

ployed for HPLC product quantitation.

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Registry No. PhOPh (radical anion), 34534-14-0; 2-H₂C=CH-(CH₂)₂C₆H₄O, 57056-96-9; PhOPh, 101-84-8; C₁₂H₁₀, 83-32-9; D₂O, 7789-20-0; 2-PhOC₆H₄(CH₂)₂CH=CH₂, 103751-30-0; (H₃C)₂CHONa, 683-60-3; 2-HOC₆H₄(CH₂)₂CH=CH₂, 14003-84-0; Ph(CH₂)₂CH=CH₂, 768-56-9; 1-methylindan, 767-58-8.

Strong Hydrogen Bonding in Gas-Phase Ions: A High Pressure Mass Spectrometric Study of Formation and Energetics of Methyl Fluoride Proton Bound Dimer

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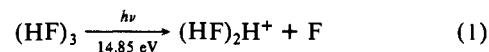
Contribution from the Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada, and the Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada.

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Abstract: The hydrogen bond energy in the proton bound dimer of methyl fluoride, (CH₃F)₂H⁺, has been determined by pulsed electron beam high pressure mass spectrometric experiments. Due to the rapid nucleophilic displacement reaction, CH₃FH⁺ + CH₃F ⇌ (CH₃)₂F⁺ + HF, the direct termolecular clustering of CH₃FH⁺ with CH₃F could not be examined. Instead the hydrogen bond energy in (SO₂)₂H⁺ was determined and then successive displacement equilibria of SO₂ by CH₃F molecules from the proton were examined. These data, coupled with the relative proton affinities of CH₃F and SO₂, yield a hydrogen bond energy in (CH₃F)₂H⁺ of 32 ± 2 kcal mol⁻¹ in good agreement with ab initio calculations for (HF)₂H⁺. Periodic trends in hydrogen bond energies in symmetric proton bound dimers of binary hydrides are discussed.

The growing body of gas-phase data from both experimental¹ and ab initio² methods recently available for hydrogen bonded cluster ions provides valuable insight into the nature of solvation of ions by both protic and aprotic solvents. To date most of the data available have been obtained for proton bound dimers of oxygen and nitrogen n-donor bases and anionic dimers of HO⁻, RO⁻, and halide ions, X⁻, with Brønsted acids. Examination of the limited amount of data available reveals a number of interesting trends. In symmetric proton bound dimers of the binary hydrides the order of hydrogen bond strengths observed is H₃O⁺-H₂O³ > NH₄⁺-NH₃⁴ > H₃S⁺-H₂S⁵ > PH₄⁺-PH₃.⁶ In symmetric anionic dimers the order of hydrogen bond strengths is F⁻-HF⁷ > HO⁻-H₂O⁸ > Cl⁻-HCl⁹ > Br⁻-HBr¹⁰ > I⁻-HI¹¹ > HS⁻-H₂S⁴ > NH₂⁻-NH₃¹² > PH₂⁻-PH₃.¹³ From these data the apparent trend is that all hydrogen bond strengths in symmetric dimers of the binary hydrides increase in proceeding from left to right across a row of the periodic table and decrease from top to bottom proceeding down a group of the periodic table. This order is known to be paralleled in neutral dimers as well with dimer bond strengths decreasing in the order (HF)₂ > (H₂O)₂ > (NH₃)₂.¹⁴ Further, a comparison of cationic and anionic dimer hydrogen bond energies reveals H₃O⁺-H₂O > HO⁻-H₂O; H₃S⁺-H₂S > SH⁻-H₂S; and NH₄⁺-NH₃ > NH₂⁻-NH₃, suggesting that cationic dimers will be more strongly bound than their anionic counterparts. This correlation has a notable omission of considerable interest in the (HF)₂H⁺ dimer. The strongest hydrogen bond known to date is that in the bifluoride ion, FHF⁻. If the above trends hold it may then be the case that the hydrogen bond strength for H₂F⁺-HF will be greater than both those of H₃O⁺-H₂O and of F⁻-HF. This possibility, that a hydrogen bond stronger than that in FHF⁻ may exist, caused us to undertake the present study.

