Variations in Reactivity of Lone-Pair Electrons due to Intramolecular Hydrogen Bonding as Observed by Penning Ionization Electron Spectroscopy

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Abstract: Helium atoms in metastable states inducing one-electron extraction upon collisions with sample molecules were used to probe the relative reactivity of lone-pair electrons in organic compounds. Considerable deactivation of the n_X orbital was observed for $HOCH_2CH_2X$ (X = Cl, Br, NH_2, and $N(CH_3)_2$) in which the group X is involved in the intramolecular hydrogen bond of the form (OH⋯X). In an H-bonded conformer, the lone-pair electrons are protected against attacks of incoming electrophiles by steric shielding effects due to the OH group. When the temperature was increased to facilitate dissociation, the reactivity of the n_X orbital was found to be recovered. The present results indicate that dynamic variations of reactivity due to conformational changes as well as differences in reactivity between chemically modified analogues can be studied by the use of metastable helium atoms.

Rare gas atoms in metastable excited states A*, such as He* (2^3S, 19.82 eV), can be used to probe the relative reactivity of molecular orbitals upon electrophilic attacks.[1,2] The probability of the one-electron-transfer reaction can be measured as a cross section for the so called Penning ionization (A* + M → A + M$^+$ + e$^-$) in which a molecule M is ionized into an ionic state. Kinetic energy analyses of ejected electrons provide an electron-energy spectrum which is called a Penning ionization electron spectrum (PIES). The reaction probability for a particular molecular orbital is observed as the intensity for the relevant band corresponding to the one-electron emission from that molecular orbital. Since occupied orbitals for closed-shell molecules usually correspond to different ionization potentials and appear as different bands in the electron energy spectrum, relative reactivities of molecular orbitals can be measured as band intensities in PIES.

The general principle that governs the relative PIES intensity has been established[1,3] based on the electron-exchange model.[4] One of the important features in Penning ionization is that metastable rare gas atoms cannot penetrate into the inside of the repulsive surface of the target molecule. This characteristic of interparticle collisions together with the short-range nature of exchange-type interactions divides the inactive part of $|\psi|^2$, which is localized in the interior region of the repulsive surface, from the active part of $|\psi|^2$, which is exposed to the exterior region. Electron densities integrated over the exterior regions, which can be defined as exterior electron densities, are thus considered to be nearly proportional to the ionization cross sections or PIES band intensities. This leads to a simple principle that an orbital exposed to the outside is more reactive than other orbitals localized in the inner part upon electrophilic attacks by metastable rare gas atoms.

A series of PIES experiments revealed that orbitals localized mostly on heteroatoms in functional groups yield generally intense PIES bands and that the relative intensity increases with a decrease in electronegativity of the relevant heteroatom.[2] This finding provides a confirmation of the simple principle that the exterior electrons govern the relative reactivity of orbitals in Penning ionization.

When a bulky group is introduced in a molecule, some target orbitals may be protected from attacks of metastable atoms. Evidences for such steric effects have been observed in applications of the PIES technique to organometallic complexes,[5,6] some

substituted anilines,[7] and nitriles.[8]

The present study is aimed at observing the effect of intramolecular hydrogen bonding on the reactivity of lone-pair electrons; the formation of an intramolecular hydrogen bond may result in a considerable reduction of the reactivity. For this purpose, PIES of some halohydrins, aminoethanols, and related molecules were measured. The results clearly demonstrate a steric effect due to the H-bond on the reactivity of lone-pair electrons.

Experimental Section

He* (2^3S) PIES and He I ultraviolet photoelectron spectra (UPS) were measured by a transmission-corrected electron spectrometer.[1,6] The helium metastable atoms, 2^3S (19.82 eV) and 2^1S (20.62 eV), were produced with an electron gun made of thoriated tungsten filaments and an anode grid. The electron gun was operated at 20 V–2 A with an accelerating voltage of about 60 V and the average emission current of 65~75 mA. Almost pure 2^3S metastable beams were obtained with a quench lamp eliminating 2^1S components. The He I resonance line (584 Å, 21.22 eV) was produced by a dc discharge in pure helium gas. The gaseous sample was introduced into the ionization chamber through a needle valve. The ionization chamber as well as the gas inlet system was heated for high-temperature measurements. Temperatures for gaseous samples were monitored with thermocouples. Electron energy spectra were obtained for electrons ejected at the angle of 90° with respect to the metastable helium beams or the photon beams by means of a hemispherical analyzer of 3-cm mean radius. A multichannel analyzer was used to accumulate signals, and the data were saved on floppy disks. Correction for the transmission of the electron spectrometer was made with a microcomputer.

