Penning ionization electron spectroscopy of organic molecules: stereochemistry of molecular orbitals

Yoshiya Harada

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

Abstract - In Penning ionization electron spectroscopy, the kinetic energy of electrons ejected by collisions between targets (gas or solid) and metastable atoms is analyzed. In a gas phase spectrum, an orbital exposed outside the repulsive molecular surface gives a stronger band than does an inner orbital localized inside the surface. Thus, the relative band intensity of the spectrum depends on the spatial electron distribution of individual molecular orbitals. Furthermore, with the introduction of a bulky group some molecular orbitals can be protected from the impact of metastable atoms and become less reactive to the metastables. Therefore, the analysis of the relative band intensity also provides information on the steric shielding effect on the molecular orbital. When Penning ionization electron spectroscopy is applied to the solid, the electron distribution of individual molecular orbitals exposed outside the outermost surface layer is selectively probed. In this case, we can see the shape of the molecular orbital from various directions, if we can control the orientation of surface molecules. The characteristics of Penning ionization electron spectroscopy stated above have been applied to the study of stereochemical properties of various organic molecules.

INTRODUCTION

Various intermolecular processes including chemical reactions start with effective overlapping of the tails of molecular wave functions. To elucidate these processes, therefore, we need information on the stereochemistry of individual molecular orbitals, especially their spatial electron distributions in the frontier region near the molecular surface. Recent studies (ref. 1, 2) have shown that such information can be obtained by Penning ionization electron spectroscopy (ref. 3, 4), in which the kinetic energy of electrons ejected by collisions between targets T and metastable atoms A* is analyzed:

$$T + A^* \rightarrow T^* + A + e^-, \quad e^- \text{for energy analysis.}$$

Usually metastable rare gas atoms such as He* (1s2s, 20.62 eV), Ne*(2p3s, 16.62 eV), and Ar*(3p4s, 19.82 eV) are used as A*.

Figure la shows the Penning ionization process due to the collision between a molecule M and a metastable helium atom. As shown in the figure, an electron in an orbital of M, $\Phi_i$, transfers to the 1s hole of He* and its 2s electron is ejected to an orbital of the continuum state, $\Phi_e$. The transition probability $\Gamma$ of this process is given by (ref. 5)

$$\Gamma \propto | \langle \phi_i(1) | z_{2s}(2) | 1/r_{1s} | z_{1s}(1) \phi_e(2) \rangle|^2.$$

Therefore, the relative intensity of the bands in a Penning ionization electron spectrum (PIES) largely depends on the overlapping of the relevant orbital $\phi_i$ and the is orbital of He*. Since the metastable atom can approach up to the repulsive surface of the molecule, which can be estimated from the van der Waals (VDW) radii of the atoms in the molecule, the degree of overlap of $\phi_i$ and $z_{1s}$ is essentially determined by the distribution of $\phi_i$ outside the repulsive molecular surface (VDW surface) (ref. 6). Thus,
He* PIES

an outer orbital "exposed" outside the VDW surface of the molecule gives a larger $r$ value and, hence, a stronger band in PIES (Fig. 1a and c) than an inner orbital localized inside the surface (Fig. 1b and c).

Let us consider an example of the ammonia molecule (ref. 6). Figure 2 shows the He*($2^3S$) PIES and He I (21.22 eV) ultraviolet photoelectron spectrum (UPS). As is seen from the figure, in the PIES the first band due to the lone pair orbital is enhanced relative to the second band due to the NH bonding orbitals. This can be explained by the electron density maps shown at the top of Fig. 2; the lone pair orbital extended outside the VDW surface interacts with He* metastables and gives a stronger band in PIES, while the bonding orbitals localized inside the VDW surface give a weaker band.

**PIES OF MOLECULES**

The features of the molecular PIES mentioned above was applied to the study of the stereochemical properties of various molecular orbitals as well as to the assignment of the UPS bands in a large number of molecules (ref. 1, 2). Some examples will be shown below.

