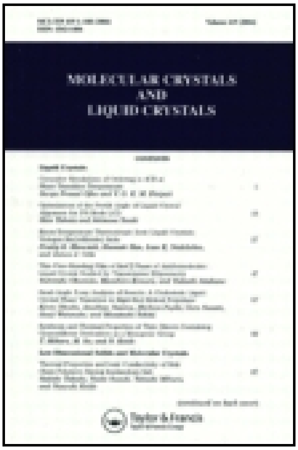

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Ionization Energies of Free Molecules and Molecular Solids

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Ionization Energies of Free Molecules and Molecular Solids

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Gas phase ionization energies I_g for compounds of interest from electrical and electronic viewpoints can be determined using photoemission techniques. Also reasonably good estimation can be obtained from oxidation potential and energy of charge-transfer absorption in solution. Photoemission techniques are also used for determining ionization energies of molecular solids I_s. These methods are reviewed, and a table of ionization energies for 120 compounds are given. The difference Δ between I_g and I_s can be ascribed to the polarization of surrounding molecules and, in some cases, intermolecular band formation. The trends in I_g, I_s, and Δ for various compounds are discussed. Finally, information from I_g and I_s is surveyed for the energetics of ionized states and the electronic structure of binary systems.

1. INTRODUCTION

Ionization energy is a leading parameter in discussing electrical and electronic phenomena in organic solids, such as charge carrier generation, charge carrier injection, and charge transfer phenomena. In the narrow sense, the term means the minimum energy required to remove an electron from a molecule or a solid (ionization threshold energy). This corresponds to the ionization from the highest occupied molecular orbital (HOMO). In a wider sense, the term also means the energy required to remove an electron from deeper orbitals. Here we will be mainly concerned with the former quantity which governs the above-mentioned phenomena, although we will also mention the latter.

In the following we discuss, with some historical comments, (1) experimental determination of ionization energies of free molecules (I_g), including indirect methods for solution, (2) methods for determining the ionization energies of molecular solids (I_s), (3) the effect of intermolecular interaction revealed by the comparison of I_g and I_s, and (4) relevance to the various electric and electronic phenomena in molecular solids.

2. IONIZATION ENERGIES OF FREE MOLECULES

2.1 Direct methods

Ionization energies of free molecule I_g have been determined by various direct and indirect methods. At first we will discuss the direct methods for vapor sample, i.e. (1) analysis of Rydberg transitions in optical absorption spectra, which converge to the ionization energy, (2) electron-impact (EI) ionization efficiency as a function of electron energy, (3) photoionization (PI) efficiency as a function of photon energy, and (4) uv photoelectron spectroscopy (UPS).

Among these, the optical and EI methods have been developed at first. The optical methods has given precise and accurate values for small molecules,[1] but its application to large molecules were generally difficult due to the diffuse nature of the spectra. The EI method[2] was not limited by such a factor, but the asymptotic rise of ionization efficiency at the onset and usually low monochromaticity of electrons hindered a precise determination of ionization energy. Such a situation was much improved in 1950s by the (PI) experiments,[3,4] where clear ionization onsets can be observed. As a result, rather detailed discussion of the relationship between I_g and molecular electronic structure was already possible at the beginning of 1960s.[3,4]

Further progress was brought about by the development of UPS, which was invented independently by the groups of Vilesov[5] and Turner.[6] By analyzing the kinetic energy distribution of photoelectrons produced by monochromatic high-energy photon (usually HeI or HeII resonance lines of 21.2 eV and 40.8 eV, respectively), it gives not only the ionization energies of the HOMO, but also those of deeper orbitals. Since the whole valence electronic structure can be studied with this technique, its impact extended over the whole field of chemistry.[6-9] Helped with the development of commercial instruments equipped with heating probe for vaporizing solids and liquid samples, most fundamental organic molecules have been studied.[10]

In discussing the results by these methods, we distinguish the vertical and adiabatic ionization energies. The former corresponds to the ionization without changing the molecular geometry, while the latter to the ionization to the fully relaxed state of the ion. Since the Franck-Condon principle requires largest ionization probability at the vertical transition, peak energy in a photoelectron spectrum gives the vertical ionization energy. The adiabatic value, which we will mainly discuss, is obtained from the onset of photoelectron band. Optical, EI, and PI methods also gives adiabatic values. The vertical values are used at the comparison with theoretical values, which are usually obtained as the negative of the orbital energies (Koopmans' theorem), implicitly assuming fixed molecular geometry.