The only experimental study to date of (HF)₂H⁺ has been that of Lee et al.^{15,16} involving photoionization appearance energy measurements of (HF)₂H⁺ from HF trimer formed in a supersonic expansion, eq 1.



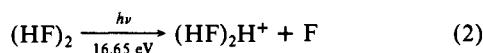
These data give a hydrogen bond energy in (HF)₂H⁺ of 25 kcal mol⁻¹. However, similar experiments involving appearance energy measurements of H₂F⁺ from HF dimer, eq 2, yield a proton affinity for HF of 96 kcal mol⁻¹, significantly lower than the currently accepted value of 121 kcal mol⁻¹.^{17,18} This discrepancy

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[†]University of Waterloo.

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has been interpreted¹⁶ as arising from a nonadiabatic ionization of $(\text{HF})_2$ to $(\text{HF})_2^+$, well above the threshold for H_2F^+ formation, giving rise to an excited state of H_2F^+ . If a similar consideration is applicable to the $(\text{HF})_2\text{H}^+$ data then a hydrogen bond strength in excess of 25 kcal mol⁻¹ may be anticipated. Large basis set ab initio calculations on H_2F^+ and $(\text{HF})_2\text{H}^+$ have been carried out by Kraemer et al.¹⁹ which yield a proton affinity for HF of 120.1 kcal mol⁻¹, in excellent agreement with experiment, and a hydrogen bond strength in $(\text{HF})_2\text{H}^+$ of 30.7 kcal mol⁻¹. Comparable calculations on $(\text{H}_2\text{O})_2\text{H}^+$ ¹⁹ gave a hydrogen bond energy of 32.4 kcal mol⁻¹ in excellent agreement with the experimental value of 31.6 kcal mol⁻¹.^{1,3}

In a comparison of periodic trends in ionic hydrogen bonds Desmeules and Allen² obtained a value for the hydrogen bond strength in $(\text{HF})_2\text{H}^+$ of 40.7 kcal mol⁻¹ using a simple 4-31G basis set. However, comparable calculations for $(\text{H}_2\text{O})_2\text{H}^+$ yielded a hydrogen bond energy of 44.7 kcal mol⁻¹, significantly in excess of the experimental value. Thus these data suggest a hydrogen bond strength in $(\text{HF})_2\text{H}^+$ slightly less than that in $(\text{H}_2\text{O})_2\text{H}^+$.

More recently Del Bene, Frisch, and Pople²⁰ carried out an examination of the hydrogen bond strengths in symmetric proton bound dimers of binary hydrides using large basis sets (6-31+G d,p) including corrections for electron correlation and zero-point energy changes. From these calculations a hydrogen bond energy for $(\text{HF})_2\text{H}^+$ of 31.9 kcal mol⁻¹ was obtained. Their value for the hydrogen bond energy for $(\text{H}_2\text{O})_2\text{H}^+$ of 33.0 kcal mol⁻¹ is in excellent agreement with experimental determination.

The ab initio calculations and periodic trends in experimental data therefore lend support to the suggestion that $(\text{HF})_2\text{H}^+$ will possess a strong hydrogen bond. However, the calculations would suggest that it will not be as strong as that in $\text{H}_3\text{O}^+-\text{H}_2\text{O}$. In either case a hydrogen bond strength in excess of 30 kcal mol⁻¹ is anticipated.

Experimental difficulties associated with handling anhydrous HF in the partially glass vacuum system of the high pressure mass spectrometer precluded direct determinations of the $(\text{HF})_2\text{H}^+$ hydrogen bond strength. However, previous studies of proton bound dimers of H_2O , CH_3OH , and $(\text{CH}_3)_2\text{O}$,^{21,22} and NH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, and $(\text{CH}_3)_3\text{N}$ ²³ have shown little, if any, effect of methyl substitution on hydrogen bond strength in symmetric proton bound dimers. It seemed reasonable therefore to expect that $(\text{HF})_2\text{H}^+$ and $(\text{CH}_3\text{F})_2\text{H}^+$ should possess comparable hydrogen bond energetics. The present manuscript describes the determination of the hydrogen bond strength in $(\text{CH}_3\text{F})_2\text{H}^+$ and its implications for the bond strength in $(\text{HF})_2\text{H}^+$.