Figure 3 shows the PIES and UPS of benzene (ref. 6, 7). A theoretical PIES (see below) and the electron density map for each molecular orbital obtained by the ab initio MO method with a 4-31G basis set are also shown. In the PIES the $\pi$ ($e_1$ and $a_2u$) bands are seen to be stronger than the $\sigma$ bands. This can be understood easily, because the $\pi$ orbitals extending out of the molecular plane interact with metastable atoms more effectively than the $\sigma$ orbitals. The electron density maps in Fig. 3 well explain this spectral feature. Furthermore, among the $\sigma$ orbitals, the $a_{1g}$ orbital gives a relatively strong band in the PIES, because it has CH bonding character and is distributed outside the molecule. On the other hand, the $b_{2u}$

---

**Fig. 2.** He*($2^3S$) PIES and He I UPS for ammonia and the electron density maps for the relevant orbitals. The thick solid curves in the maps indicate the molecular surface.

**Fig. 3.** Theoretical PIES (upper), He*($2^3S$) PIES (middle), and He I UPS (lower) of benzene together with the electron density maps for the relevant orbitals. The maps are drawn for a plane 1.7 Å above the molecular plane.

**Fig. 4.** He*($2^3S$) PIES (upper) and theoretical PIES (lower) of anthracene.
Penning electron spectroscopy of organic molecules

band is almost missing in the PIES, although the corresponding band has appreciable intensity in the PIES. This is ascribed to the distribution of the \( b_z \) orbital localized along the carbon skeleton (see the electron density map) and shielded by the \( \pi \) orbitals. As was described above, the relative intensity of the PIES band can be estimated from the distribution of molecular orbitals outside the repulsive molecular surface (VDW surface). Hence, we have defined the exterior electron density (EED) for each MO \( \phi \), by (ref. 7)

\[
\text{(EED)} = \int_\Omega |\phi_i(r)|^2 dr,
\]

where the integration is taken over the region \( \Omega \) outside the VDW surface of the molecule. The theoretical PIES in Fig. 3 was synthesized from Gaussian-type bands with area proportional to the respective EED's and is seen to be in good agreement with the observed PIES.

Figure 4 shows the observed and theoretical PIES of anthracene (ref. 8). As is seen in the figure, the theoretical PIES well reproduces the relative intensity of the observed bands. Thus, the EED analysis allows us to assign all the bands in the He I UPS, where only the highest five \( \pi \) bands have been assigned previously.

With the introduction of a bulky group some orbitals can be protected from the impact of metastable atoms and become less reactive in Penning ionization. Such a steric shielding effect has been found in the PIES of organometallic complexes (ref. 9) and also of some substituted anilines (ref. 10) and nitriles (ref. 11). Figure 5 shows the PIES of carbon monoxide (ref. 9) and chromium hexacarbonyl (ref. 12). In the case of CO the first band is enhanced relative to the other bands, because the corresponding \( 5\sigma \) orbital protrudes largely outside the molecular surface. In the PIES of \( \text{Cr(CO)}_6 \) band 1 due to \( 3d \) orbitals is much weaker than the other bands, since the \( \text{Cr} \) atom is surrounded by six CO molecules and, hence, the electrons in the atom cannot interact effectively with metastables. On the other hand, bands 9 and 10 related to the \( 4\sigma \) orbital of \( \text{CO} \) is much enhanced in comparison with bands 2 to 8 originated from the \( 5\sigma \) and \( 1\pi \). This is ascribed to the character of the \( 4\sigma \) orbital, which has large electron density on the oxygen atom (see the top of the figure). Thus, orbitals of \( \text{Cr(CO)}_6 \), predominantly \( 4\sigma \) in character, are exposed in the outermost region of the molecule.