Calculations

Ab initio SCF MO calculations were made at the computer center of the University of Tokyo. A library program GSCF2[9] was used with 4-31G basis sets.[10] Electron density maps were drawn for some molecular orbtials. The density of the nth line from the outside is $k \times 2^n \times 10^{-4}$ au^{-3}, where k is chosen to be 0.5 so that at least three lines may be found in the exterior region. In the electron density maps, thick solid curves indicate repulsive molecular surfaces which are approximated by composition of spheres with van der Waals radii of atoms (r_C = 1.70 Å, r_O = 1.40 Å,

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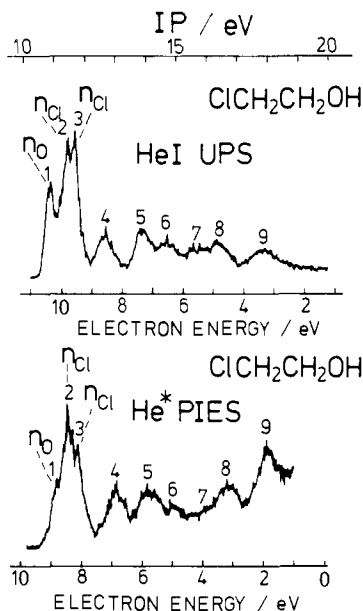(2) Ohno, K.; Imai, K.; Matsumoto, S.; Harada, Y. *J. Phys. Chem.* **1983**, *87*, 4346–4348.

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Table I. Observed Vertical Ionization Potentials (IP_v/eV)[a] and Calculated Ionization Potentials (IP_{calcd}/eV) for Nonbonding Orbitals[c]

compound	IP_v/eV
CH_3CH_2OH	10.64 (11.89, n_O)
CH_3CH_2Cl	11.06 (11.53, n_{Cl}), 11.06 (11.53, n_{Cl})
$HOCH_2CH_2OH$	10.55 (11.84, n_O), 11.22 (12.45, n_O)
$ClCH_2CH_2OH$	10.91 (12.68, n_O), 11.48 (11.95, n_{Cl}), 11.71 (12.11, n_{Cl})
CH_3CH_2Br	10.30 (n_{Br}),[b] 10.60 (n_{Br})[b]
$BrCH_2CH_2OH$	10.62 (n_{Br}),[b] 10.92 (n_{Br}),[b] 11.32 (n_O)
$CH_3CH_2OCH_2CH_3$	9.61 (11.24, n_O)
$BrCH_2CH_2OCH_2CH_3$	9.94 (n_O), 10.42 (n_{Br}),[b] 10.68 (n_{Br})[b]
$BrCH_2CH_2Cl$	10.63 (n_{Br}),[b] 10.93 (n_{Br}),[b] 11.61 (n_{Cl})
$CH_3CH_2NH_2$	9.50 (10.19, n_N)
$CH_3CH_2N(CH_3)_2$	8.40 (n_N)
$H_2NCH_2CH_2OH$	9.88 (10.78, n_N), 10.71 (11.72, n_O)
$(CH_3)_2NCH_2CH_2OH$	8.80 (n_N), 10.32 (n_O)
$H_2NCH_2CH_2OCH_3$	9.40 (n_N), 10.00 (n_O)

[a] IP_v listed are obtained from the UPS at room temperature. In calculations for $ClCH_2CH_2OH$ and $H_2NCH_2CH_2OH$, H-bonded structures determined from microwave studies are used. [b] A couple of observed bands is due to spin–orbit interactions as well as ionization from n_{Br} orbitals. [c] IP_{calcd} are shown in parentheses with the orbital characters.