Experimental Section

All experiments were carried out with use of a pulsed electron beam high pressure mass spectrometer described in detail previously.²⁴ Techniques for carrying out termolecular clustering equilibria and bimolecular solvent exchange equilibria have been outlined extensively elsewhere.²¹

Methyl fluoride and sulfur dioxide were obtained from Matheson Canda Ltd. and were used without further purification. All gases were flowed from a gas handling vacuum line to the high pressure ion source through a U trap cooled to -95 °C with use of an acetone slush to remove traces of water. Water, even in trace amounts, contributed to loss of signal intensity due to exothermic proton transfers to H_2O and subsequent clustering to H_2O .

Ion source temperatures were varied over the range 140 to 240 °C to obtain van't Hoff plots for $\text{SO}_2\text{H}^+-\text{SO}_2$ clustering and $\text{SO}_2-\text{CH}_3\text{F}$ exchange.

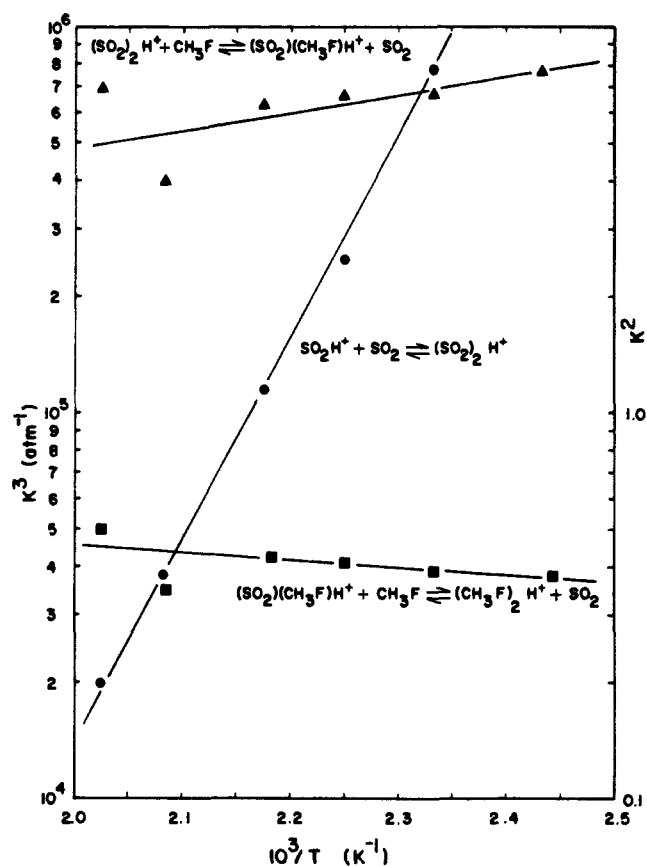
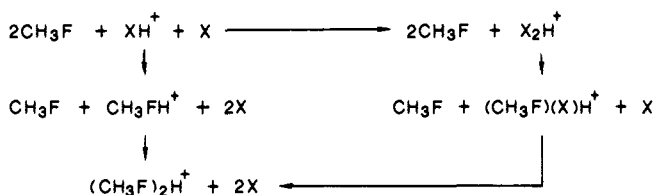
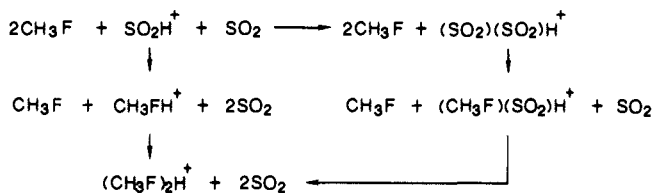


Figure 1. van't Hoff plots for the following equilibria: $\text{SO}_2 + \text{SO}_2 \rightleftharpoons (\text{SO}_2)_2\text{H}^+$; $(\text{SO}_2)_2\text{H}^+ + \text{CH}_3\text{F} \rightleftharpoons (\text{CH}_3\text{F})(\text{SO}_2)\text{H}^+ + \text{SO}_2$; $(\text{CH}_3\text{F})(\text{SO}_2)\text{H}^+ + \text{CH}_3\text{F} \rightleftharpoons (\text{CH}_3\text{F})_2\text{H}^+ + \text{SO}_2$.