In contrast to the case of \( \text{Cr(CO)}_6 \), the \( 3d \) orbitals of dibenzene chromium are not well shielded by the benzene rings (ref. 12). As shown in Fig. 6, bands 1 and 2 in the PIES due to the \( 3d \) orbitals are relatively strong. In particular, band 1 originated from the \( 3d_{\sigma} \) orbital is stronger than a \( \pi \) band of the benzene ring; the intensity of band 1 is larger than a quarter of the integrated intensity of bands 3 and 4, which are related to four \( \pi \) orbitals. This shows that the \( 3d_{\sigma} \) orbital is distributed outside the molecule, penetrating the planes of the benzene rings. Chromium hexacarbonyl and dibenzene chromium are model compounds for carbon monoxide and benzene adsorbed on a metal surface. It is interesting to note that our results are consistent with those observed in the PIES of metal surfaces; \( \text{CO} \) molecules adsorbed perpendicularly on a metal surface shield the metal orbitals, while benzene molecules adsorbed flat on the surface do not (ref. 13).

Finally the study of hydrogen bonding by PIES will be described (ref. 14). When an intramolecular hydrogen bonding of the OH-X
type is formed in $\text{XCH}_2\text{CH}_2\text{OH}$ molecules, the intensity of the $n_x$ band is found to be much less than that of the corresponding $n_x$ band in $\text{XCH}_2\text{CH}_2$ molecules. This is due to the fact that upon the formation of the hydrogen bonding the access of metastable atoms to the $n_x$ orbital becomes difficult owing to the sterical shielding effect of the $\text{OH}$ group. In the case of $\text{N,N'}$-dimethylaminoethanol, the temperature dependence of the $n_x$ band intensity, which is an average of the intensities for bonded and dissociated forms, was analyzed and the population of the bonded conformer ($0.83 \pm 0.03$ at $23 \, ^\circ\text{C}$, $0.29 \pm 0.03$ at $300 \, ^\circ\text{C}$) and some thermodynamic data for the dissociation of the hydrogen bonding ($\Delta H = 1.25 \, \text{kJ mol}^{-1}$, $\Delta S = 28 \, \text{J K}^{-1} \, \text{mol}^{-1}$) were obtained.

**PIES OF SOLID SURFACES**

When PIES is employed for the study of a solid surface, the following two characteristics are displayed (ref. 1, 2, 15). Firstly, PIES probes the outermost surface layer of the solid surface selectively because metastable atoms do not penetrate into the inner layers. This is not the case in other electron spectroscopies such as photoelectron, Auger, and electron impact spectroscopies, where photons or electrons used for the excitation sources penetrate into the inner layers. Secondly, PIES enables us to study the electron distribution of individual orbitals in the exterior region outside the solid surface. In gas-phase molecules, which are randomly oriented with respect to the direction of the metastable beam, the relative intensity of the PIES bands reflects the overall spread of individual orbitals. On the other hand, the PIES of the solid surface provides information on the wave function tails of individual orbitals at a definite molecular part exposed outside the surface. This character of surface PIES can be used to probe the geometrical orientation of surface molecules.

Figure 7 shows an example of benzene layers adsorbed on a graphite cleavage plane at 130 K (ref. 16). The spectrum (a) was measured for a clean graphite substrate and spectrum (b), (c), and (d) were obtained from substrates exposed to benzene vapor of $5 \times 10^{-7}$ Torr for 10, 100, and 400 s, respectively. The thicknesses of the adsorbed layers were estimated to be a few monolayers at a 10 s exposure and more than several tens of monolayers at a 400 s exposure. In Fig. 7(a) the relative intensities of the $\pi$ bands are much stronger and those of the $\sigma$ bands are much weaker compared to the case of the gas-phase PIES in Fig. 3. This is accounted for, if we assume that the benzene molecules are oriented flat to the substrate. As can be seen from Fig. 8(a), if a metastable atom approaches a benzene molecule oriented parallel to the graphite cleavage plane, a $\pi$ orbital exposed outside the surface should interact effectively with the metastable atom and give a strong band in the PIES, while a $\sigma$ orbital shielded by the $\pi$ should give a weak band. When the surface molecule is tilted on the substrate, the $\sigma$ bands are expected to become stronger in the spectrum, because the $\sigma$ orbitals are also exposed outside (Fig. 8(b)). In fact, the intensity of the $\sigma$ bands gradually increases with increasing exposure time (see Fig. 7(b) to (c)), showing that molecules at the outermost layer gradually become tilted with increasing film thickness.

