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The Ultraviolet Photoelectron Spectroscopy of Aliphatic Hydrocarbons and Tetramethylsilane in the Solid State

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He I, Ne I, and Ar I ultraviolet photoelectron spectra were measured for solid hexane, 3-methylpentane, 2,2-dimethylbutane, neopentane, tetramethylsilane, cyclohexane, and 1-hexene deposited on a substrate at the temperature of liquid nitrogen. The spectra of all the compounds except hexane showed valence-band features. The threshold ionization potential was 7.6—8.9 eV, with a lowering of the threshold from the gas to the solid phase (polarization energy P_S) of 1.2—1.8 eV. These P_S values are in reasonable agreement with theoretical model calculations. To clarify the effect of intra- and intermolecular factors on P_S, the observed P_S values were compared with those of liquid-phase and solid-aromatic hydrocarbons. For compounds in which the bottom of the conduction band lies above the vacuum level, the polarization energy data showed that electrons with energies between these states are also emitted, possibly without any excitation of electrons to the conduction band in the bulk of the solid.

Ultraviolet photoelectron spectroscopy (UPS) is a powerful tool for studying the electronic structure and electron-transport properties of solids, including organic compounds.[1] Although extensive studies have been carried out on aromatics,[2–4] however, few results have been reported for aliphatics. We have already reported UPS studies of long-chain alkanes (n-$C_{28}H_{58}$, n-$C_{36}H_{74}$, and polyethylene),[5–9] whilst others[10] have concentrated more on small compounds containing one or two carbon atoms. We wish here to report a UPS study of aliphatic hydrocarbons containing five to seven carbon atoms, and of tetramethylsilane.

This work has two aims. One is to study the energetics of the ionized states of these solids. An important quantity obtained by UPS is the threshold ionization potential of a solid, which gives the location of the top of the occupied valence band. Together with the reported energy of the bottom of the conduction band, V_0 (relative to the vacuum level),[11,12] it gives a basic picture of the electronic structure of these solids. Further, a comparison of the threshold with that in the gas phase gives the interaction energy between the ionized molecule and the surroundings. This is mainly to be ascribed to the electric polarization of the surroundings and is called the polarization energy.[13,14] It is a fundamental quantity in discussing the ionized state of molecular solides.[14] However, the values of the polarization energies of aliphatic solids have not been experimentally determined except in a few small-molecule compounds. The experimental values observed here are discussed in comparison with theoretical-model calculations, the polarization energies in liquid phase,[15,16] or aromatic hydrocarbon solids.[3]

The second aim of this study is to obtain information as to the photoemission mechanism from aliphatic solids. In most of the solids studied here, the bottom of conduction band has been reported to lie above the vacuum level ($V_0>0$), with no bulk electronic state inbetween.[11,12] Some compounds have V_0's as high as ≈ 1 eV (1 eV=0.1602 aJ). It is of interest to determine whether or not electrons which do have energies between these two levels are emitted. This problem could be elucidated by the measured photoemission threshold and the polarization energies.

There is also a question about the origin of features in the photoelectron spectra. In our previous studies of long-chain alkane solids,[6,7] the UPS spectra for 11 eV $\leq h\nu \leq 21$ eV were dominated by conduction-band features, unlike those of most other organic solids, dominated by valence-band features.[1–4] The present study will elucidate if similar behavior is also exhibited by smaller aliphatic compounds.

Since the electronic properties of aliphatic compounds in the condensed phase are known to depend significantly on the molecular structure,[11,12,17,18] we chose to study the following species: hexane, 3-methylpentane, 2,2-dimethylbutane, neopentane, tetramethylsilane, cyclohexane, methylcyclohexane, and 1-hexene.

Experimental

The samples were commercially obtained, of the purity indicated: Hexane (99.8%, gas chromatographic standard), cyclohexane (99.7%), and tetramethylsilane (99.7%, NMR standard) from Merck; 3-methylpentane (99%), 2,2-dimethylbutane (99.8%), and methylcyclohexane (99.9%) from Tokyo Kagaku Seiki; neopentane (96.3%) and 1-hexene (99%) from Tokyo Kasei. All were further purified by vacuum distillation and the freeze-and-thaw technique in a system with a base pressure of 5×10^{-6} Pa.

