Two-dimensional Penning Ionization Electron Spectroscopy of CH$_3$I and CH$_2$I$_2$ by He*(2$^3$S) Metastable Atoms

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Abstract. Penning ionization of iodomethane (CH$_3$I) and diiodomethane (CH$_2$I$_2$) upon collision with metastable He*(2$^3$S) atoms was studied by collision-energy/electron-energy resolved two-dimensional Penning ionization electron spectroscopy (2D-PIES) over a wide range of collision energies (20 – 350 meV). Collision energy dependence of partial ionization cross sections (CEDPICS) indicates that the interaction with He*(2$^3$S) atoms around the valence molecular orbitals is attractive at low collision energies except for the only $\sigma_{CH}$ molecular orbital region of iodomethane which has a repulsive character in the normal collision energy range (70 – 350 meV). Large bands at lower electron energies (3.7 – 5.5 eV) in PIES spectra were ascribed to autoionization from a transient ion-pair. The related entrance ionization channel has an attractive character. The excitation transfer, which is responsible for the I** autoionization, takes place in regions close to carbon atoms and is repulsive towards He*(2$^3$S) in the normal collision energy range. The superexcited complex of (He–CH$_2$I$_2$)** autoionizes via the excitation transfer occurring close to the $\sigma_{CI}$ regions of the targets.

1. Introduction

Unraveling the dynamics of chemical reactions is of fundamental importance. In the case of chemi-ionization process known as the Penning ionization (A* + M → A + M$^+$ + e) [1], the ionization of a target atom or molecule (M) occurs by collision with a metastable atom (A*). Important information on the dynamics of this process can be obtained by resolving the collision energy between reactants and analyzing the energy distributions of ejected electrons. Usually, ionic states can be related to valence molecular orbitals (MOs). In the Penning ionization, an electron in MO having higher electron density outside the boundary surface of M is transferred to the inner-shell orbital of the probe atom A*, which results in a high-intensity band in Penning ionization electron spectroscopy (PIES) according to the electron exchange model [2].

Extensive studies have been made for Penning ionization with a metastable A* beam, and the collision energy dependence of total ionization cross sections ($\sigma_I$) by product-ion detection [3] as well as the scattering angular distribution [4] have been measured. Olson showed that the experimental collision energy dependence of the total ionization cross section for He*(2$^1$S) + Ar was well reproduced by semiempirical calculations [5]. In collision energy region lower than 100 meV, the ionization cross section decreases with the increase of collision energy, and then starts to increase to 15 Å$^2$ around a collision energy of 10 eV. The general features of the collision energy dependence of
Penning ionization cross sections can be classified into three types as follows. The first type (I) shows negative collision energy dependence, and it was related to the attractive interactions. If the long-range attractive part of the interaction potential $V^*(R)$ as a function of inter atomic distance $R$, with the potential well $\varepsilon$, plays a dominant role and its function form is the type of

$$V^*(R) \propto R^s, \quad (1)$$

$\sigma_i(E_c)$ can be expressed by

$$\sigma_i(E_c) \propto E_c^{2s}. \quad (2)$$

This formula for Langevin-type cross section is derived from the impact parameter value at which orbiting occurs. The potential parameter $s$ can be related to interaction forces such as dispersion forces or induced dipole interactions ($s = 6$) and ionic interactions ($s = 4$). In the second type (II), the repulsive part of interaction potential governs the collision energy dependence. In the simple theoretical model introduced by Illenberger and Niehaus [6], $\sigma_i(E_c)$ can be expressed as

$$\sigma_i(E_c) \propto \left[ \ln (A/E_c) \right]^3 E_c^{(b+d)/(b+d)}, \quad (3)$$

where simple analytical forms of the interaction potential $V^*(R)$ and the ionization width $\Gamma'(R)$ are assumed by

$$V^*(R) = A \exp(-dR), \quad (4)$$

and

$$\Gamma(R) = B \exp(-bR). \quad (5)$$

When the minor contribution of the first factor in Eq. (3) is neglected, the collision energy dependence can be related to $d$ and $b$ via the slope $m$ in a plot of $\log \sigma_i$-$\log E_c$ by

$$m = (b/d) - (1/2). \quad (6)$$

Here, $d$ and $b$ are effective decay parameters of repulsive potential wall ($V^*$) and ionization width ($\Gamma$), respectively. The third type (III) corresponds to the hard core limit of Eq. (6); the parameter $d$ becomes considerably large and slope $m$ of a log $\sigma_i$-$log E_c$ plot is nearly $-1/2$. In this case, the effective interaction time deceases with the increase of $E_c$.