The photon energy scale in optical and PI methods are rather accurate (±0.01 eV), while the energy scale of UPS at low I_g usually has an ambiguity of 0.1 eV or so, since it is calibrated with Xe/Ar internal standards at large I_g (12–16 eV). This situation can be improved with He II light source, since self ionization of He gives a peak at 5.00 eV in the He I spectrum.

With these methods, values of I_g have been determined for many molecules. As lists of these values, References 11 and 12 are available, but many other molecules have been measured after their pubication. In Table I we list selected values of I_g for compounds of interest from the viewpoint of electrical phenomena. Although we preferred values determined by UPS for uniformity, they agree with available values by PI technique within 0.2 eV.

Next we will examine the trends in these values. As is well known, molecules with delocalized π electron systems have small I_g, which can be further reduced with substitution by electron-releasing groups such as NH_2, CH_3, and CH_3O, as seen in *N*,*N*,*N'*,*N*-tetramethyl-*p*-phenylenediamine (TMPD) and tetrakis-(dimethylaminoethylene) (TMDA). There are also molecules with very small I_g for their molecular size, such as tetrathianaphthacene (TTN), tetrathiafulvalene (TTF), and metallocenes, which include hetero- or metal-atoms. These molecules are good electron donors. In contrast, electron acceptors with electron-withdrawing subsitituents, such as halogens, NO_2, and CN groups have large values of I_g, as seen e.g. in quinones, tetracyanoquinodimethane (TCNQ), and tetracyanoethylene (TCNE).

2.2 Indirect methods

The direct methods described in 2.1 are not applicable for molecules which decompose on vaporization. Further, the sophisticated apparatuses for these methods are not usually easy to access for the people synthesizing new interesting materials. These factors led to the development of auxiliary techniques using solution. Two most popular ones are the measurements of (1) electrochemical oxidation potential E_{ox}[13,14] and (2) energy of charge-transfer (CT) absorption $h\nu_{CT}$.[15] Also there is a trial by measuring (3) threshold energy of photoconduction in nonpolar solvent E_{pc}.[16] In all cases, correction is necessary for solvation energies etc., which introduces some inaccuracy to the estimated value of I_g.

The oxidation potential can be measured with a conventional apparatus. The disadvantage is that it is applicable only to reversible oxidation processes. The correction term contains the difference of the solvation energy of neutral and ionized species, the potential of the electrode to the vacuum level, the reorientation energy of solvents,[17] and so on.

CT spectra can be also measured with conventional apparatus. The drawback is that a simple linear relation between $h\nu_{CT}$ and I_g holds only for weak complexes. For example, amine-I_2 complexes show large deviation from the correlation for almost all other I_2 complexes.[15b] The correction term includes factors such as the solvation energy and the coulomb interaction of the CT pair, which may depend on the detailed structure of the complex.

In Figure 1, we show the correlation between I_g and E_{ox} as an example of such correlation. It is a combined and expanded version of the results of References 13, 15, 18 and 19, with the values of E_{ox} in Table I. We see that a semiquantitative correlation exists, which allows an estimation of I_g within 0.5 eV or so. However, we note that some show larger scatter, in particular in the small I_g region.[18,19] Further, the slope deviates from unity. Similar deviation has been also observed for $h\nu_{CT}$ and between the reduction potential and electron affinity,[20] and ascribed to the solvation energy.

TABLE I

Ionization energies of free molecules (I_g) and molecular solids (I_s), oxidation potentials (E_{ox}) vs saturated calomel electrode, and gas-to-solid reduction of ionization energy (Δ).