Table II. Relative Band Intensities in PIES[a]

compound	intensities
$CH_3CH_2NH_2$	2.4 (1, n_N), 1.0 (2)[b]
CH_3CH_2Cl	1.7 (1, n_{Cl}),[c] 1.7 (2, n_{Cl}),[c] 1.0 (3)[b]
CH_3CH_2OH	0.76 (1, n_O), 1.0 (2)[b]
$ClCH_2CH_2OH$	0.76 (1, n_O), 1.1 (2, n_{Cl}),[d] 0.78 (3, n_{Cl}),[d] 1.0 (4)[b]
$H_2NCH_2CH_2OH$	1.0 (1, n_N),[d] 0.71 (2, n_O), 1.0 (3)[b]
$H_2NCH_2CH_2OCH_3$	2.3 (1, n_N), 0.77 (2, n_O), 1.0 (3)[b]

[a] Band labels are shown in parentheses. Relative band intensities in PIES indicate relative reactivities for the relevant orbitals in Penning ionization (see text). [b] A band due to ionization from a bonding orbital is used as a reference, since the intensity for that band is considered to be insensitive to the functional groups. [c] Bands 1 and 2 for EtCl were assumed to have the same intensities. [d] These bands are suppressed by the steric shielding effect due to the intramolecular hydrogen bonding (see text).

Figure 1. Transmission-corrected He* (2^3S) PIES (lower) and He I UPS (upper) for 2-chloroethanol.

$r_N = 1.50$ Å, $r_{Cl} = 1.80$ Å, $r_H = 1.20$ Å).
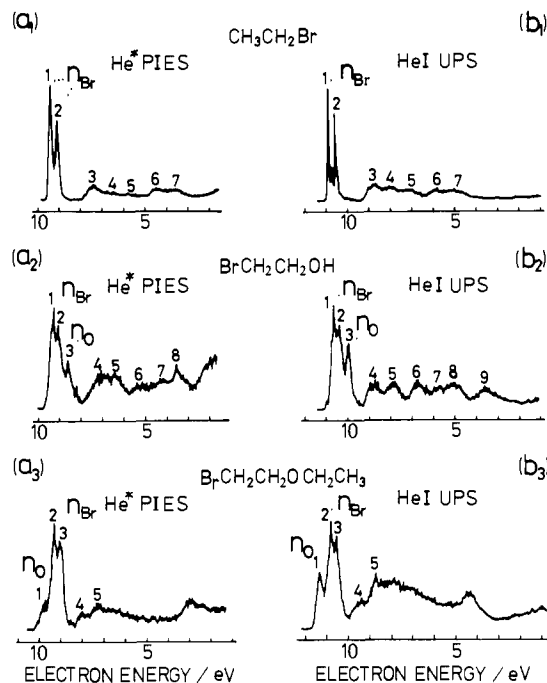
Results and Discussion

1. Assignments. For nonbonding orbitals of some molecules related to halohydrins and aminoethanols, Table I lists vertical ionization potentials (IP_v) obtained from UPS and ionization potentials (IP_{calcd}) obtained from ab initio MO calculations via Koopmans' approximation. On this basis assignments of the observed bands in PIES were also made.

Figure 1 shows He I UPS and He* (2^3S) PIES for 2-chloroethanol (ethylenechlorohydrin). The bands are labeled from the left by numbers as well as by orbital characters. Kimura et al.[11] assigned the first two bands to nonbonding orbitals localized on the Cl atom. However, the present results lead to different assignments as shown in Figure 1 and Table I from the following reasons: (i) The observed lowest IP for n_{Cl} orbitals are 11.06 eV for CH_3CH_2Cl and 11.41 eV for $ClCH_2CH_2Cl$. The observed

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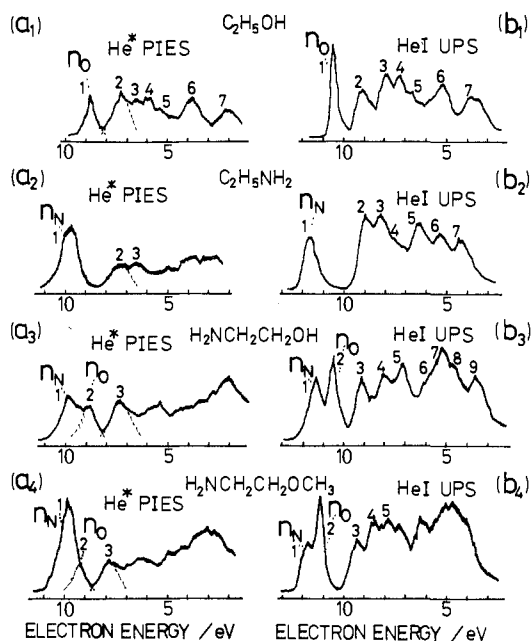
Figure 2. Transmission-corrected He* (2^3S) PIES (left, a_1–a_3) and He I UPS (right, b_1–b_3) for ethyl bromide (a_1, b_1), 2-bromoethanol (a_2, b_2), and 2-ethoxyethyl bromide (a_3, b_3).