Combining an electron energy analysis with a velocity selection of the metastable incoming atomic beams [7,8] enables us to measure the collision energy dependence of partial ionization cross-sections (CEDPICS) by collision-energy/electron-energy-resolved two-dimensional Penning ionization electron spectroscopy (2D-PIES) [8,9]. Since the asymptotic decay of all MOs is directly related to the lowest ionization energy ($I_0$) of the target molecule [10-12] by an expression of $\exp\{-2(2I_0)^{1/2}R\}$ for the distance $R$, the radial dependence of the ionization width in Eq. (5) for all MOs should be the same. However, the reaction probability to each ionic state was found to show a difference in the collision energy dependence with the change of $E_c$ [7]. This difference can be ascribed to the highly anisotropic interactions around the target molecule, where trajectories of the metastable atoms are deflected variously around the reactive region depending on the collision energy, the impact direction, and the impact parameter. For the target molecule, since the electron distributions of individual MOs are more or less localized on the spatial parts of the molecule, different CEDPICS for various ionic states can be connected to the anisotropy of interaction between a target molecule $M$ and a metastable atom $A^*$ [7-9]. In the case of positive CEDPICS, the metastable atom with larger kinetic energy reaches the inner region of the target against a repulsive interaction. Thus, a positive CEDPICS implies that the interaction around the region where a corresponding MO spatially extends is repulsive. On the other hand, negative CEDPICS can be related to an attractive interaction around the region where the corresponding MO distributes, since the metastable atom is deflected towards the target molecule by the attractive interaction. In this case, the extent of the deflections decreases with the increase of collision energy.

The interaction between a metastable atom and a target molecule does not necessarily lead to a direct Penning process, and two further sequences also can lead to electron ejection when a molecular target collides with a metastable $\text{He}^*(2^3S)$ atom; (i) Electron ejection can be achieved through autoionization via an ionic reaction channel. In this channel, the $\text{He} 2s$ electron transfers to the target which results into the formation of an ionic pair $\text{He}^–\text{M}^+$. Then the $\text{M}^+$ component autoionizes in a
subsequent step, and the ionic pair He\(^{\pm}\)–M\(^{-}\) transforms into He, M\(^{+}\), and e\(^{-}\). Dissociation of M into some fragments can occur. (ii) A more complicated autoionization reaction channel can involve an electronic excitation transfer: the He 2s electron transfers to an unoccupied target molecular orbital accompanied by a filling of the He 1s hole orbital by an electron of M. The produced intermediates are electronically excited M\(^{*}\) species which can autoionize; or alternatively, undergo dissociation in excited fragments that can also autoionize. Moreover for some substances such as compounds containing halogen atoms, complicated and various autoionization processes can also play an essential role and lead to spectral bands with large ionization cross section. Broad intensive bands were observed in the PIES spectra of Cl\(_2\), Br\(_2\), and I\(_2\) [13,14]. It is interesting that for heteronuclear halogen compounds (ICl and IBr), the autoionization structure can be in general represented as a simple superposition of corresponding bands of related homonuclear compounds (Cl\(_2\), Br\(_2\), and I\(_2\)) [14]. For HCl, HBr, and HI, the excitation transfer has been observed [15-17], and PIES measurements with high electron energy resolution led to observation of a series of small peaks in the low electron energy region (0 – 3.7 eV), which was assigned to the autoionization of the Rydberg series of the dissociated halogen atom.

Our group has applied 2D-PIES to some methyl compounds containing halogen such as bromo methanes, CH\(_2\)ClI, CH\(_2\)BrI, CHBrCl\(_2\) in order to investigate the reaction dynamics and anisotropic interactions with He\(^{*}\) atoms [18-20]. In this study, we have investigated the anisotropic interaction with He\(^{*}\) atoms and autoionization process for Penning ionization of CH\(_3\)I and CH\(_2\)I\(_2\) with the 2D-PIES technique.