			I_s/eV^b					
	I_g/eV^a	Ref.	UPS	Yield	Ref.	E_{ox}/V (vs SCE)	Ref.	Δ/eV
Methane	12.70	10	11.2		97			1.2
Hexane	10.2_5*	10	8.5_5		121			1.7
Iodine	9.26*	10	6.3_4		44			2.9
CI_4	9.00	101	5.5_0		47			3.5
C_2I_4	8.57	102	5.04		47			3.5
Benzene	9.17	69	7.3		118	2.30	13	2.1
Naphthalene	8.12*	69	6.4		43	1.54	13	1.7
Anthracene	7.36*	69	X5.6_7		24	1.09	13	1.7
Naphthacene	6.89*	69	5.10		43	0.77	13	1.8
Pentacene	6.58*	69	4.85		90			1.7
Phenanthrene	7.86	73	X6.0_8		25	1.50	13	1.8
Chrysene	7.51	73	5.8		43	1.35	13	1.7
Benz[a]anthracene	7.38	73	5.64		90	1.18	13	1.7
Triphenylene	7.81	75	6.2		91	1.55	13	1.6
Dibenz[a,h]anthracene	7.35	43	5.55		91	1.19	13	1.8
Picene	7.5	73	5.7		91	1.33	13	1.8
Pyrene	7.37	75	X5.5_8		25	1.16	13	1.7
Benz[a]pyrene	7.12	73	5.4		124	1.27	13	1.7
Perylene	6.90*	43	X5.1_2		18	0.85	13	1.8
Benzo[ghi]perylene	7.12*	73	X5.2_6		25	1.01	13	1.9
Coronene	7.25*	75	5.52		90	1.23	13	1.7
Ovalene	6.86	73						
Violanthrene A	6.42	43	4.8_6		43			1.6
Tetrabenzo[a,cd,j,lm]perylene	6.58	125	5.3_4		125			1.2
Tetrabenzopentacene	6.13	125	4.9_8		125			1.2
Quaterrylene	6.11	78	4.76		96			1.4
Graphite			4.7		141			
Biphenyl	8.2	83						
Sexiphenyl	7.2	126	5.9		126			1.3
Azulene	7.43	72				0.71	13	
Fluoranthene	7.95	72				1.45	13	
Acenaphthene	7.82	72						

Acenaphtylene	8.22	72				1.21	13	
Toluene	8.67	80	7.28		132	1.98	13	1.4
o-Xylene	8.4*	103				1.89	13	
m-Xylene	8.5*	103				1.91	13	
p-Xylene	8.3*	103				1.77	13	
α-Methylnaphthalene	7.95v	95				1.43	13	
β-Methylnaphthalene	7.93v	95				1.45	13	
9-Methylanthracene	7.23	57	5.7_5	5.6_8	57	0.96	13	1.5
Rubrene	6.41	135	5.3		135			1.1
Phenol	8.48	84						
Fluorobenzene	8.9*	74						
Chlorobenzene	8.9*	74						
Bromobenzene	9.0*	74						
Iodobenzene	8.4*	74						
Anisole	8.0*	74						
Cyanobenzene	9.2*	74						
Nitrobenzene	9.6*	74						
p-Dinitrobenzene	10.3	82						
9,10-Dichloroanthracene	7.5*	134	5.8	5.7_5	94			1.7
9,10-Dibromoanthracene	7.5*	134		6.08	108			1.4
1,3,6,8-Tetracyano*pyrene*			6.21	6.35	57			
Pyridine	9.26	6	7.3*		142	2.12	14	2.0
Pyrrole	8.209	79				1.06	14	
Thiophene	8.87	84				1.90	14	
Quinoline	8.5*	139						
Carbazole	7.53	92	5.87	ca.6.2	56			1.5
Acridine	7.88	92		ca.7.1	108			
Phenazine	8.4	110			108			
Phenothiazine	6.82	93	$X5.1_5$		25	0.58	143	1.5
Tetraphenyl[3,4-c] thienothiophene	6.1	111						
1,2,5,6-Tetramethyl-6a-thia-1,6-diazapentalene	6.3*	87						
1,8-Dithianaphthalene	7.0*	121	5.75		121			1.3
Tetrathianaphthacene (TTN)	6.07	47	4.4		47	0.25	143	1.7
Tetraselenonaphthacene			4.45		127			