The photoelectron spectra were recorded on a retarding-potential-type photoelectron spectrometer. The base pressure of the vacuum chamber was 2×10^{-8} Pa. A copper substrate 12 mm in diameter was located at the center of a nearly spherical collector coated inside with gold. The sample vapor was deposited through a variable-leak valve onto a substrate cooled to about 80 K by means of liquid nitrogen. The light source was a dc discharge lamp capable of He I (21.22 eV), Ne I (16.67 and 16.85 eV), and Ar I (11.62 and 11.83 eV) emission. For Ne I and Ar I, the mean values, 16.8 and 11.7 eV, were taken to be the incident energies respectively. As an exception, the higher energy components were used to calculate the photoemission thresholds. The energy analysis was performed by means of the ac-modulated retarding-potential technique reported previously,[2a] with a 0.2 V peak-to-peak modulation of 4 Hz. The energy resolution was 0.2—0.3 eV, determined by the Fermi edge of gold.

Although the film thickness was not measured, it was increased step-by-step until no essential change in the spectra could be observed on further deposition. Figure 1 shows such

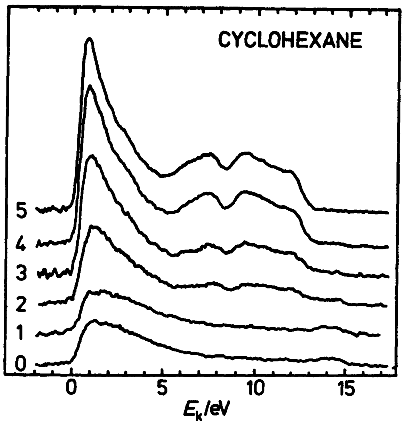

Fig. 1. He I photoelectron spectra of condensed cyclohexane against kinetic energy of electron E_k with a different degree of sample deposition. 0, copper substrate; 1 to 5, spectra showing the larger amount of condensation of cyclohexane.

a series for the He I photoelectron spectra of cyclohexane, plotted against the kinetic energy of photoelectrons E_k. The spectral profile appears to become settled at Curve 5, apart from the increasing secondary electron peak at $E_k \approx 0$ eV. A further increase in thickness resulted in the charging of the deposited sample, which could be detected as the tailing at the left-hand cutoff of the spectrum. Since 3-methylpentane, methylcyclohexane, and 1-hexene are known to form glass on rapid cooling, with their glass-transition temperatures above the temperature of liquid nitrogen,19) they should form such glasses under the present experimental conditions. For the other compounds, it is not clear whether they form crystalline films or become a morphous.

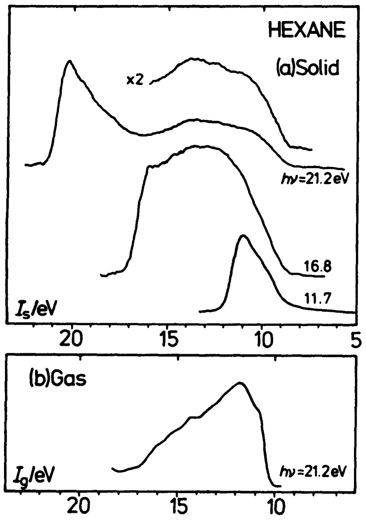

Fig. 2. Photoelectron spectra of hexane in solid (a) and gas (b) phases. Energy scales are shifted by 0.6 eV. The correspondence between the spectra of the two phases is dubious for this compound. The units of the ordinate are arbitrary and not common to the different curves (the same also in Figs. 5(a)—9(a)).

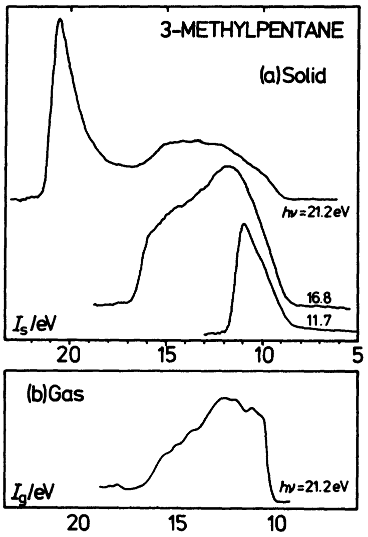

Fig. 3. Photoelectron spectra of 3-methylpentane in solid (a) and gas (b) phases. Energy scales are shifted by 0.8 eV for a good peak correspondence between the two phases.

