Hypervalent Carbon and Iodine Compounds Investigated by Cryogenic Gas-Phase Spectroscopy

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Hypervalent compounds possess a main group element that formally has more than eight valence electrons, apparently exceeding the Lewis octet rule. Their characteristic electronic states that realize the "hypervalent state" have been intensively studied from a viewpoint of theoretical chemistry [1], while few attempts were made toward their spectroscopic identification. In this talk, we present our recent achievements in experimentally characterizing electronic states and bonding natures of following hypervalent carbon [2] and iodine [3] compounds, by using our spectroscopic techniques under cryogenic gas-phase conditions.

(1) Carbon compound [4] Yamamoto and co-workers have recently synthesized hypervalent pentacoordinate carbon compounds bearing a flexible 7-6-7 membered ring (Figure 1a) [2]. It was revealed that their bonding nature, penta-coordinate (hypervalent) versus tetra-coordinate (normal-valent) of the central carbon atom, is dependent on electron donating ability of substituent on ligands, X (Figure 1a). However, the structure of a compound with moderately electron donating one, X = SMe, remained ambiguous. Herein, our combined study of photodissociation spectroscopy (PDS), ion mobility-mass spectrometry, and density functional theory calculations demonstrated the coexistence of penta- and tetra-coordinate forms as isomers in solution and gas phase. It is in sharp contrast to the exclusive presence of the latter one in crystal, highlighting the effects of environment on stability of the hypervalency.

(2) Iodine compound We extend our study to an iodine compound, which has a colinear "N–I–N" moiety: $[(C_5H_5N)_2I]^+$ (Figure 1b) [3]. PDS of the cryogenically (~10 K) cooled $[(C_5H_5N)_2I]^+$ ion identified well-resolved vibronic bands, where N–I symmetrical stretching mode was observed at 168 cm⁻¹. It corresponds to an effective spring constant of $132 \text{ N} \cdot \text{m}^{-1}$ for the N–I bond in the electronically excited state. This study provides a clue toward quantitative understanding of the hypervalency.



Fig. 1 Hypervalent (a) carbon and (b) iodine compounds used in this study.

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