

Anisotropic interaction between iodomethanes and He* (2³S) metastable atoms
and autoionization processes studied by
collision-energy-resolved Penning ionization electron spectroscopy
in the energy range of 20 - 350 meV

(Department of Chemistry, Graduate School of Science, Tohoku University)

○ Andriy Borodin, Takuya Horio, Masakazu Yamazaki, Naoki Kishimoto, and Koichi Ohno

Penning ionization of iodomethanes (CH_xI_{4-x}) upon collision with metastable He*(2³S) atoms was studied by collision-energy/electron-energy resolved two-dimensional Penning ionization electron spectroscopy (2D-PIES) in the collisional energy range from 20 to 350 meV.

The initial guess for the electronic structure of iodomethane and diiodomethane was made by the *ab initio* calculation. The main difference between band positions observed by UPS and calculated by the OVG method is the splitting of non-bonded MOs caused by spin-orbit interaction and Jahn-Teller effect,¹ those are known, in particular, for 5p band of I (5p_{1/2} - 5p_{3/2}) and can also be observed for related MOs in many compounds containing Iodine. The PIES spectra of iodomethane and diiodomethane are similar to the UPS spectra except for the relative band intensities. In PIES, some additional structures caused by the interaction with metastable He* can be noticed.

The Figure 1 shows the HeI UPS and He* (2³S) PIES spectra of iodomethane. The calculated positions of valence bands (by OVG) are presented below the spectra. The electron density maps related to that are also shown in the figure. The MOs 9e and 8e are degenerated in OVG, so the OVG positions and electron density maps cannot be divided between them. Unlike UPS, a strong additional structure (marked by S*) stretching from E_e ~ 0.5 eV to E_e ~ 4.5 eV can be noticed in PIES. A peak at E_e ~ 4.2 eV as well as several small irregular peaks in region of 1–4 eV reproducing themselves from one measurement to other belong to this structure. A similar additional broad band was already observed by PIES for HI.² In that case the enhanced peak can be assigned to ionic states of I⁺ produced via autoionisation within the potential energy surface of a transient HI–He⁺ ionic pair. In case of bromomethanes (CH_xBr_{4-x}) a similar process can be observed in PIES: the autoionization of the Br^{**} Rydberg atom produced at the dissociation of molecular target caused a similar S* band.³ On that way, the neutral dissociation followed by autoionization processes can also

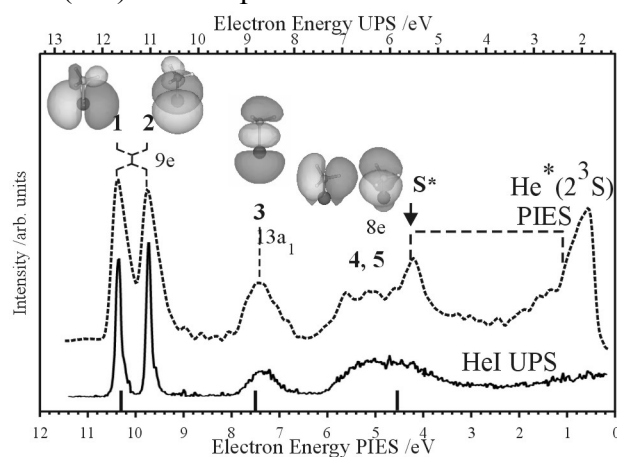


Figure 1. He* (2³S) PIES and HeI UPS of iodomethane

explain well the appearance of the S^* - band for iodomethane.

As can be seen in the Figure 2, the collision-energy-dependences of the partial ionization cross sections (CEDPICS) for all MOs of iodomethane have negative slopes indicated an attractive character of interaction with $\text{He}^*(2^3S)$ in low collision energy range. In the full collision energy range, these dependences are negative for MOs 1 – 3, with slopes of -0.30 – -0.38. The slopes 4 and 5 should rather be related to the autoionization band S^* , which is tightly surrounded by the satellite bands. And the shape for the slope of band S^* , in its turn, is similar to that of band 3, which is a σ band of C–I bond, which may be connected to the autoionisation from σ_{CI}^* excitation states (LUMO, next to LUMO) caused the appearance of band S^* .

The anisotropy of the interaction potential between CH_3I and metastable $\text{He}^*(2^3S)$ is shown in Figure 3 by the model potential calculation with a $\text{Li}(2^2S)$ -atom. The curve denoted by (\square) for the He^* ($\text{Li } 2^2S$) approaching towards the I atom from directions which are perpendicular to the C–I bond are most attractive (the well depth of 318 meV); while the curve (\bullet) for direction along the C–I bond has a weakly negative or rather neutral character (the interaction potential of -20 – -30 meV). The curve (\blacktriangledown) for the direction towards methyl group has a repulsive character. The behavior of the interaction potential is well correlated with the slopes of CEDPICS in the range of the collision energy of 150 – 300 meV.

The diiodomethane (CH_2I_2) shows a similar behavior in interaction with the metastable $\text{He}^*(2^3S)$: The bands indicating the autoionization can be observed; the ionization from all MOs has negative CEDPICS by attractive interactions; the interaction potential has similar values of the well depth in regions around the I atoms and close to the methyl group.

Thus the collision-energy-resolved Penning ionization electron spectroscopy in connection with the *ab initio* calculations gives us a good means to study the collisional ionization dynamics in detail such as the dissociation following autoionization observed in the present study.

References:

- (1) Ehland, J. H. D. *Photoelectron Spectroscopy: An introduction to Ultraviolet Photoelectron Spectroscopy in Gas Phase* (Butterworth, London, 1974).
- (2) Yench, A. J.; Ruf, M. W. and Hotop, H. Z. Phys. D. 1994, 29, 163.
- (3) Kishimoto, N.; Matsumura, E.; Ohno, K.; Deleuze, M. S. J. Chem. Phys. 2004, 121, 3074.

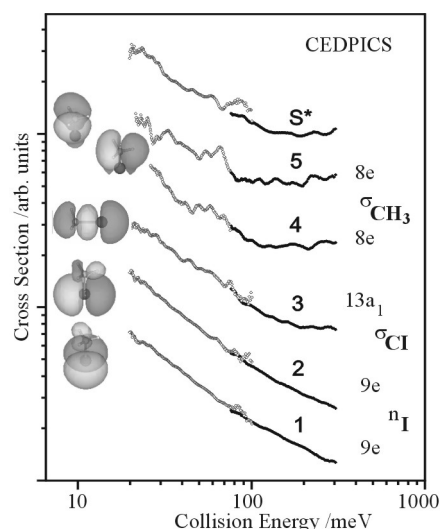


Figure 2. CEDPICS for $\text{He}(2^3S)+\text{CH}_3\text{I}$

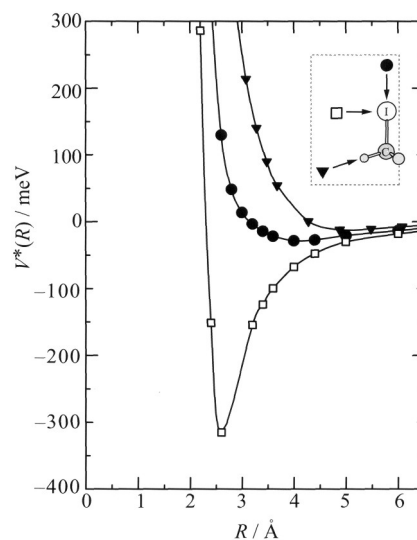


Figure 3. Interaction potential curves for $\text{Li}(2^2S) + \text{CH}_3\text{I}$