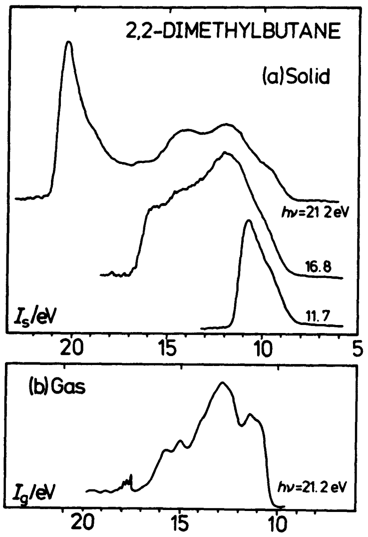

Fig. 4. Photoelectron spectra of 2,2-dimethylbutane in solid (a) and gas (b) phases. Energy scales are shifted by 0.9 eV for a good peak correspondence between the two phases.

Results and Discussion

General Aspects of the Photoelectron Spectra. Figures 2—9 (a) show the solid UPS spectra of the aliphatic compounds studied here. The abscissa is the solid ionization potential, I_s, relative to the vacuum level of the sample, converted from E_k as:

$$I_s = h\nu - E_k. \qquad (1)$$

For all the compounds some features in the low I_s region correspond to constant values of I_s, independent of $h\nu$. which indicates that they originate from valence bands. In particular, the right-hand edge of the spectrum corresponds to the top of the valence bands, and its I_s gives the threshold ionization potential of the solid. For the sake of comparison, the gas-phase photoelectron spectra reported by other workers20) are shown in Figs. 2—9 (b). The valence-band features of a solid corre-

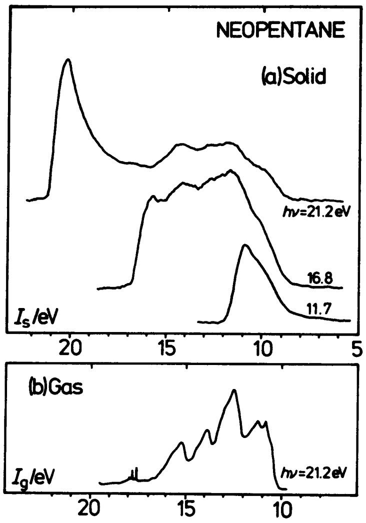

Fig. 5. Photoelectron spectra of neopentane in solid (a) and gas (b) phases. Energy scales are shifted by 1.1 eV for a good peak correspondence between the two phases.

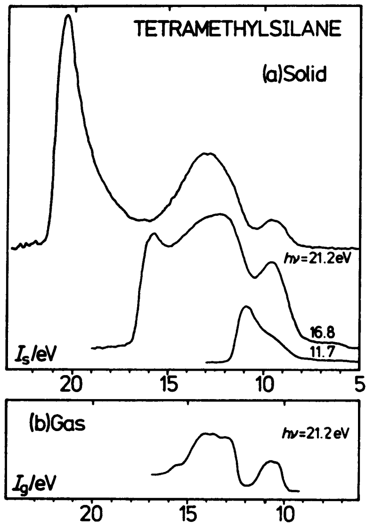

Fig. 6. Photoelectron spectra of tetramethylsilane in solid (a) and gas (b) phases. Energy scales are shifted by 1.1 eV for a good peak correspondence between the two phases.

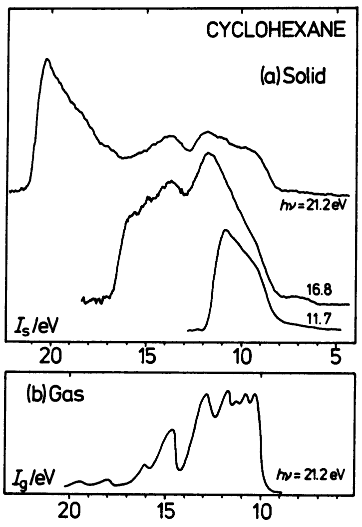

Fig. 7. Photoelectron spectra of cyclohexane in solid (a) and gas (b) phases. Energy scales are shifted by 1.0 eV for a good correspondence between the two phases.