TABLE I

continued

Tetrathiafulvalene (TTF)	6.4	89	5.0		112	0.31	143	1.4
Dimethyl TTF (DMTTF)	6.00	47	5.1		47			0.9
Tetramethyl TTF (TMTTF)	6.03	47	4.9		47	0.24	143	1.1
Hexamethyl TTF (HMTTF)	6.06	18	4.6_3		18	0.33	129	1.4
Dibenzo TTF (DBTTF)	6.68	47	4.4		47	0.53	122	2.3
Bis(ethylenedithiolo) TTF (BEDT-TTF)	6.21	18	4.7_8		18	0.53	122	1.4
Tetraselenafulvalene (TSF)	6.68	133	4.9_9		18	0.44	122	1.7
Tetramethyl TSF (TMTSF)	6.27	88	4.8_4		18	0.41	143	1.4
Hexamethyl TSF (HMTSF)	6.12	18	4.7_5		18	0.41	122	1.4
Tetrathiomethoxy TSF (TTMTSF)	6.29	18	5.0_0		18	0.50	122	1.3
Hexamethylenetetratellurafulvalene (HMTTeF)	6.81	19	4.87		19	0.40	129	1.9
Methylamine	8.95	137						
n-Butylamine	8.59	137						
Triethylamine	7.37	137				1.15	14	
Aniline	7.71	84						
N-Methylaniline	7.4*	6	5.9		118			1.5
p-Phenylenediamine (PD)	6.84	136	5.2		98			1.7
N,*N*′-Dimethylaniline	7.1	82						
N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine (TMPD)	6.2	82		4.7	98	0.10	143	1.5
				4.63	124			
Tetrakis(dimethylamino)ethylene (TDAE)	5.36	77						
1-Naphthylamine	7.1*	107				0.54	13	
2-Naphthylamine	7.5*	107				0.64	13	
1,5-Diaminonaphthalene	6.74	107				0.46	13	
1,8-Diaminonaphthalene	6.65	107				0.47	13	
Triphenylamine	6.82	119	5.4_2		119			1.4
Benzidine			5.10		124			
p-Quinone	9.95	81						
p-Chloranil (CA)	9.74	46	8.1		46			1.6
p-Iodanil (IA)	8.58	46	5.6		46			3.0
Anthraquinone	9.05	106	7.6		114			1.5
Violanthrone			5.10		23			
Tetracyanoethylene (TCNE)	11.7	99						
Tetracyanoquinodimethane (TCNQ)	9.5	99	7.4		99			2.1

Tetracyanonaphthoquinodimethane (TNAP)	8.5	100	6.0		100	2.5
Pyromellitic dianhydride (PMDA)	10.9*	86	8.0*		86	2.9
Metal-free Phthalocyanine (PC)	6.1*	71	5.15		140	1.0
				M5.20	31	
Cu-PC	6.1*	71	(α)4.8_8		49	1.2
			(β)4.6_2		49	1.5
Tetraphenylporphyrine (TPP)	6.39v	104				
Zn-TPP	6.2	104	5.0		128	1.2
Chlorophyll *a*			4.8		140	
Chlorophyll *b*			5.25		113	
Cytochrome *c*			(ox)6.1		105	
			(red)5.8			
Cytochrome c_3			(ox)5.4		105	
			(red)4.6		128	
Ferrocene	6.72	117	5.4		116	1.3
Decamethylferrocene	5.7	76	4.7		116	1.0
Decamethylnickellocene	4.4	76				
β-Carotene	6.5	115		5.4	138	1.1
Methyl viologen			(red)3.6		109	
			(ox)4.8	4.8 – 9	109	
Rhodamn B				M5.10	32	
polyethylene			8.48	8.50	85	
polyacetylene			5.24		131	
Poly(*p*-phenylene)			5.65		59	
Polythiophene			5.65		59	
Poly(*N*-vinyl carbazole)			5.85		130	

[a] *: read from the spectrum. v: vertical I_g.

[b] *: read from the spectrum. X: single crystal. M: Millikan method.