Scheme I

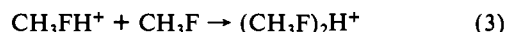


Scheme II



Results and Discussion

Direct determination of the clustering equilibrium, eq 3, leading to the proton bound dimer of CH_3F was precluded due to the rapid nucleophilic displacement reaction, eq 4, which made simultaneous observation of CH_3FH^+ and $(\text{CH}_3\text{F})_2\text{H}^+$ impossible. In order to circumvent this difficulty it was postulated that if methyl fluoride



is a very strong hydrogen bond acceptor despite its low Brønsted basicity than it should be possible to find some species, X, with a proton affinity greater than that of methyl fluoride but with a poorer hydrogen bonding ability. Measurement of the clustering equilibrium leading to the proton bound dimer of such a species and determination of the subsequent displacement equilibria by

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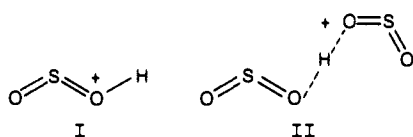
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Table I. Thermochemical Data Derived from Equilibria in the SO₂/CH₃F System

reaction	ΔH° (kcal mol ⁻¹)	ΔS° (cal mol ⁻¹ K ⁻¹)
SO ₂ H ⁺ + SO ₂ ⇌ (SO ₂) ₂ H ⁺	-23.2	-27.4
(SO ₂) ₂ H ⁺ + CH ₃ F ⇌ (SO ₂)(CH ₃ F)H ⁺ + SO ₂	-2.1	-1
(SO ₂)(CH ₃ F)H ⁺ + CH ₃ F ⇌ (CH ₃ F) ₂ H ⁺ + SO ₂	+0.8	0

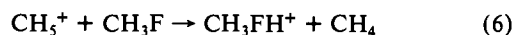
methyl fluoride from this proton bound dimer would then lead to the energetics of (CH₃F)₂H⁺. Such a means of determination of the hydrogen bond strength in the proton bound dimer a methyl fluoride was found to be possible with use of SO₂ as the companion compound, X. Measurement of each of the equilibria outlined in Scheme II could then be used to determine the hydrogen bond strength, $\Delta H^\circ_c(\text{CH}_3\text{F})$.

Equilibrium data used to obtain $\Delta H^\circ_c(\text{SO}_2)$, $\Delta H^\circ_{\text{ex}_1}$ and $\Delta H^\circ_{\text{ex}_2}$ are shown in the van't Hoff plots of Figure 1. The enthalpy and entropy changes associated with each of these processes are summarized in Table I. The enthalpy change associated with the clustering of SO₂H⁺ with SO₂ of -23.2 kcal mol⁻¹ is lower than those of most symmetric proton bound dimers containing oxygen functional groups such as alcohols, ethers, aldehydes, ketones, carboxylic acids, and derivatives which all tend to be -32 ± 2 kcal mol⁻¹. The reason for the large difference between proton bound dimer energetics for SO₂ and organic oxygen functional groups may likely be found in the different nature of the molecular orbitals involved in the hydrogen bond. In the organic oxygen bases the orbital involved in hydrogen bonding is principally oxygen nonbonding. Thus neither protonation nor hydrogen bond formation will affect the structure of the oxygen base to any appreciable degree. However, in the case of SO₂ the highest occupied molecular orbital has weak antibonding character²⁵ with electron density on sulfur and oxygen. Ionization of SO₂ from this orbital leads to excitation of ν_2 , the bending mode, with a large increase in O-S-O, the bond angle.²⁵ The large geometry changes accompanying hydrogen bond formation may then contribute to the overall lowering of the energy of the hydrogen bond interaction. Previous correlations of oxygen 1s binding energies with proton affinities of oxygen bases¹⁸ show that SO₂ appears to be an oxygen base. Protonation of SO₂ therefore most probably occurs at oxygen as does hydrogen bond formation to yield structures I and II, respectively.

