

Theoretical analysis on inner shell excitation dynamics of acetylene

Victor Kimberg¹, Faris Gel'mukhanov², and Nobuhiro Kosugi^{1,3}

¹*Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*

²*Theoretical Chemistry, Royal Institute of Technology, S-106 91 Stockholm, Sweden*

³*The Graduate University for Advanced Studies, Japan*

e-mail address: viktor@ims.ac.jp

Recent experimental results of high resolution angle-resolved photoion-yield spectra (ARPIS) of acetylene [1, 2] show significant changes in fine structure of the spectra profile for core-to-valence excitation measured at 0 and 90 degrees regarding to the direction of x-ray photon polarization. This phenomenon can be explained by the vibronic coupling in the core-to-valence state due to strong Renner-Teller effect [3]. The present poster proposes theory of NEXAFS of fixed-in-space polyatomic molecule which explains in details the experimental observations using the analysis of the inner-shell excitation dynamics.

Our theoretical approach employs *ab initio* configuration interaction (CI) method implemented in GSCF3 [4] – a program package for molecular inner-shell ionization and excitation. We performed calculation of the potential energy surfaces of the ground and core-excited states, as well as transition dipole moments, including two-dimensional calculation for symmetric and antisymmetric bending modes to account for Duschinsky effect. Vibrational energies and wave functions are found as solution of time-independent Schrödinger equation. The angle-resolved photoion-yield spectra are obtained by evaluation of ion flux, which can be found as a projection of the excited state wave packet on particular direction in molecular frame. The model was applied to study of the acetylene $1s \rightarrow 1\pi_u^*$ and $1s \rightarrow 3\sigma_g^*$ transitions. The core-to-valence excited states has bent geometry due to vibronic coupling, and especially bending modes play a key role in changing anisotropy of the ARPIS, while stretching modes define a dominant part of the spectral profile. The effect of the lifetime of the core-excited state, direction of ion flux and transition dipole moment on spectra formation is also discussed.

- [1]. J. Adachi, N. Kosugi, and A. Yagishita, J. Phys. B: At. Mol. Opt. Phys. **38**, R127 (2005).
- [2]. J. Adachi, N. Kosugi, E. Shigemasa, and A. Yagishita, Chem. Phys. Lett. **309**, 427 (1999).
- [3]. J. Adachi, N. Kosugi, E. Shigemasa, and A. Yagishita, J. Chem. Phys. **107**, 4919 (1997).
- [4]. N.Kosugi and H.Kuroda, Chem. Phys. Lett. **74**, 490 (1980); N.Kosugi, J. Comput. Phys. **55**, 426 (1984); N. Kosugi, Thoret.Chim. Acta **72**, 149 (1987).