lowest IP for n_O orbitals are on the other hand much lower, as 10.64 eV for CH_3CH_2OH and 10.55 eV for $HOCH_2CH_2OH$. This tendency supports the fact that band 1 is due to the n_O orbital. (ii) When one compares IP_v with IP_{calcd} in Table I, it is noted that the IP_{calcd} for n_O orbitals are too large by about 1.3 eV for CH_3CH_2OH and $HOCH_2CH_2OH$. The corresponding differences for the n_{Cl} orbitals of CH_3CH_2Cl and $ClCH_2CH_2Cl$ are, however, only about 0.4–0.5 eV. Such a tendency for calculated IP values leads to a set of deduced IP values (IP_d) for $ClCH_2CH_2OH$ from the following equation: $IP_d = IP_{calcd} - \delta$, where δ is the difference between IP_v and IP_{calcd} for related molecules. The deduced IP values are 11.5 eV (n_{Cl}), 11.6 eV (n_{Cl}), and 11.38 eV (n_O), respectively. These values support the ordering in the present assignments. (iii) The calculated splitting for the two n_{Cl} orbitals is 0.16 eV which is in good agreement with the observed separation between bands 2 and 3 (11.71 − 11.48 = 0.23 eV) and much smaller than the corresponding value for bands 1 and 2 (11.48 − 10.91 = 0.57 eV). (iv) In most organic molecules, the band shape for the n_O orbital is rather broad in both UPS and PIES in comparison with the case for n_{Cl} orbitals. This propensity clearly indicates that the rather sharp doublet of bands 2 and 3 in UPS is due to n_{Cl} orbitals. (v) It is also suggested that the first band in PIES must be ascribed to the n_O orbital, based on the propensity found in the PIES for CH_3CH_2X (X = OH, Cl, NH_2, etc.).[2] The relative enhancement of the band due to the n_X orbital with respect

Figure 3. Transmission-corrected He* (2^3S) PIES (left, a_1–a_4) and He I UPS (b_1–b_4) for ethanol (a_1, b_1), ethylamine (a_2, b_2), 2-aminoethanol (a_3, b_3), and 2-methoxyethylamine (a_4, b_4). The dashed curves in a_1–a_4 indicate the deconvoluted envelopes for the overlapping bands.

to other bands was found to be in the following order: $n_N > n_{Cl} > n_O$. This propensity is also confirmed in the present results, as can be seen in Table II.

Figure 2 shows He I UPS and He* (2^3S) PIES for CH_3CH_2Br, $BrCH_2CH_2OH$, and $BrCH_2CH_2OCH_2CH_3$. Bands 1 and 2 for CH_3CH_2Br are assigned to a couple of bands due to spin–orbit splittings.[11] These bands are also ascribed to ionization from nonbonding orbitals localized on the Br atom. Bands 1 and 2 for $BrCH_2CH_2OH$ can also be assigned to the ionized states involving spin–orbit interactions as well as a couple of n_{Br} orbitals. Electron inductive effects of the OH group on the IP values are about 0.4–0.6 eV from a comparison between IP values for n_{Cl} orbitals of CH_3CH_2Cl and $ClCH_2CH_2OH$ (Table I). Similar effects are also seen for CH_3CH_2Br and $BrCH_2CH_2OH$ where shifts of IP values are 0.32 eV. In Table I, the first three bands for $BrCH_2CH_2OH$ should be compared with those for $BrCH_2CH_2Cl$. An observed tendency for IP values, IP(n_{Cl}) > IP(n_O, OH group) > IP(n_{Br}), supports the present assignments for $BrCH_2CH_2OH$ (Figure 2, Table I). For $BrCH_2CH_2OCH_2CH_3$, one must note that the n_O orbital corresponds to a lower IP(9.94 eV) in comparison with the n_O orbitals for molecules containing the OH group (IP = 10.4~11.3 eV). The former IP can be compared to that for the n_O orbital of $CH_3CH_2OCH_2CH_3$ (9.61 eV).