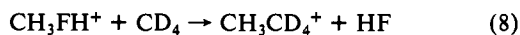
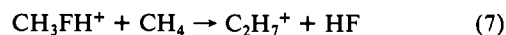


The exchange of SO₂ for CH₃F in the proton bound dimer complex is of interest because of the known lower proton affinity of CH₃F relative to SO₂.²⁷ The fact that the two exchanges are nearly thermoneutral despite a 7 kcal mol⁻¹ difference in proton affinities is indicative of the enhanced hydrogen bonding ability of fluorine relative to compounds of similar basicity containing other heteroatoms.

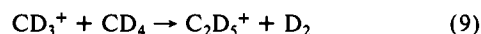
Some note should be made of the discrepancy between the value of the proton affinity of CH₃F quoted here of 148 ± 2 kcal mol⁻¹ and that reported by Lias et al.²⁸ in the recent compilation of gas-phase basicities of ≈ 132 kcal mol⁻¹. This latter value is based on the reported observation of reaction of CH₃FH⁺ with CH₃F to produce CH₂F⁺, eq 5, and of the simple proton transfer from CH₅⁺, eq 6.



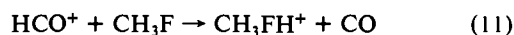
On the basis of the known heats of formation of CH₂F⁺,²⁹ the proton affinity of CH₃F was thus assigned as ≈ 132 kcal mol⁻¹. However, an investigation of the original reference to observation of this reaction³⁰ reveals that in fact a mixture of CD₄ and CH₃F was examined. The methylation of alkanes has been under investigation in our laboratory, and it has been found that CH₃FH⁺ readily transfers a CH₃⁺ to both CH₄, eq 7, and CD₄, eq 8.³¹ In



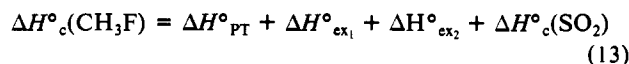
the CH₄-CH₃F mixture at low CH₃F partial pressures no *m/z* 33 (CH₂F⁺) was observed. However, in CH₃F-CD₄ mixtures an appreciable *m/z* 33 ion was formed. We have determined that this species is in fact the result of isotope exchange by C₂D₅⁺, eq 10, formed from ion molecule reaction in CD₄, eq 9, rather than CH₂F⁺ production. Thus the deduced proton affinity of CH₃F



based on supposed observation of eq 5 is very probably in error. Efficient proton transfer to CH₃F from HCO⁺, eq 11, and C₂H₇⁺, eq 12, has been observed both by HPMS and ICR, supporting the assignment of proton affinity of CH₃F as 148 ± 2 kcal mol⁻¹.²⁷



Taking this value of proton affinity for CH₃F, the clustering enthalpy change for the proton bound dimer, ΔH°_c in Scheme II, may be determined from eq 13 as -32 ± 2 kcal mol⁻¹.



This value of the hydrogen bond strength in the proton bound dimer of CH₃F is in excellent agreement with the early calculation for (HF)₂H⁺ of 30.7 kcal mol⁻¹ by Kraemer et al. and with the more recent calculations by Pople et al.²⁰ of 31.9 kcal mol⁻¹. Their calculations and the previous observations that alkyl substitution on a heteroatom does not affect the hydrogen bond strength in proton bound dimers lead to a high degree of confidence in this experimental value of 32 ± 2 kcal mol⁻¹ in the hydrogen bond in (CH₃F)₂H⁺.

It is of some interest to attempt to compare the magnitude of this hydrogen bond strength relative to those in symmetric proton bound dimers involving oxygen and nitrogen bases. It has previously been demonstrated that despite their greater Brønsted basicity nitrogen bases are intrinsically poorer hydrogen bonding entities than organic oxygen bases. Furthermore, the enhanced hydrogen bonding ability of oxygen bases in proton bound dimers cannot be ascribed to greater electrostatic interactions in these compounds since no dependence of hydrogen bond strength on dipole moment within a homologous series of bases is evident. Indeed all oxygen n-donor bases have nearly identical hydrogen bond strengths in their proton bound dimers. Desmeules and Allen² in an analysis of proton bound dimers of binary hydrides have concluded that whenever the distance between heavy atoms is less than 2.55 Å there is a significant covalent contribution to the bond. In more simple terms this statement implies that such hydrogen bonds are indeed something more than electrostatic in origin. These authors also concluded that such covalent bonds are most evident in species containing more electronegative

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heteroatoms. The highest level calculations of Pople et al.²⁰ corroborate this by showing that H_5O_2^+ , H_3F_2^+ , and H_3Cl_2^+ have single minimum potential energy wells with the proton symmetrically bound by the two monomer bases. Further, even through N_2H_7^+ is predicted to have a double minimum potential energy well, the central barrier is only 1.0 kcal mol⁻¹, indicating that the zero-point energy of the vibrations about the hydrogen bond will readily carry the proton over the maximum.

