrations in the neutral state, (b) the energy loss of the photoelectrons during their transport to the surface as a result of the excitations of the intramolecular vibrations of neutral molecules, and (c) the difference in the ionization potential between the surface and the bulk. The FWHM of the solid band expected from the mechanism (a) may be a few tenth of a relaxation energy R.[††] Therefore, it is possible in the present case that the mechanisms (b) and (c) also contribute to the bandwidth (≈0.9 eV) which amounts to about 70% of the relaxation energy (1.2—1.3 eV). The fact that the FWHM's of the solid phase bands are nearly constatnt irrespective of those of the gas phase bands suggests that the mechanism (b) involving the energy loss due to the intramolecular vibrations makes considerable contribution to the broadening of the solid bands.

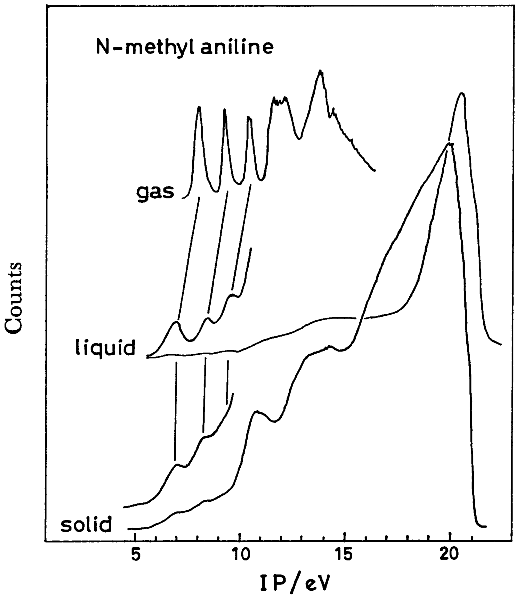

Fig. 4. He I spectra of *N*-methylaniline in the gas,[8] liquid[1] and solid phases.

Table 4. The vartical ionization potentials of gas, liquid, and solid *N*-methylaniline together with the relaxation shifts

Orbital	IP(gas)[13] eV	IP(liquid)[1] eV	IP(solid) eV	R_l[a)] eV	R[b)] eV
π_4	7.65	7.1	7.0	0.5_5	0.6_5
π_3	9.05	8.6	8.4	0.4_5	0.6_5
n	10.20	9.8	—	0.4	—
σ	11.5	—	(11.0)	—	(0.5)

a) $R_l = IP(\text{gas}) - IP(\text{liquid})$. b) $R = IP(\text{gas}) - IP(\text{solid})$.

N-*Methylaniline* ($C_6H_5NHCH_3$). Figure 4 shows the He I spectrum of *N*-methylaniline condensed on the gold substrate together with the spectra in the gas[8] and liquid[1] phases. To our knowledge, *N*-methylaniline is the first compound whose ultraviolet photoelectron spectrum has been measured in all the three phases of gas, liquid, and solid. As is seen in Fig. 4, the bands are more diffuse in the order of gas, liquid and solid, the order of increasing intermolecular interaction.

Table 4 gives the vertical IP's of *N*-methylaniline in the three phases together with the relaxation shifts, R_l and R for the liquid and solid phases. In the table we find that the value of R_l (0.4—0.5 eV) is

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[††] For example, in the case of solid naphthacene, the estimated FWHM due to the machanism (a) is 0.3 eV, the relaxation energy being *ca.* 1.2 eV.[12]

not much different from that of R ($\approx$0.6 eV). Since the relaxation shift is mostly due to the polarization energy of the neutral molecules surrounding a molecular ion, the small difference between the two sets of values suggests that no large change in the intermolecular distance arises on going from liquid to solid.

Pentane (C_5H_{12}). Figure 5 shows the He I spectrum of pentane condensed on the gold substrate. Since the gas phase spectrum of pentane is diffuse and its band assignment has not been well established, we compared the positions of prominent features of the gas phase spectrum[14] with those of the solid phase one (Table 5).

As is shown in Table 5, the relaxation shift of pentane is 0.7 eV, which is small compared with those of the other samples studied (1.1—1.3 eV), except for the case of *N*-methylaniline (0.6 eV). The molecule of pentane is chain-like and has freedom of rotation about its CC single bonds. When such molecules are solidified, especially at low temperature, they are expected to be loosely packed in solid. This may be the reason why pentane shows a small relaxation shift. In the case of *N*-methylaniline, its large substituent of the benzene ring may hinder a close packing of molecules in solid, also leading to a small relaxation shift.

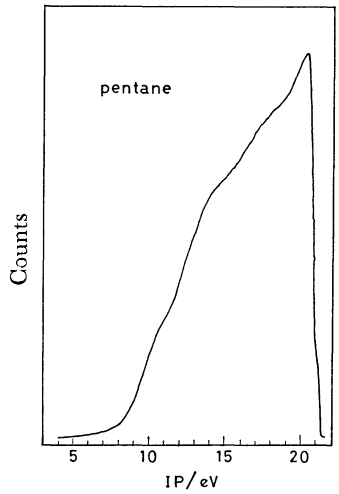

Fig. 5. He I spectrum of pentane condensed on Au at 77 K.

Table 5. The prominent features in the spectra of gas and solid pentane together with the relaxation shifts

E(gas)[14] eV		E(solid) eV	R[a)] eV
10.8 11.4 12.05	11.1[b)]	10.4	0.7
15.1		(14.4)	(0.7)

a) $R=E$(gas) $-E$(solid). b) Centre of the overlapping features.

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