Figure 3 shows He I UPS and He* (2^3S) PIES for CH_3CH_2OH, $CH_3CH_2NH_2$, $H_2NCH_2CH_2OH$, and $H_2NCH_2CH_2OCH_3$. Bands 1 and 2 for 2-aminoethanol can be assigned to the n_N and the n_O orbitals, respectively. This is supported by the following propensity, IP(n_O, OH group) > IP(n_N), which can be seen for CH_3CH_2OH and $CH_3CH_2NH_2$. Bands 1 and 2 for $H_2NCH_2CH_2OCH_3$ are also assigned with the same ordering. The rather diffuse nature for bands due to n_N orbitals also gives support to the present assignments in Figure 3. It must be noted that the PIES intensity of band 1 (n_O) for ethanol (a_1 in Figure 3) is not so strong as that of band 1 (n_N) for ethylamine (a_2 in Figure 3). This tendency also supports the present assignments for aminoethanol and its methoxy analogue (a_3 and a_4 in Figure 4).

2. Relative Reactivity of Halogen-Nonbonding Orbitals. On the basis of the simple principle observed for band intensities in PIES,[1] one can compare relative reactivity of nonbonding orbitals upon electrophilic attacks of metastable helium atoms. Figure 4 shows He* (2^3S) PIES for $ClCH_2CH_2OH$ and CH_3CH_2Cl. As studied in earlier work,[2] bands 1 and 2 for ethyl chloride are due to almost degenerate n_{Cl} orbitals and are very much enhanced with
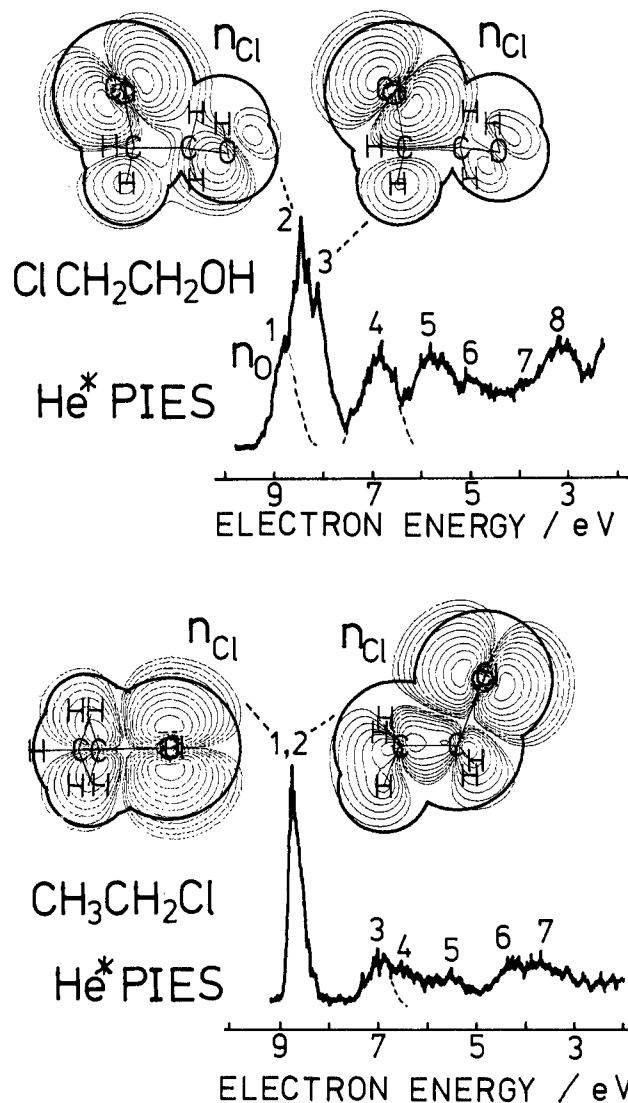

Figure 4. Transmission-corrected He* (2^3S) PIES for 2-chloroethanol (upper) and ethyl chloride (lower). Electron density maps are drawn for the n_{Cl} orbitals at a plane including the Cl atom (and the hydroxyl H atom). The density of the most outer line is 1.0×10^{-4} au^{-3}. Thick solid curves indicate the repulsive molecular surface (see text). The dashed curves indicate components of overlapping bands in the spectra.