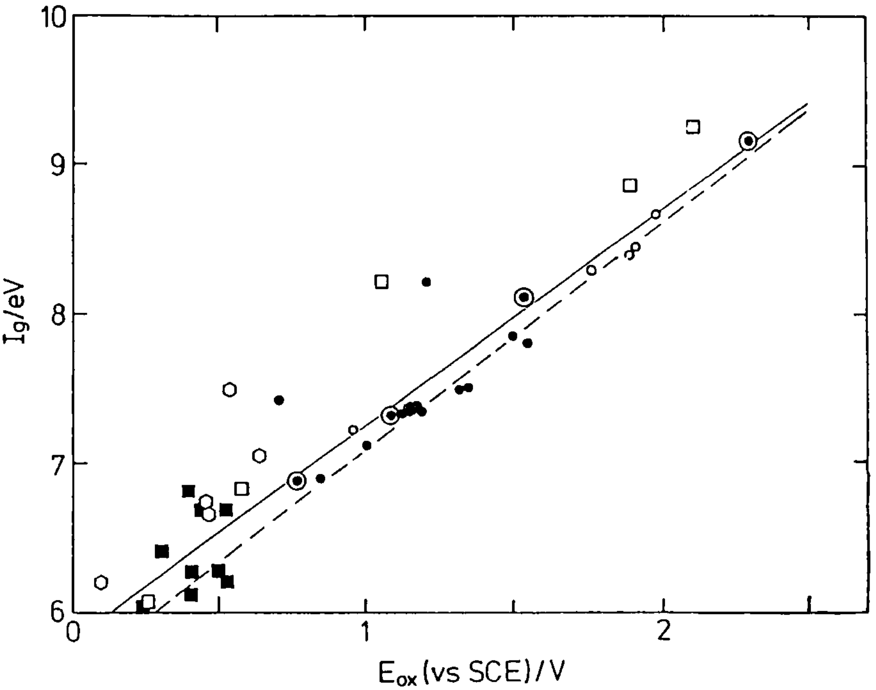

FIGURE 1 Correlation between the ionization energies of a free molecule (I_g) and oxidation potential (E_{ox}) vs saturated calomel electrode (SCE) for aromatic polycyclic hydrocarbons (⊙ for acenes and ● for others), methyl-substituted hydrocarbons (○), amines (O), TTF-related donors (■), and other heterocyclics (□) in Table I listed with values of E_{ox}. Solvent for electrochemical measurements is acetonitrile in most cases. The dotted line (I_g = 5.615 + 1.506 E_{ox}) and the real line (I_g = 5.832 + 1.442 E_{ox}) are the least-square fit for hydrocarbons and all compounds in the figure, respectively.

3. IONIZATION ENERGY OF MOLECULAR SOLIDS

3.1 Experimental methods

Ionization energy of a molecular solid I_s can be determined by various techniques using photoemission: (1) spectral dependence of photoemission efficiency, (2) uv photoelectron spectroscopy, and (3) the Millikan method. For all of them, clean sample surface is required due to the rather short escape depth (nm order) of photoelectrons. Fortunately, this is often achieved without ultrahigh vacuum thanks to the rather inactive nature of organic solid surfaces.

The first two techniques, pioneered by Lyons[21,124] and Vilesov,[22] are similar to the PI and UPS methods in the gas phase, and have been employed by most workers. In photoemission efficiency measurements, main difficulty lies in the slow decrease of efficiency with the decrease of photon energy. Thus either some cutoff value is employed[21] or an extrapolation formula such as[23]

$$Y \propto (h\nu - I_s)^{1/n} \qquad (1)$$

is used, with n being an adjustable parameter between 2 and 3.

In UPS measurements of clean specimen, the ionization onset is fairly sharp, and a reliable value of I_s can be obtained. The main difficulty in UPS comes from the charging of the sample by the accumulation of positive charge, which deforms the observed spectrum. Usually thin films of several tens nm thick is used for avoiding this effect. Since preparation of such thin and uniform films forms an essential part of the UPS experiments, various methods have been applied, e.g. vacuum evaporation, solution casting, chemical vapor deposition, and Langmuir-Blodgett technique for multilayer films. Recently measurements of single crystals and thick layers have been also carried out[24-26] using auxiliary light causing photoconduction and thin Au overlayer.