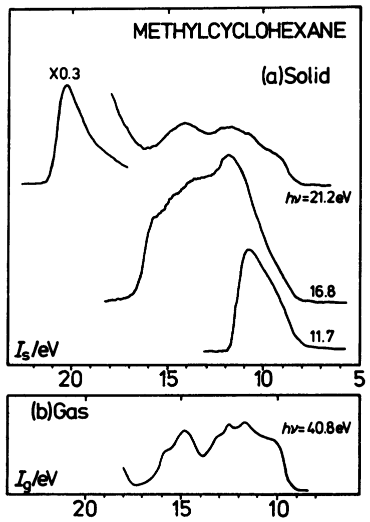

Fig. 8. Photoelectron spectra of methylcyclohexane in solid (a) and gas (b) phases. Energy scales are shifted by 0.7 eV for a good peak correspondence between the two phases.

spond well with the gas-spectrum features, when we make a shift between I_s and the gas-phase ionization potential I_g, as is indicated in each figure caption. Such a good correspondence shows that the photoemission from an organic solid may be regarded as the ionization of a molecule in the solid.[2,3]

If the conduction band gives rise to a band in the photoelectron spectrum its value of E_k should be independent of $h\nu$.[6,21] No such features are seen except for the secondary-electron peak at $E_k \approx 0$ eV. The features in the spectra of 1-hexene and hexane at $I_s \approx 9$ eV cannot be ascibed unambiguously to either the valence- or the conduction-band. These results show that the dominance of conduction-band features observed in the spectra of long-chain alkanes for $h\nu \leq 21.2$ eV[6,7] is not common to aliphatic compounds. Rather, they suggest that linear-chain aliphatics, maybe including hexane and 1-hexene, form a special group in terms of the photoemission from organics. Naturally, the cause of such variation in valence- or conduction-band dominance is of great interest, but here we will not discuss this point in detail, leaving it to a later publication.

The relative intensity of the secondary-electron peak at $E_k \approx 0$ eV is much larger in the He I spectrum than in the Ne I spectrum. This intensity difference can be ascribed to inelastic electron-electron (e-e) scattering, which can occur only when the photon energy exceeds the threshold energy E_1 given by:[21,22]

$$E_1 = E_g + E_x, \qquad (2)$$

where E_g and E_x are the band gap and the energy of the lowest electronic excitation in the solid respectively. The values of E_1 in condensed aliphatic compounds are

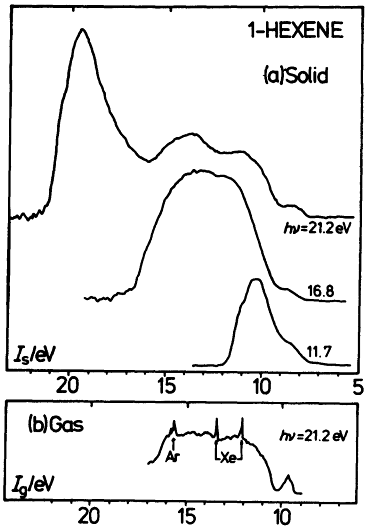

Fig. 9. Photoelectron spectra of 1-hexene in solid (a) and gas (b) phases. Energy scales are shifted by 1.0 eV for a good correspondence of the lowest ionization potential peaks between the two phases. The correspondence is dubious for the region of $I_s > 9$ eV.

estimated to be ≈16 eV (*e.g.*, for liquid hexane, $E_g = 8.7$ eV[16] and $E_x = 7.4$ eV).[23] In the Ne I ($h\nu = 16.8$ eV) spectra, $h\nu$ is comparable with E_1, and most of the photoexcited electrons cannot undergo e-e scattering. In the He I spectra, $h\nu$ is sufficiently large to cause appreciable e-e scattering, and hence secondary-electrons. In contrast to the present results, the smaller E_1 values of 4—8 eV in aromatics result in strong secondary-electron bands, even in the Ne I spectra.[2b]

Photoemission Threshold and Polarization Energy. Table 1 lists the values of the threshold ionization energy I_s^{th} determined as the intercept of the low I_s linear extrapolation of the spectrum with the energy axis. The values obtained from the spectra for three photon energies agreed within ±0.1 eV, including a reproducibility for several samples.

There is a problem in the determination of the I_s^{th} of amorphous solids, for the ionization potential of a molecule in the solid may depend on the arrangement of the surrounding molecules. However, the onsets in the lowest I_s region of the observed spectra are fairly distinct, which suggests that the fluctuation of this kind is minimal.

Using these values and the reported values of V_0,[11,12] which are also listed in Table 1, we can construct basic energy diagrams for these compounds. The band gap between the valence and conduction bands is 8—9 eV, which is consistent with the onset energies of the electronic absorption[23] and the photoconduction[16,24] of these compounds in the condensed phase.