respect to other bands (bands 3–7) which are due to bonding orbitals having electron distributions mostly on the ethyl group. The electron density maps in Figure 4 show that the n_{Cl} orbitals are exposed to the outside beyond the repulsive molecular surface indicated by solid curves. Therefore, the strong intensities for the n_{Cl} bands were explained from the large exterior electron distributions of the n_{Cl} orbitals. In the PIES for $ClCH_2CH_2OH$, however, the relative enhancement of the n_{Cl} bands with respect to bands 4–8 is not so striking as the case of EtCl (Table II). Microwave studies[12] revealed that an intramolecular H-bonded conformer is likely to be most populated. The electron density maps in Figure 4 exhibit how the exterior electron distributions for the n_{Cl} orbitals are geometrically placed in the H-bonded form of $ClCH_2CH_2OH$. The OH group located just on the side of the Cl atom may protect the Cl atom against attacks by metastable helium atoms incoming through that direction and cause a suppression of the one-electron-transfer reaction. It is noted that the steric shielding effect due to the OH group is larger for band 3 assigned to the n_{Cl} orbital whose electron distributions are much more shielded by the OH bond, in comparison with band 2 for which the corresponding n_{Cl} orbital is much less covered by the OH group.
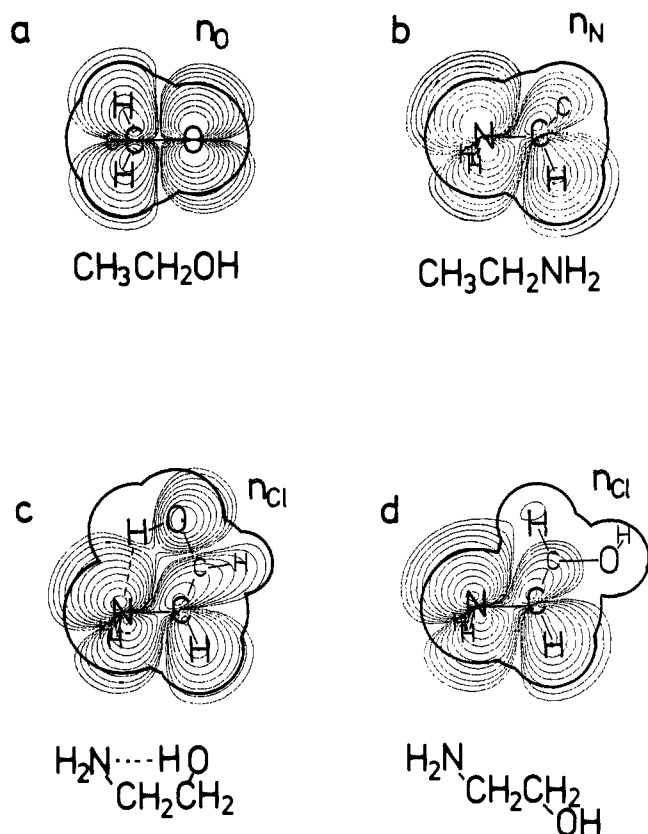
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Figure 5. Electron density maps for the n_O orbital of ethanol (a), the n_N orbital of ethylamine (b), the n_N orbital of ethanolamine in the H-bonded conformation (c), and the n_N orbital of ethanolamine in a nonbonded conformation (d). The density of the most outer line is 1.0×10^{-4} au^{-3}. Thick solid curves indicate the repulsive molecular surface.

Figure 6. He* (2^3S) PIES for N,N-dimethylaminoethanol at 23, 100, 200, and 300 °C.

Table III. Temperature Dependence of the Integrated Intensity Ratio and the Population for the H-Bonded Conformer

temp, °C	$I(n_N)/I(n_O)$	C_B
300	0.80	0.29
200	0.77	0.42
100	0.71	0.63
23	0.66	0.83

In Figure 2 one can see similar H-bond effects for BrCH$_2$CH$_2$OH. In the PIES (a$_1$–a$_3$) the relative enhancement of bands due to n_{Br} orbitals with respect to other bands is suppressed for bromohydrin (a$_2$) in comprison with the cases for ethyl bromide (a$_1$) and the ethoxy analogue (a$_3$). This must also be due to the shielding effect due to the OH group. However, in this case the relative degrees of suppression are nearly the same for bands 1 and 2 (a$_2$) in contrast with the case for chlorohydrin. This behavior of the first two bands of bromohydrin is consistent with the cause of the splitting which is mostly due to the spin–orbit interaction. It is thus indicated that orbital characteristics must be nearly the same for the two ionized states corresponding to bands 1 and 2 in BrCH$_2$CH$_2$OH. In the case of BrCH$_2$CH$_2$OCH$_2$CH$_3$, one cannot expect a strong steric shielding effect on the n_{Br} orbitals, since the ethoxy group cannot be bound to the Br atom. This is clearly demonstrated in the PIES in Figure 2 in which the enhancement of bands 2 and 3 for BrCH$_2$CH$_2$OCH$_2$CH$_3$ (a$_3$) is comparable with the case of EtBr (a$_1$). This may provide a chemical verification of the steric effect due to the OH group in bromohydrin.