2. Methods

The experimental apparatus used for the measurements is described in detail in previous papers [8,9]. Briefly, metastable He\(^{*}\)(2\(^3\)S) atoms were produced by a discharge nozzle source. In addition, a water-cooled helium discharge lamp was used for quenching the metastable He\(^{*}\)(2\(^3\)S) atoms generated as a byproduct in the source. To obtain the collision-energy-resolved spectra, a chopper disk rotating with a frequency of about 350 Hz modulated the beam of the metastable helium atoms. For the UPS measurements, the apparatus was equipped with an additional source of photons from the He I resonance line (584 Å, 21.22 eV). The interaction between the molecules under investigation and the metastable He\(^{*}\)(2\(^3\)S) atoms as well as with the He I photons occurred in a small collision cell (20 mm in diameter). A hemispherical electrostatic deflection type analyzer connected to the collision cell was used to measure the kinetic energy of the ejected electrons. The transmission curve for the energy analyzer was calibrated on the basis of the relative peak intensities for various compounds with respect to known UPS data [21,22].

The collision energy dependence of the partial ionization cross-section was obtained for a specific ionic state in 2D-PIES accumulated as functions of two parameters; the electron kinetic energy (E\(_e\)) and the collision energy (E\(_c\)) between A\(^{*}\) and M. The 2D-PIES measurements in the low collision energy range have been performed with slow metastable He\(^{*}\) atoms produced by discharge between the skimmer and a nozzle cooled by liquid nitrogen [23]. The retarding type electron analyzer based on the ‘magnet bottle effect’ has been utilized for collecting electronic counts at lower collision energy region. The velocity distribution of the metastable He\(^{*}\) beam was monitored by secondary electrons emitted from a stainless steel plate inserted in the reaction cell. Then we obtained CEDPICS in lower (20-100 meV) and higher (60-300 meV) collision energy range.

We performed ab initio molecular orbital calculations with the Gaussian 03 package of programs [24]. The geometries of the neutral target molecules were obtained by microwave spectroscopy for CH\(_3\)I [25] and optimization with second-order Møller-Plesset perturbation theory (MP2) with 6-311G** basis functions. In the electron density contour maps, thick solid curves indicate the repulsive molecular surface approximated by atomic spheres of van der Waals radii [26]. For the ionization potential energies, the outer valence Green’s function (OVGF) [27] calculations were performed. Based on the well-known resemblance between He\(^{*}\)(2\(^3\)S) and Li(2\(^{2}\)S) [3], a Li(2\(^{2}\)S) atom in the ground state was utilized in place of a He\(^{*}\)(2\(^3\)S) atom for model potential surface calculations for the
interacting system He*-M. The basis set superposition error was corrected by counterpoise method [28].

According to the electron exchange model [2,8] of Penning ionization process, the probability of partial electron emission intensities for ionization from selected electronic states are thought to be proportional to the overlap between the unoccupied 1s MO of the He*(23S) atomic probe with the ionized target MO ($\phi_i$) within the subspace ($\Omega$) outside the collision boundary surface:

$$ (EED)_i = \int_{\Omega} |\phi_i(r)|^2 \, dr $$

In practice, the collision boundary surface is equated to a rigid van der Waals surface assuming a hard sphere depiction [2,8]. Exterior electron density values (EED), from which partial ionization cross sections can be estimated, have been calculated at the HF/6-311G** level. In that way, on the basis of known (from UPS or ab initio calculations) ionization potentials we can simulate the Penning ionization electron spectra from investigated target. By comparison of this spectrum with real PIES data we can distinguish bands caused by other ionization channels.

3. Results and Discussion

3.1. Valence ionic states observed by UPS and PIES

It is well-known that the first and second bands in the UPS of iodomethane (CH$_3$I) show spin-orbit splitting (5P$_{1/2}$ and 5P$_{3/2}$) of degenerate 9e orbitals [30], which emerges as two peaks in almost equal intensities at 9.5 and 10.8 eV in the UPS spectrum (Figure 1(a)). The strong intensity of bands 1 and 2 in PIES indicates spatial extending of large electron density outside of the collision limit (molecular surface) as shown in the EED spectrum. Band 3 was assigned to 12a$_1$ MO which also has relation with the iodine lone-pair electron. Degenerate 8e orbitals having $\sigma_{CH}$ character were observed as bands 4, 5 for which broadening was induced by the Jahn-Teller effect. Observed band intensity of band 3 and bands 4, 5 is not so large as bands 1, 2, which can be ascribed to bonding character of 12a$_1$ MO between the iodine atom and the methyl group ($\sigma_{CI}$) and 8e MO ($\sigma_{CH}$) with small spatial extending outside the molecular surface.

