Réunions scientifiques

Séminaires

Séminaire SOLEIL

Threshold and Imaging Photoelectron Photoion Coincidence Spectroscopy Experiments for High-Accuracy Thermochemistry

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Invité par Laurent NAHON

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Petit Amphi SOLEIL – Bât. Accueil

Photoelectron photoion coincidence (PEPICO) spectroscopy is a marriage of photoelectron spectroscopy and mass spectrometry. Electron / ion pairs are created by single photon ionization and the two charged species are measured in delayed coincidence with each other. Ions are selected in narrow range of internal energy by collecting only ions created in delayed coincidence with the photoelectrons. In threshold PEPICO, only the initially zero-energy electrons are detected, while in imaging PEPICO (iPEPICO), a whole velocity image is detected in coincidence with the photoions. These photoelectrons provide the start signal for measuring the ion time of flight (TOF) distributions. All the kinetics information about dissociation rate constants and translational energy release in the dissociation is contained in these TOF distributions. Recent developments in the experimental technique, including velocity focusing optics, as well as advances in data analysis that take into account the initial thermal energy distribution of the molecules, has permitted the extraction of dissociation limits and, therefore, bond energies to within 10 meV (0.5 kJ/mol) using the lab-based TPEPICO experiment. With the recent commissioning of the VUV beamline at the Swiss Light Source (SLS) synchrotron, both the energy resolution and the photon energy range of these experiments have been considerably extended, allowing bond energies to be determined with close to meV accuracy.

The use of the PEPICO technique is be demonstrated on a number of mid-size organometallic complexes, where thermochemistry is correlated with results on the electron structure using photoelectron spectroscopy, as well as on small molecules, where the existing gaps in high-accuracy thermochemistry is filled using the numbers from T- and i-PEPICO: A) A recent TPEPICO study on mixed Cl and Br haloforms show how accurate heats of formations can be determined using multiple thermochemical anchors. B) From a temperature-dependent series of TPEPICO experiments, the most reliable numbers on the heats of formation of ethyl halides is obtained through the common Et^+ cation dissociation product. C) In order to obtain reliable thermochemical data on atmospherically relevant mixed sulfur-chloride oxoions, iPEPICO and TPEPICO experiments have been performed on SCl_2, S_2Cl_2, $SOCl_2$, and SO_2Cl_2 to derive heats of formation of the various $S_xO_yCl_z^+$ fragment ions. These experiments were also used to address the open problem of the number of translational degrees of freedom in product energy distributions of the dissociating photoions. D) To complement recent high-accuracy results on the dissociation energy of the neutral water molecule, the appearance energy of the OH^+ or OD^+ fragment ion from four isotopomers of water is determined to meV accuracy.

Formalités d'entrée *: accès libre dans l'amphi du Pavillon d'Accueil. Si la manifestation a lieu dans le Grand Amphi Soleil du Bâtiment Central, merci de vous munir d'une pièce d'identité (à échanger à l'accueil contre un badge d'accès).*

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