The ionization potential of a molecule in the bulk of a solid is determined as the gas-phase ionization potential lowered by the polarization energy, P_s of the surroundings.[13,14] We can determine P_s from a comparison of the gas and solid-state photoelectron spectra. According to an analysis of the contribution of molecules in the bulk and at the surface, we have already noted[3] that we should compare the thresholds of these spectra, rather than the peak energies, to obtain the bulk polarization energy. That is, P_s should be determined as:

$$P_s = I_g^a - I_s^{th}, \tag{3}$$

where I_g^a is the threshold (adiabatic) ionization potential

Table 1. Observed photoemission thresholds and related energy-structure parameters

Compound	$I_s^{\mathrm{th\,a)}}$ / eV	$V_0^{\mathrm{b)}}$ / eV	$I_g^{\mathrm{a\,c)}}$ / eV	$P_s^{\mathrm{d)}}$ / eV	$P_s^{*\mathrm{e)}}$ / eV
Hexane	8.5_5	$0.62^{\mathrm{f)}}$	10.2_5	1.7(2.1)	2.3
		$0.98^{\mathrm{g)}}$			2.7
		$0.9^{\mathrm{i)}}$			2.6
3-Methylpentane	8.8_5	$1.29^{\mathrm{g)}}$	10.2	1.3(1.7)	2.6
		$1.20^{\mathrm{h)}}$			2.5
		$0.6^{\mathrm{i)}}$			1.9
2,2-Dimethylbutane	8.8	$-0.013^{\mathrm{f)}}$	10.2	1.4	—
		$0.59^{\mathrm{g)}}$			2.0
Neopentane	8.7	$0.33^{\mathrm{g)}}$	10.2	1.5	1.8
		$<0^{\mathrm{i)}}$			—
Tetramethylsilane	8.2	$0.440^{\mathrm{f)}}$	9.79	1.6	2.0
		$<0^{\mathrm{i)}}$			—
Cyclohexane	8.2	$0.47^{\mathrm{f)}}$	9.88	1.7(1.7)	2.2
		$0.9^{\mathrm{i)}}$			2.6
Methylcyclohexane	8.3	$1.00^{\mathrm{g)}}$	9.5	1.2(1.6)	2.2
		$1.43^{\mathrm{f)}}$			2.6
		$1.24^{\mathrm{h)}}$			2.4
1-Hexene	7.6	$0.6^{\mathrm{i)}}$	9.37	1.8(2.4)	2.4

a) Photomission threshold observed in the present study. b) Energy of the bottom of the conduction band relative to the vacuum level. c)Gas-phase adiabatic (thereshold) ionization potential taken from Ref. 20. The values of hexane, 3-methylpentane, and 2,2-dimethylbutane were read from the spectra. d) Polarization energies calculatcd from Eq. 3 (correct values). The values in parentheses are from Ref. 12. e) Polarization energies calculated from Eq. 6 (wrong values, see text). f—i) Values from Refs. 11a,b,c, and 12 respectively.

TABLE 2. POLARIZATION ENERGIES CALCULATED BY MEANS OF Eq. 5 AND PARAMETERS USED

Compound	ε[a]		ρ[b]	P_s[c]
	Crystal	Glass	pm	eV
Hexane	2.33 (A)	2.23 (B)	214	1.92 (A) 1.86 (B)
3-Methylpentane	—	2.31 (A) 2.24 (B)	214	1.91 (A) 1.86 (B)
2,2-Dimethylbutane	2.18 (A)	2.23 (B)	219	1.78 (A) 1.81 (B)
Neopentane	1.98 (A)	2.14 (B)	216	1.65 (A) 1.78 (B)
Tetramethylsilane	2.19 (A)	2.20 (B)	225	1.74 (A) 1.75 (B)
Cyclohexane	2.48 (A)	2.39 (B)	213	2.02 (A) 1.97 (B)
Methylcyclohexane	—	2.53 (A) 2.38 (B)	213	2.04 (A) 1.96 (B)
1-Hexene	—	2.36 (A) 2.28 (B)	210	1.98 (A) 1.92 (B)

a) Optical permittivity estimated as described in the Appendix. Symbols in the parentheses indicate the methods given there. b) Effective radius of the cation evaluated from the density. c) Polarization energy estimated using Eq. 5.

in the gas phase. The values of I_g^a reported by other workers and the P_s values calculated by means of Eq. 3 are listed in Table 1. The maximum error in P_s is estimated to be ±0.2 eV from those (±0.1 eV) for both I_g^a and I_s^{th}. As has already been noted, the shift between I_s and I_s to give the best peak correspondence (relaxation shift) is shown in each caption of Figs. 2—9, which may be convenient in comparing our results with those of other workers.