![Figure 1. He I UPS, He*(23S) PIES, and EED simulation of (a) CH$_3$I and (b) CH$_2$I$_2.$](image-url)
The four bands corresponding to lone-pair MOs of diiodomethane (CH$_2$I$_2$) were assigned to 19b$_2$, 9b$_1$, 8a$_2$, and 21a$_1$ in the order calculated with the OVGF method (Figure 1(b)). Our assignment is consistent with an earlier UPS study [30]. However, ionization energy values of these lone-pair MOs of CH$_2$I$_2$ can be difficult to estimate by the quantum chemical theory because of spin-orbit splitting effects in ionization from iodine lone-pair orbitals. Next three bands (bands 5, 6, and 7) were observed in He I UPS spectrum at the electron energy of 4–9 eV, and they were assigned to $\sigma_{CI}$ and $\sigma_{CH}$ MOs based on the results by the OVGF calculation as shown in Table 1. Contrary to the UPS and the EED spectrum (Figure 1(b)), these bands show strong intensity in PIES. The reason for this strong intensity in PIES will be discussed in Section 3.3.

3.2. Collision-energy-resolved measurements of PIES

Negative slope of CEDPICS for CH$_3$I (Figure 2 (a)) for bands 1 and 2 ($n_i$, $m$(higher) =$-0.60$, $m$(lower) = $-0.40$) can be ascribed to attractive interaction between the target molecule and He*($2^3S$) atoms around the $n_i$ orbital region. It is known that slower He* atoms can penetrate into the inner reactive region than the faster He* atoms because of the lower centrifugal barrier, which can lead to negative CEDPICS [7,8] as described in Section 1. Attractive interaction was found by the model potential calculation for the perpendicular direction around the C-I axis (Figure 3(a)). The small well depth (ca. 10 meV) of the interaction potential may be due to the Li-model potential calculation with insufficient basis set for the I atom. On the other hand, repulsive interaction was obtained around the $\sigma_{CH}$ orbital region, which is consistent with the small positive slope of CEDPICS at higher collision energy region (60-300 meV) for bands 4,5 ($\sigma_{CH}$, $m$ = +0.04). The bending shape of CEDPICS for bands 4,5 may be influenced by the attractive interaction around the iodine atoms in spite of the ionization from $\sigma_{CH}$ MOs for slower metastable He$^-$ atoms. The negative slope of CEDPICS for band 3 ($\sigma_{CI}$, $m$(higher) =

![Figure 2. CEDPICS of (a) CH$_3$I and (b) CH$_2$I$_2$ by collision with He*($2^3S$) atoms.](image-url)
−0.09) is smaller than that for \( n_I \) bands, which is consistent with the weaker interaction potential along the C-I axis rather than the perpendicular direction around the C-I bond. For this band, weak bending shape of CEDPICS was observed.

For the case of CH\(_2\)I\(_2\) (Figure 2(b)), similar negative collision energy dependence was observed for bands 1, 2 and bands 3, 4. Influence of attractive interactions was calculated around the iodine atoms of CH\(_2\)I\(_2\) (Figure 3(b)) rather than CH\(_2\) group. It is interesting that the shape of CEDPICS was bending at lower collision energy region. The CEDPICS for other bands will be discussed in the following Section 3.3.

### 3.3. Autoionization bands

Former studies on iodine compounds have pointed out the presence of autoionization bands (\( S^* \) in this study) in PIES of HI [17], I\(_2\), IBr, and ICl [14]. The position of \( S^* \) bands depend on the energy curve for the dissociation of the intermediate ionic pair He\(^-\)···I⁻·R [17]. For CH\(_3\)I, small \( S^* \) band can be found around \( E_e = 4 \) eV in PIES, and no counter part band structure was observed in He I UPS. The strong \( S^* \) band of CH\(_2\)I\(_2\) (Figure 1(b)) relating to the formation of intermediate ionic pair (He\(^-\)···I⁻·CH\(_2\)I) is located at electron energy \( E_e = 3.94 \) eV in PIES, which is close to the diatomic iodine molecule cases (3.75 eV for HI [17], 3.2 eV for I\(_2\), IBr, and ICl [14]). Band shoulder with no strong counter part was observed at \( E_e = 5.1 \) eV in He I UPS for CH\(_2\)I\(_2\) in this study and other diatomic iodine molecules (I\(_2\), IBr, and ICl) [14]. Observed intensity of \( S^* \) band is extensively large compared with band 7 in the EED spectrum (Figure 1(b)). The shape of CEDPICS for the \( S^* \) band of CH\(_3\)I and CH\(_2\)I\(_2\) is bending with large negative slope at lower collision energy region and small positive slope at higher
collision energy region, which can be explained by the collision dynamics around the crossing point of interaction potential energy curves for intermediate ionic pair He + ∙∙∙I - R and normal Penning ionization collision of He* M. These results indicate that metastable atoms at lower collision energy are strongly influenced by the attractive force on the interaction potential energy curve for the ionic pair. In addition, small positive collision energy dependence was observed for the normal Penning ionization process around the C-I axis at higher collision energy region than E_c ~ 150 meV.