As for energy analyzers, simple retarding-field type of medium resolution (0.2 eV or so) gives accurate energy scale, since the low-energy cutoff of the spectrum, which determines the origin of the kinetic energy, is clearly seen due to its simple construction. On the other hand, in sophisticated electrostatic-deflection type, despite its high-resolution (0.1 eV or less), the low-energy electrons are easily affected by weak residual field around the analyzer, leading to ambiguity in the energy scale. Further, the detection of charging is also easy with retarding-field type analyzers. These factors make retarding-field type analyzers suitable for determining accurate ionization energies. For more details of the UPS of organics, including the use of synchrotron radiation for detailed study of the occupied and vacant electronic structures of molecular and polymeric solids, see the review articles.[26-30]

In the Millikan method, developed by the groups of Pope[31] and Gerischer,[32] a fine particle is suspended between two electrodes, and photoemisison from the particle is detected by monitoring the electric field required to keep the particle still.

In Table I, we list values of I_s obtained with these methods, for compounds selected from over 200 for which values are reported. The results for complexes and most simple molecules, dyes and polymers are omitted. Although only one value is listed for each compound, other values usually agree within 0.2 eV or so. A more complete list is now under preparation.

3.2 Interpretation of solid-state ionization energy

The values of I_s are generally smaller than the corresponding value I_g of a free molecule, being expressed as:

$$I_s = I_g - \Delta \tag{2}$$

The values of Δ are also listed in Table I. Such a reduction can be discussed with the model of localized charge carrier in molecular solids, which was proposed by Lyons in 1957.[33,34] He pointed out that (a) the photoformed hole should be mostly localized in a molecule due to the weak van der Waals intermolecular interaction, and (b) this will lead to a reduction of ionization energy from gas phase, since the cation is stabilized by the electronic polarization of the surrounding molecules.

This stabilization energy is called polarization energy P_+. We also note that (c) according to this model, the ionization energy should be larger for the molecules at the surface than for the bulk, because of the lack of polarizable molecules.[35]

This picutre has been well confirmed by later studies. As for (b), photoemission work by his[21,124] and other groups[22,35,36] gave I_s values actually smaller than I_g by a comparable magnitude to the calculated energy among the charge and the induced dipoles.[34] Theoretical treatment was further developed by several workers[37,38] to predict fairly correct values for simple compounds.

As for (a), in Figure 2 we show the UPS spectra of naphthacene in gaseous and solid states. A good one-to-one correspondence can be seen when a shift of 1 eV is allowed for the energy scale. This reflects the preservation of the occupied electronic states of a molecule in the solid, which corresponds the hole localization.[39] We note that a breakdown of such good correspondence has been observed