Recently Hiraoka[12] estimated the P's for several of the compounds studied here. He estimated I_s^{th}, from the values of E_g and V_0 measured by an electron-transmission experiment, as:

$$I_s^{th} = E_g - V_0, \tag{4}$$

and used Eq. 3. His values are also listed in Table 1. They are, on the average, 0.4 eV larger than the present directly measured ones, but the latter are within the estimated error of his values, ±0.4 eV for E_g and $^{+0.2}_{-0.3}$ eV for V_0.

We will discuss the observed values of the polarization energy P_s in some detail, for it is an important quantity in the energestics of the ionized state of a molecular solid.

Comparison with Theoretical Models. Two models have been reported for the theoretical estimation of the polarization energy. In the first model, by Lyons and his-coworkers,[13,25,26] the polarization energy is calculated as the sum of the interaction energy between the cation and the multipoles induced on surrounding molecules. Lyons and Mackie[25] reported P_s=1.7 eV for hexane, which is in good agreement with the present experimental result. Unfortunately, no calculations are reported for the other compounds studied here.

In the second model, by Born,[27] the ion is treated as a point charge at the center of a spherical cavity, while the surrounding molecules are regarded as a continuous medium. The polarization energy is given by:

$$P_s = (e^2/2\rho)(1-1/\varepsilon), \tag{5}$$

where e is the electronic charge: ρ, the effective radius of the ionic cavity, and ε the optical permittivity of the medium. This model can be applied not only to crystals but also to liquids[15—17] and amorphous solids.[11,12]

In order to calculate P_s by means of this model, the values of ρ and ε are needed. We estimated ε (solid) at the temperature of liquid nitrogen in two ways (A and B), as will be described in the Appendix. For compounds whose state of aggregation is not clear, ε was evaluated for both crystalline and glassy states. The effective radius was calculated as $v^{1/3}/2$, where, $v=1/N$ and where N is the number density of molecules, as evaluated from the density; this gave a reasonable agreement with the experimental values in the case of aromatic hydrocarbons.[3] The values of these parameters and of P_s as calculated by means of Eq. 5 are listed in Table 2.

The agreement between the experimental and calculated values is reasonable, considering the estimated error of ±0.2 eV in the observed values. The state of aggregation or the method of estimation of ε do not affect the calculated P_s so much. Calculations using two other kinds of effective radius: (1) the van der Waals radius used in the hard-core model of the critical volume[28] and (2) the electron-molecule hard-core radius,[16,27] gave larger P_s values, with poorer agreement with the experimental values. We note that the above trends are common in molecules from spherical to linear, which have varying degrees of matching to the assumption of spherical cavity. This suggests that the anisotropy in the molecular shape of these compounds is not yet so large as to break the validity of this model.

The reasonable success of the present way of evaluating ρ tempts us to calculat the ρ of TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine), which has been frequently used as a photoionizing dopant in these compounds. The crystal structure[30] gives 316 pm, which is comparable with one of the previous estimates, 324 pm,[31a] but which shows a discrepancy from the 249 and 193 pm in Refs. 31b and 11c.

In conclusion, theoretical calculations, both the Lyons model and Born's, predict reasonably accurate values for P_s. However, a very detailed discussion of the correlation between the calculated and observed values does not appear feasible at this time.

Comparison with Aromatic Hydrocarbons. Aromatic hydrocarbons form another representative group of organic compounds. The P_s values of aliphatics range from 1.2 to 1.8 eV, which is, on the average, a little smaller than the almost constant value of $\approx$1.7 eV for condensed aromatic hydrocarbons with planar structures.[3]

We can analyze these values in terms of molecular polarizability and molecular packing.[3] In aliphatics, ε is much smaller than those in aromatics (ε=4.8—5.9 from naphthalene to coronene). As may be seen in Eq. 5, this will make the P_s values of aliphatics smaller. However, ρ is also smaller in aliphatics than in aromatics (ρ=280—360 pm for the aromatics described above). This tends to increase the P_s. The observed P_s values should be the result of the balance between these two factors.

Such a difference in P_s preserves or even enlarges the difference between the I_g^a's of aliphatics and aromatics in going to the solid phase. Thus, the I_s^{th} values of saturated compounds exceed 8 eV and are higher than those of aromatics (*e.g.*, 7.1 eV for benzene[32]). A similar preservation also exists between saturated and unsaturated (*e.g.*, 7.1 eV for 1-hexene) aliphatic hydrocarbons.