3. Relative Reactivity of Nitrogen-Nonbonding Orbitals. Microwave studies[13,14] showed that an intramolecular hydrogen bond is formed in the equilibrium conformation for aminoethanols. In Figure 3 as well as in Table II one can see the effects of intramolecular H-bonding on the PIES intensities for bands corresponding to n_N orbitals. For aminoethanols and their analogues, Leavell et al.[15] made studies by UV photoelectron spectroscopy. They compared IP values of H-bonded molecules with those of nonbonded analogues. In the present study, interests are focused on the differences in the PIES intensities. For the non-
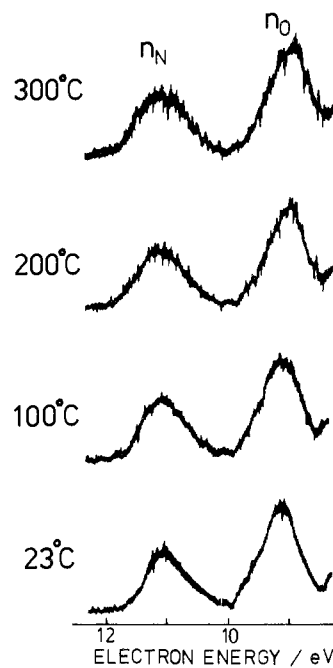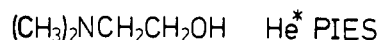
bonded molecules, EtNH$_2$ and H$_2$NCH$_2$CH$_2$OCH$_3$, band 1 in the PIES (a$_2$ and a$_4$ in Figure 3) is enhanced with respect to other bands. Band 1 in the PIES for H$_2$NCH$_2$CH$_2$OH (a$_3$ in Figure 3) is, on the other hand, considerably suppressed. Figure 5 shows electron density maps for relevant molecular orbitals. One can see that exterior electron distributions are large for the n_N orbitals for the nonbonded conformer of aminoethanol d as well as for EtNH$_2$ b and that exterior electron distributions are quite suppressed for the n_N orbital for the H-bonded conformer of aminoethanol c. In the bonded confomer, the effective solid angle open to incoming metastable atoms is also decreased for the exterior electron distributions around the N atom by the shielding effect due to the OH group.

4. Temperature Dependence and Dissociation Equilibrium. One would imagine that when the temperature is increased populations of nonbonded conformers are increased, which would result in an increase of the PIES band intensity for the nonbonding orbital relating to the H-bond. For such a study N,N-dimethylaminoethanol is an ideal system, because the bands of interest are clearly isolated and analyses leading to thermodynamic properties can be made effectively. Figure 6 shows the temperature dependence (23–300 °C) of bands 1 and 2 in the PIES for (CH$_3$)$_2$NCH$_2$CH$_2$OH. As has been indicated by Leavell et al.,[15] slight peak shifts as well as modification of band shapes were observed with an increase in temperature. Here the stress must be placed on the considerable changes in the relative intensities. Table III lists the ratios of integrated band intensities, $I(n_N)/I(n_O)$, as a function of the temperature. The increase of this ratio with an increase in temperature indicates that populations of nonbonded conformers increase at the higher temperature. Therefore, one may be led to the following analyses: for a given temperature the observed intensity is assumed to be a weighted average of those values for the bonded and the nonbonded conformers

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$$I(n_N) = C_B I_B(n_N) + C_N I_N(n_N)$$

$$I(n_O) = C_B I_B(n_O) + C_N I_N(n_O)$$

where C_B and C_N are the relative populations for the bonded (B) and nonbonded (N) conformers, respectively, and they satisfy $C_B + C_N = 1$. One must here note that the relative PIES intensity for the n_O oribtal remains nearly the same for the bonded and nonbonded conformers (a_1 and a_3 in Figure 4, a_4 in Figure 3, and Table II). MO calculations also showed that exterior electron distributions for the n_O orbitals are rather insensitive to the changes in conformation. Thus one may assume that

$$I_B(n_O) = I_N(n_O)$$

and one obtains

$$I(n_N)/I(n_O) = C_B I_B(n_N)/I_B(n_O) + C_N I_N(n_N)/I_N(n_O)$$

One may then introduce a relationship with the enthalpy and entropy changes due to dissociation of the hydrogen bond

$$\ln K = \ln (C_N/C_B) = -\Delta H/RT + \Delta S/R$$

A least-squares fit to this equation with the observed ratios of $I(n_N)/I(n_O)$ in Table III leads to the following results:

$\Delta H = 1.25$ kJ mol^{-1} (3.0 kcal/mol)

and $\Delta S = 29$ J K^{-1} mol^{-1}

The relative populations of the bonded conformer C_B were also obtained and listed in Table III. The present result for ΔH is in good agreement with the earlier value (2.8 kcal/mol) obtained for a tetrachloroethylene solution by infrared spectroscopy.[16]

The above analyses also yields the following ratios:

$I_N(n_N)/I_N(n_O) = 0.88$ and $I_B(n_N)/I_B(n_O) = 0.62$

It is noted that even in the nonbonded conformation $I(n_N)$ is smaller than $I(n_O)$. This is apparently contrary to the observed ratio for $H_2NCH_2CH_2OH$ ($I(n_N) > I(n_O)$) in Figure 3. However, an explanation can be made in terms of effective solid angles open to incoming metastable atoms. In the dimethyl analogue, the effective solid angle for the n_N orbital is decreased, as observed for some substituted anilines with methyl groups.[7] Such a steric effect may occur to a larger extent than one would expect for a small reagent like a proton, since the radius for He* (2^3S) is estimated to be as large as 2.5 Å. This estimate can be made from the van der Waals radius of Ne (1.5 Å) together with the fact that the He* (2^3S)–Ne potential becomes repulsive even at a large distance of about 4.0 Å.[17]

5. Concluding Remarks. Formation of intramolecular hydrogen bonding was found to cause a considerable deactivation of the nonbonding orbitals in Penning ionization. Helium atoms in metastable states attack easily the nonbonding orbitals when (i) the molecule has no hydroxyl group accessible to the *n* orbitals or (ii) the molecule is in a nonbonded molecular conformation. For an intramolecular H-bonded conformer, however, the nonbonding orbital involved in the hydrogen bond is geometrically placed in the "shadow" of the OH bond and shows a considerably suppressed activity in electrophilic attacks by metastable helium atoms. When the dissociation equilibrium is shifted at higher temperatures and the steric shadow effect by the OH bond is decreased, the reactivity of the *n* orbitals increases, since much more electron density is then exposed to the exterior region accessible to the incoming species.

It is noted that Penning ionization is a typical process of electron-transfer reactions; an electron in an occupied molecular orbital of the sample molecule is extracted by an electrophile. The Penning process may thus be used to study relative reactivities of sample molecules. In this use, metastable rare gas atoms may be considered to be microscopic probes of the stereochemical properties of molecular orbitals in the sample molecule. The present study demonstrates that Penning ionization electron spectroscopy may find its applications not only to the comparative study of relative reactivities of orbitals for various molecules but also to the study of dynamic variations of reactivity due to conformational changes.

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Study of Stereochemical Properties of Molecular Orbitals by Penning Ionization Electron Spectroscopy. Effects of Through-Space/Through-Bond Interactions on Electron Distributions

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Abstract: Experimental evidence for effects of through-space/through-bond interactions on electron distributions of molecular orbitals was observed by Penning ionization electron spectroscopy. For norbornadiene, the next highest occupied molecular orbital, which has high electron densities in the endo face augmented by the through-space interactions between π electrons on the double bonds, showed a large reactivity upon electrophilic attacks by metastable helium atoms. In the case of 1,4-diazabicyclo[2.2.2]octane, the highest occupied MO composed of a symmetric coupling of the lone-pairs on nitrogen atoms, which has a smaller exterior electron density than the next HOMO because of the strong through-bond interactions, was found to give the smaller reactivity in Penning ionization.

Molecular orbitals have profound scientific meanings as they explain varieties of experimental results in systematic ways. Recent progress in the chemical orbital theory has made it possible to elucidate chemical reactions on the basis of MO calculations.

Even though such a relationship between theory and experiment is approximate, the relation cannot be limited to one way. One may, therefore, expect that an experimental study is able to elucidate a theoretical construct. A concrete example of this