Conclusions

Experimental evidence has been presented to show that the proton bound dimer of methyl fluoride, $(\text{CH}_3\text{F})_2\text{H}^+$ (and by implication that of $(\text{HF})_2\text{H}^+$), exhibits a very strong hydrogen bond of 32 ± 2 kcal mol⁻¹. Such strong hydrogen bonding involving monomers of very low base strength offers strong support for Allen's contention that hydrogen bonding will be greatest for

species involving electronegative atoms. Available experimental data and ab initio calculation show a strong correlation between electronegativity and hydrogen bond strength in symmetric proton bound dimers. Work is currently in progress on binding energies of proton bound dimers of a variety of sulfur, phosphorus, chlorine, and bromine bases to determine effects of substitution on the heteroatom on hydrogen bond strength.

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Registry No. $\text{CH}_3\text{F}\cdot\text{H}^+$, 59122-96-2; CH_3F , 593-53-3; $\text{SO}_2\cdot\text{H}^+$, 103905-48-2; SO_2 , 7446-09-5; H^+ , 12408-02-5.

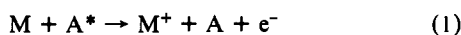
Penning Ionization Electron Spectroscopy of Monohalobenzenes: $\text{C}_6\text{H}_5\text{F}$, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{Br}$, and $\text{C}_6\text{H}_5\text{I}$

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Contribution from the Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan, and Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komba, Meguro, Tokyo 153, Japan. Received January 2, 1986

Abstract: $\text{He}^*(2^3\text{S})$ Penning ionization electron spectra (PIES) and He I ultraviolet photoelectron spectra (UPS) were measured to study the electronic structures and reactivities of monohalobenzenes. On the basis of the feature of PIES which provides direct information on the spatial distribution of individual molecular orbitals, all the bands in the UPS were assigned. Since Penning ionization can be interpreted as an electrophilic reaction in which a metastable atom extracts an electron from an occupied orbital of a molecule, the relative reactivity of the orbital upon electrophilic attack can be studied from the relative intensity of the bands in PIES. It was found that the reactivity of the n and π orbitals of monohalobenzenes depends on the electronic factor due to the size of the halogen p orbitals and the conjugation between the benzene ring and the halogen atoms, and also on the steric factor due to the benzene ring shielding some orbitals from the impact of metastable atoms.

Penning ionization electron spectroscopy is based on the energy analysis of electrons released in the ionization of atoms or molecules M by impact of metastable atoms A^* :¹



In this process an electron in an orbital of M transfers into the vacant orbital of A^* and its excited electron is ejected.² Since the probability of the electron transfer is essentially determined by spatial overlap of the relevant orbital of M and the vacant orbital of A^* , an outer orbital exposed outside the repulsive (van der Waals) surface of the molecule gives a stronger band in the Penning ionization electron spectrum (PIES) than does an inner orbital localized inside the surface.³ Thus, the relative band intensity of the spectrum depends on the spatial electron distribution of individual molecular orbitals. Using this feature of PIES, we have successfully assigned the bands in ultraviolet photoelectron spectra (UPS) of various organic molecules.³⁻¹¹ Furthermore, the studies of the electron distribution of individual orbitals exposed outside solid surfaces have enabled us to probe the geometrical orientation and electronic state of molecules at the outermost surface layer.^{12,13}

From a chemical point of view, Penning ionization process 1 is regarded as an electrophilic reaction of an excited atom A^* with a molecule M ; the reagent A^* attacks an orbital of M and extracts an electron into the vacant orbital of A^* yielding an ionic state

of M^+ .^{3,10} In this respect, the intensity of a band in PIES is connected with the reactivity of the corresponding orbital upon

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