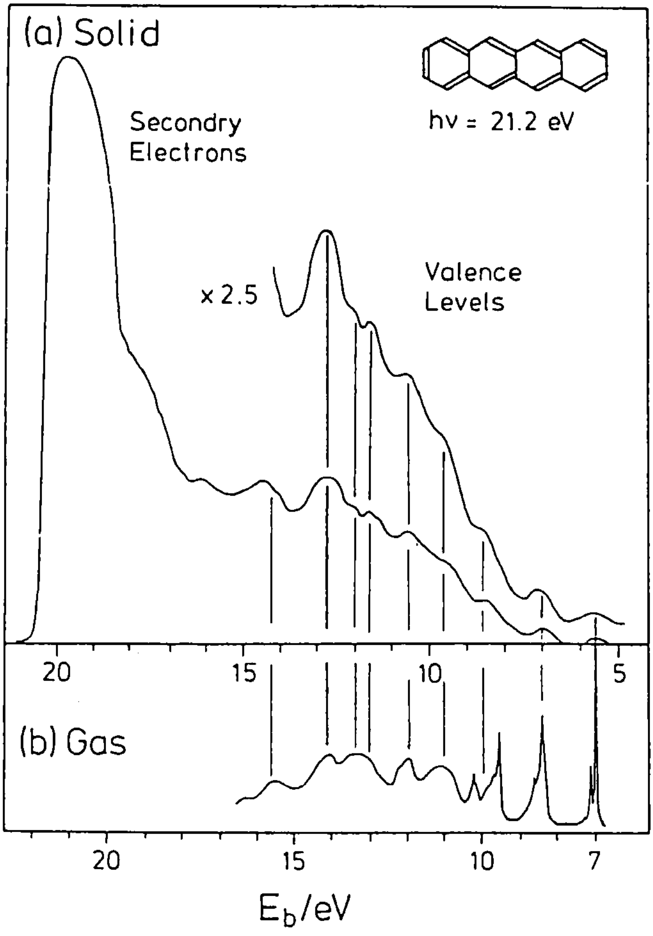

FIGURE 2 Comparison of UPS spectra of naphthacene in gaseous[69] and solid[70] states for $h\nu = 21.2$ eV. The solid-state spectrum is an angle-resolved spectrum with synchrotron radiation.

in the cases where geometrical or chemical changes between the two phases. For examples, see Reference 27.

Finally, the difference of the ionization energy between molecules at the surface and in the bulk (c) was also verified for anthracene by varying the sampling depth of UPS.[40] Recent experiments of Penning ionization electron spectroscopy (PIES), which uses metastable rare gas atoms instead of photons, gave a reliable value of 0.3 eV as this difference for pentacene.[41] The localized charge model thus established was further developed by Duke[42] for various phenomena in molecular solids.

We note that the shift of 1 eV in Figure 2 for peak allignment does not directly give the polarization energy P_+ for a molecule in the bulk, due to the ambiguity in the physical meaning of the peak energy in the solid spectrum. The peak is formed by overlapping contribution from the bulk and the surface, where molecules have different ionization energies. Considering this point, we pointed out that the value of P_+ for the bulk should be derived as the difference Δ between the ionization thresholds.[43]

Sato *et al.*[43] studied many of the materials in Table I, and showed that the trends in Δ for simple van der Waals solids can be well explained with the above-mentioned picture. Simple approximations give an expression of P_+ as[43]

$$P_+ = K\alpha e^2 n^{4/3}, \tag{3}$$

where α is the mean molecular polarizability, e is unit charge, n is the number density of molecules, and K is a constant. This predicts that P_+ should be large for compounds with (1) large α and (2) compact packing in the solid, which results in strong electric field in the surrounding molecules. Such a trend is clearly seen in Table I. At first we note that most aromatic hydrocarbons have nearly constant value of $\Delta = 1.7$ eV. This constancy should result from the balance between the increase in α and the elongated intermolecular distance with increasing molecular size. Further, compounds containing easily polarizable iodine atoms (I_2,[44] CI_4, C_2I_4[45] and iodanil[43]), have large values of $\Delta = 2.9$–3.5 eV. On the other hand, compounds with intricate molecular structures (e.g. rubrene, $\Delta = 1.1$ eV) or overcrowded nonplanar molecules (e.g. tetrabenzopentacene, $\Delta = 1.2$ eV) give much smaller values than the above-mentioned common value of 1.7 eV, probably due to the loose molecular packing and reduced molecular polarizability.[46] Also the values of α of important donors were estimated from the observed values of Δ by using Equation (3).[18,19,45,47] Studies were also carried out on the difference between amorphous and crystalline states,[48] solid and liquid states[51] and polymorphs.[49]

For compounds with strong intermolecular interactions, we must also take account of the effect of intermolecular band formation on the ionization energy. The band model predicts a reduction in ionization energy due to the splitting of energy levels by intermolecular interaction. Possible contribution from band formation to Δ have been reported for iodine compounds (partially covalent intermolecular bonding),[44,45] TTF derivatives with long-alkyl chains (molecular fasteners TTC_n-TTF),[50,51] and stearic acid (dimer formation via hydrogen bonding).[52] In the case of TTC$_n$-TTF, where n stands for the number of C atoms in each alkyl chain, the value of I_s shows a large variation of 0.5 eV which parallels the large n-dependence of electric conductivity, while E_{ox} is independent of n within 0.1 V for $n = 1$ to 18. Such an anomaly disappears on melting, showing that the strong intermolecular interaction is specific to the crystalline state.[51]

4. APPLICATIONS

Here we will briefly discuss several subjects on molecular crystals, where ionization energy is playing an important role.