Comparison with Polarization Energies of Liquid Phase. Recently, data have accumulated on the polarization energies of pure liquid P_l. Schmid *et al.*[15] and Casanovas *et al.*[16] measured the band gap of tetramethylsilane and some alkanes as the photoconduction thresholds. The polarization energies were calculated by means of Eqs. 4 and 3 using reported values of I_g^a and V_0. Their results are listed in Table 3, together with the $\Delta P_{sl}=P_s-P_l$ calculated with P_s in Table 1. For most compounds, P_s and P_l are rather similar, indicating that the polarization energy and the ionization threshold do not change very much in these condensed states. The small positive values of ΔP_{sl} (except for 2,2-dimethylbutane) may be understood as being due to the decrease in density, and thus in ε, at the transition from the solid to the liquid phase. The calculation of ΔP_{sl} by means of Eq. 5, using the ρ and ε of these two states, gives an almost common value of 0.2—0.3 eV. Considering the possible errors in P_l and P_s, however, it is difficult to discuss these values further.

TABLE 3. POLARIZATUION ENERGIES OF LIQUID PHASE AND THEIR DIFFERENCES FROM SOLID PHASE

Compound	$P_l^{a)}$ / eV	$\Delta P_{sl}^{b)}$ / eV
Hexane	1.61[c)]	0.1
2,2-Demethylbutane	1.46[c)]	−0.1
Neopentane	1.2_6[e)]	0.2
Tetramethylsilane	1.17[c)]	0.4
	1.12[d)]	0.5
Cyclohexane	1.46[c)]	0.2

a) Polarization energy of the liquid phase. b) $\Delta P_{sl}\equiv P_s-P_l$. c) Ref. 16. The values are slightly different from theoriginal values due to the use of the I_g's in Table 1 instead of tho se used in Ref. 16. d) Ref. 15.

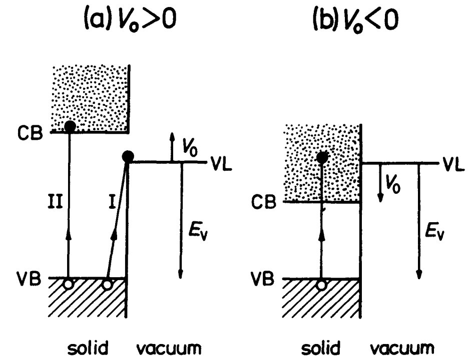

Fig. 10. Schematic energy diagram of photoemission process. VB, top, of the valence band; CB, bottom of the conduction band; VL, vacuum level; V_0, the energy of CB relative to VL; E_v, the energy differnce between VL and VB. (a) The case of $V_0>0$. I denotes the direct photoemission into vacuum and II denotes the photoexcitation process in the rigorous three-step model. (b) The case of $V_0<0$.

Interpretation of the Observed Photoemission Threshold Energies. Most of the compounds studied here have been reported to have fairly large positive V_0 values (Table 1). This means that the lower boundary of the conduction band (CB) lies above the vacuum level (VL) (Fig. 10), with no bulk electronic states in between. This raises a question as to whether photoelectrons with energies between CB and VL may be emitted by direct photoemission from the valence band into the vacuum (Case I), or whether the electron must first be excited to the conduction band in the bulk of the solid, and hence may not possess an energy between the two levels (Case II). The latter case was favored by Delahay[33] and by Less and Wilson[24] on the basis of a three-step photoemission model (photoexcitation in the bulk/electron transport/escape into the vacuum).[21]

An examination of the photoemission thresholds and polarization energies enables us to determine which model is most probably correct. In Case I, the experimentally observed threshold I_s^{th} corresponds to the excitation energy from the top of the valence band to the vacuum E_v (VB→VL in Fig. 10(a)), as in the case of $V_0<0$ (Fig. 10(b)). This was our assumption in the preceding part of this paper. In Case II, I_s^{th} gives the band gap $E_g=E_v+V_0$ (VB→CB in Fig. 10(a)). Since the polarization energy is defined as $I_g^a-E_v$, the "true" polarization energy in Case II, P_s^*, is:

$$P_s^* = I_g^a - (I_s^{th} - V_0), \tag{6}$$

instead of $I_g^a-I_s^{th}$ (Eq. 3). The values of P_s^* calculated using the reported V_0's are listed in Table 1.