Autoionization bands like band S for CH2I2 in this study were observed at the shoulder of valence bands for CHBr3 [20] and HX [14-17], and they were assigned to ionization from superexcited states of a complex (He-M)** to highly excited vibrational states of ion. The large negative CEDPICS for band S of CH2I2 can be ascribed to attractive interaction around the iodine at generating the superexcited states. The observed intensity of band 6 for CH2I2 is also different from the EED spectrum, and observed CEDPICS for band 6 is very similar to that for band 5. Judging from the similar MO distribution of 18b2 and 20a1 and CEDPICS for bands 5 and 6, the additional signals around the band 6 also can be assigned to autoionization (S band) related to bands 5 and 6.

For lower electron energy region in PIES of HI, sharp lines by autoionization of [1S0]ns and [1S0]np series Rydberg I** atom into the 1D2 I+ state were observed [17]. Thus, signals in lower electron energy region than 3.6 eV in PIES of CH2I2 may be ascribed to Rydberg 1** (S_r) atoms induced by the dissociation of the C-I bond of (CH2-I)**. At the low electron energy region in PIES for CH3I, electronic counts are low, and the band structure was not significant. The small or indistinct S_r band for CH3I may be related to small transition probability to excited (CH3-I)** states by the approach of He (2S) atoms. The positive slope of CEDPICS for the S_r** band of CH2I2 at higher collision energy region (m = + 0.09) may indicate collision dynamics for generating the (CH2-I)** states. When we assume the anisotropy of interaction potential for the He**-CH2I2 system in the excitation transfer from He* to CH2I2, the He* approaching direction can be dominant around the σ_CH bond region.

| Table 1. Ionization potentials (eV) by He I UPS and theoretical calculations, band assignments, EED values (%) and slope parameter (m) of CEDPICS at lower (20-100 meV) and higher (60-300 meV) collision energy region for CH3I and CH2I2 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Band | IP | Koopmans | OVGF | EED | m(lower) | m(higher) |
|---|---|---|---|---|---|---|
| CH3I |
| 1 | 9.48 | 9.85(9e, n_i) | 9.50 (0.93)* | 6.51 | -0.60 | -0.40 |
| 2 | 10.11 | 9.85(9e, n_i) | 6.51 | -0.62 | -0.40 |
| 3 | 12.40 | 12.67(12a1, σCI) | 12.31 (0.92) | 3.00 | -0.54 | -0.09 |
| 4 | 15.1 | 16.59(8e, σCH) | 15.28 (0.89) | 3.26 | -0.53 | +0.04 |
| 5 | 16.59(8e, σCH) | 3.26 | |
| S* | (15.8) | -0.50 | +0.03 |
| CH2I2 |
| 1 | 9.36 | 9.86(19b2, n_i) | 9.36(0.92) | 5.45 | -0.65 | -0.26 |
| 2 | 9.70 | 10.24(9b1, n_i) | 9.68(0.92) | 6.52 | -0.65 | -0.26 |
| 3 | 10.14 | 10.39(8a2, n_i) | 9.82(0.92) | 6.02 | -0.65 | -0.26 |
| 4 | 10.50 | 10.52(21a1, σCI) | 9.95(0.92) | 6.23 | -0.65 | -0.26 |
| S | (11.2-12.6) | -0.68 | -0.17 |
| 5 | 12.68 | 13.23(18b2, σCI) | 12.54(0.91) | 2.48 | -0.62 | -0.16 |
| 6 | 13.48 | 14.43(20a1, σCI) | 13.39(0.89) | 2.82 | -0.62 | -0.15 |
| 7 | 15.50 | 17.65(8b1, σCI) | 15.82(0.88) | 2.62 | -0.68 | +0.02 |
| S* | (15.9) | -0.68 | +0.02 |
| S_r | (18.1-19.8) | -0.70 | +0.09 |

* Pole strengths are shown in the parentheses.
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