4.1 Energetics of ionized states in molecular solids

According to the molecular approach described above, electron in the lowest conducting state should be also localized in a molecule, which is stabilized by surrounding molecules by polarization energy P_-.[33,34] Then the energy for producing a pair of charge carriers ("band gap") E_g can be evaluated to be

$$E_g = I_s - A_s = (I_g - P_+) - (A_g + P_-) = (I_g - A_g) - (P_+ + P_-). \quad (4)$$

This forms the basis for discussing the energetics of ionized states in molecular crystals. This expression has been often further simplified by assuming $P_+ = P_-$, leading to $E_g = 2I_s - I_g - A_g$. However, theoretical works by Munn and coworkers[38] indicates that charge-quadrupole interaction will give opposite contribution to P_+ and P_-, casting doubt on the validity of this assumption. Recently Sato *et al.*[53] evaluated the value of P_- for polyacenes from the reported experimental values of E_g. From the values $I_g = 7.39$ eV and $I_s = 5.86$ eV, $P_+ = 1.53$ eV is obtained. Combination of this value with $A_g = 0.60$ eV and $E_g = 4.40$ eV led to $P_- = 1.01$ eV, which is smaller than P_+. These values are in fair good agreement with theoretical results by Munn *et al.*[38] Accumulation of reliable E_g will be useful for further clarification of the energetics of the ionized states.

4.2 Binary systems: complexes, doped system, and interface

It is a challenging subject to study how the electronic structure of a binary system is formed from those of component molecules, and how charge carriers are transferred between them.

CT complexes can be regarded as binary systems where component molecules are mixed in the molecular level. It is well known that the degree of charge transfer in molecular complexes depends on the combination of ionization energy of the donor and the electron affinity of the acceptor. There have been several attempt for classifying the complexes in (ionization energy) vs (electron affinity) diagram,[54,122] including the criterion for donor-acceptor pairs with partial charge-transfer, which is closely related to metallic behavior of the complex.[122] In these works, electrochemical or CT absorption techniques were used, taking advantage of their convenience.

Ionization energy of complexes also gives information. The weak CT interaction was analyzed in a series of anthracene complexes, by comparing the ionization energies with those of components.[55,56] In ionic compounds, the occupation of the LUMO of the acceptor lead to a drastic decrease in ionization energy (e.g. from 6.2 eV of 1,3,6,8-tetracyanopyrene[57] to 1.3 eV of its Cs complex[58]).

Another class of binary system is formed by using polymer as one of its components. Many conjugated polymers are known to become conducting on acceptor doping, and I_s is expected to be a good measured of the easiness for doping. Good correlation has been actually found with experimental findings on doping.[59] In relation to this, the decrease of ionization energy from that of a monomer gives a measure of the width of the topmost band in a polymer chain, which governs the intrachain carrier transport. Such decrease can be studied by using various oligomers[60,61] or by pursuing the change on polymerization.[62-64]

Systems with minor component doped in host material form third class of binary systems. Such a situation happens e.g. in hole-trapping impurities and carrier transport layer in electrophotography. Karl *et al.* estimated the depth of hole-traps (e.g. phenothiazine in anthracene) as the difference between I_s of each component, which was consistent with electrical observations.[56] The ionization energies of aromatic molecules embedded in polymer matrix were also measured.[65,27] Experimental difficulty in such measurements is the weak signal from the minor component.

Finally, we will consider about interfaces. They are important in fields such as electrophotography (hole injection from carrier-generation layer into the transport layer), solar cell, and spectral sensitization in photography and photoelectrochemistry. In these cases, comparison I_s of materials at the two sides gives a rough idea about the relative location of the HOMOs of these materials.[66] However, care should be paid that such a simple picture assuming a common vacuum level does not necessarily hold.[67] Our recent study about dyes on silver halide[68] verified this, indicating that direct measurements of the interface are necessary in discussing such systems.

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