The theoretical results of Lyons and Mackie[25] give the polarization energies for hexane and anthracene as 1.7 and 2.1 eV respectively. This indicates that the polarization energy of hexane is unlikely to exceed that of anthracene. For anthracene, the negative value of V_0[14] assures that Eq. 3 gives the polarization energy. The observed P_s=1.7 eV for anthracene[3] shows that the idea that $P_s^*=2.3_2$ to 2.6_8 eV for hexane is very improbable, while $P_s=1.7$ eV in Table 1 is reasonable. Therefore, Case I applies, and I_s^{th} corresponds to the VB→VL excitation. Thus, the discussion in the preceding part of this paper is substantiated. To support this, Koch *et al.*[34] showed that $E_g>I_s^{th}$ for solid Ne and Ar, from independent measurements of E_g and I_s^{th} by means of optical spectra and photoemission respectively. This gives another example where Case I applies.

It was shown that the photoemission experiment can provide the energy of electrons relative to the vacuum level, even for organic solids with positive V_0 values. Considering that an advantage of UPS is that one can get the absolute energy of electrons relative to the vacuum level, this is an important conclusion. Furthermore, the above discussion suggests that the photoemission in aliphatic solids most probably cannot be rigorously divided into three steps (only because at present we cannot exclude the possibility of the existence of defect states between CB and VL, which may allow optical excitation and the transport of electrons in this energy range[12]).

Concluding Remarks

The ultraviolet photoelectron spectra of seven aliphatic hydrocarbons and tetramethylsilane were measured in an attempt to elucidate the energetics of the ionized state and the photoemission mechanism. Most of the spectra revealed valence-band features, but linear compounds (hexane and 1-hexene) showed some spectral features which may be due to conduction-band structures. Together with the dominance of the conduction band observed in longer-chain normal alkanes, this suggests that long linear aliphatics may form a special group in terms of photoemission from organics.

Although it has been reported that the conduction bands lie above the vacuum level, with no bulk electronic states in between, electrons with energies between the two levels are emitted. That is, we can determine the location of the valence-band features relative to the vacuum level. This ensures the usefulness of UPS as a tool for probing the electronic structures of organic solids with positive V_0 values. By virtue of this fact, the experimental values of the photoemission thresholds and the polarization energies could be obtained directly from the observed spectra.

The reasonable agreement of the observed polarization energies with the model calculations confirmed the validity of these models, and also indicated that both aliphatics and aromatics can be treated in a common theoretical frame. Further studies of other aliphatics are desired in order to confirm this point.

Although the present study gave these important pieces of general information on the electronic structure and photoemission mechanism of aliphatic solids, more studies are required in order to clarify such problems as the peculiarity of long-chain molecules and the difference between solid and liquid states. The accumulation of data on other compounds is required for the former, while the continuous examination of the solid and liquid states, using the same photoelectron spectrometer, will be useful for the latter. We have already started these kinds of studies.

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Appendix

Here we will describe the two methods[11] of evaluating the optical permittivity ε of aliphatic solids at the temperature of liquid nitrogen, methods which were used for the calculation of P_s by means of Eq. 5.

One of them (Method A) applies the Clausius–Mosotti relation $(\varepsilon-1)/(\varepsilon+2)(M/d)=N_A\alpha/3$, where M is the molecular weight; d, the density; N_A, the Avogadro constant, and α, the molecular polarizability. Assuming that α is independent of the temperature, we first calculated its value using ε and d[35] for the liquid at room temperature. The value of ε was taken as the square of the refractive index n for the Na D emission lines.[35] The procedure was then reversed to obtain ε at low temperatures from the solid density.

In the other method (Method B), the value of n at a low temperture was estimated by the extrapolation of n using $\mathrm{d}n/\mathrm{d}T$ (liquid), and ε was taken as equal to n^2.

Method A is applicable for both crystalline and glassy states, while B may be used only for the glassy state because of the discrete change in n at the liquid-crystal transition. For compounds whose state of aggregation was not clear, ε was evaluated for both states. The low-temperature values of d for crystalline states were calculated for the nearest temperature phase whose crystal structure data are available.[36] For tetramethylsilane, a directly measured value for d is available.[37] For glasses, d and $\mathrm{d}n/\mathrm{d}T$ are available for several compounds.[19,36] For compounds with no observed data, $\mathrm{d}n/\mathrm{d}T$ of similar compounds were used. The various values of ε thus obtained are listed in Table 2.

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