Figure 9 shows the PIES of two kinds of iron phthalocianine (FePc) films (ref. 17). Film A is a monolayer prepared by vacuum sublimation onto a graphite substrate held at 213 K. Film B is a crystalline one deposited on a stainless steel substrate at room temperature. As illustrated on the right of the figure, molecules are arranged flat to the substrate in film A and are tilted in film B. In the flat molecular orientation, $\pi$-type orbitals extending normal to the molecular plane (xy plane) effectively interact with metastables, whereas $\sigma$ orbitals distributed within the molecular plane and shielded by the $\pi$-type orbitals scarcely interact with metastables. Among the $\pi$-type orbitals, those mainly originated from the iron $3d_{x^2}$, $3d_{z^2}$, or $3d_{xy}$ MO ($3d_{xy}$-like MO) should interact with meta-
Penning electron spectroscopy of organic molecules

Fig. 8. Interaction between a metastable helium atom and a benzene molecule. (a) The molecule is oriented parallel to a graphite cleavage plane, (b) the molecule is tilted to the plane.

stables more effectively than those derived from the carbon and nitrogen 2p AO, because the former orbitals protrude outside the molecular surface more prominently than the latter ones. On the other hand, in the tilted molecular orientation, the \( \sigma \) orbitals as well as the \( \pi \) should be effectively attacked by metastables, but the 3d-like orbitals with little distribution outside the film surface is expected to be scarcely attacked. As can be seen from Fig. 9, the relative intensity of the PIES bands for films A and B substantiate the above expectations regarding the distributions of the surface orbitals.

Fig. 10 shows the PIES of two evaporated films (films I and II) of a long-chain alkane, tetratetracontane (n-C\(_{34}H_{70}\)) (ref. 18). Film I is a polycrystalline film prepared on a metal substrate at room temperature. Film II is a monolayer deposited on a graphite cleavage plane at low temperature (-60 °C). Since in the crystalline film (film I) molecules stand upright with their chains
perpendicular to the substrate, metastable atoms effectively interact with the terminal methyl moieties (see the right part of Fig. 10). In fact, according to ab initio MO calculations, the features of the PIES are essentially due to molecular orbitals having a large distribution on the terminal methyl group. On the other hand, in the monolayer (film II) molecules lie flat on the substrate with their long chains parallel to the substrate plane. In this case, the features of the spectrum are due to molecular orbitals distributed on the side of the chain. For example, the peak located around 10 eV is originated from pseudo-π orbitals comprised of the C 2p and H 1s AO's and the peak at ca. 2.5 eV is attributed to orbitals due to the C 2s and H 1s AO's. The results shown here have been applied to the characterization of Langmuir-Blodgett (LB) films (ref. 18, 19). The LB films of cadmium stearate, for example, give almost the same PIES as that of Film I, which means that hydrocarbon chains of cadmium stearate stand upright exposing their methyl ends outside the film surface (ref. 18).

The examples shown in Figs. 9 and 10 indicate that surface PIES reflects the local distribution of individual orbitals at a definite molecular part exposed outside. If we can control the orientation of the surface molecules by means of the selections among various substrates, film preparation methods (vacuum deposition, adsorption, Langmuir-Blodgett technique etc.), deposition conditions (substrate temperature, deposition speed), and film treatments (e.g. annealing), we can probe the distribution of molecular orbitals from various direction and approach their "shape" or whole picture.

CONCLUDING REMARKS

We have shown that Penning ionization electron spectroscopy enables us to study the spatial electron distribution of individual molecular orbitals outside the molecular surface. From a chemical point of view, Penning ionization process 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'. In this respect, the intensity of a band in PIES is connected with the reactivity of the corresponding orbital upon electrophilic attack by metastables. For solids, Penning spectroscopy probes the distribution of orbitals penetrated outside the outermost layer that essentially determines the properties of the solid surface. This unique feature of Penning spectroscopy should be further explored by its application to various solid surfaces.

REFERENCES