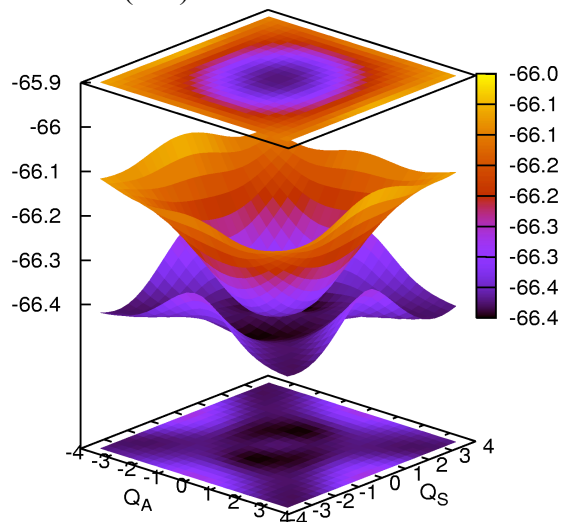# 1P120

アセチレンの内殻励起ダイナミクスの理論解析

（分子研、総研大、**KTH**）**V. Kimberg, F. Gel'mukhanov,** ○小杉信博

The present paper proposes theory of NEXAFS of fixed-in-space polyatomic molecule. The theory explains qualitatively spectra formation in recent ARPIS measurements near 1s→1π_g* and 1s→3σ_u* transitions of acetylene. Our theoretical approach employs ab initio calculation of the potential energy surfaces (PES) of the ground and core-excited states, as well as transition dipole moments, including two-dimensional (2D) calculation for symmetric and antisymmetric bending modes to account for Duschinsky effect. 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 effect of the lifetime of the core-excited state, direction of ion flux and transition dipole moment on spectra formation is also discussed.

Angle-resolved photoion-yield spectra[1] are measured in the direction parallel and orthogonal to the electric vector of the linearly polarized X-ray radiation. This technique allows us to observe polarized XAS even of free molecules. Resent experimental results on ARPIS of core-to-valence excitation in acetylene show significant changes in fine structure of the spectral profile measured at 0 and 90 degrees regarding to the direction of x-ray photon polarization. In particular, high resolution measurements in the region of acetylene core-to-π* excited state show that the relation of the intensities of spectra obtained at 0 and 90 degree is modulated with vibrational frequency of the excited state. This phenomenon can be explained by the vibronic coupling in the core-to-valence state due to strong Renner-Teller (RT) effect[2]. Similar effect was observed near core-to-σ* transition of acetylene[3]. Present work proposes a theoretical model for qualitative explanation of angle-resolved x-ray absorption fine structure measurements.

The important part of our theoretical approach is based on accurate *ab initio* calculations of PES for ground and excited state and dipole matrix elements using configuration interaction (CI) method implemented in GSCF3 program package, which has been developed by one of the authors (NK) for molecular inner-shell ionization and excitation since 1980[4]. In most cases, a rather simple approach based on one electron picture is successful. However, Hartree-Fock (HF) solution fails to interpret in detail high-resolution molecular spectra measured at recent advanced SR facilities in case of vibronic coupling in the core-excited state. In such a case, we have to go beyond HF; that is, electron correlation approaches such as CI. In the C1s→1π_g* excited state, twofold degeneracy of the bending modes is removed due to vibronic coupling with bending vibrations through the RT effect. The 1π_g* excited state is split into in-plane π* and out-of-plane π* excited states with bent and linear equilibrium geometry, respectively (Fig.1). The strong Duschinsky effect motivates us to use 2D picture for symmetric Q_S and antisymmetric Q_A

Fig.1. PES of 1s→π* excited state.

bending modes to be able to reproduce ARPIS profile. At the next step, vibrational wave functions and eigen energies are computed using time-independent solution of Schrödinger equation, which allows us to evaluate the wave packet of the core-excited state.

Due to RT effect acetylene is bent in the core-excited state (Fig.1) and during the lifetime the molecule is able to perform bending vibration and align the C-H bond along new equilibrium geometry. After decay of the molecule to the dissociative final state due to Auger process, hydrogen ion leaves the molecule and is detected by ion detector, which measures the absolute value of the ion flux J. The numerical solution of the obtained nonlinear equation for the cases of parallel and orthogonal orientation of J relative to polarization vector results in ARPIS profiles, which are shown in Fig.2 and 3 for $1s \rightarrow 1\pi^*_g$ and $1s \rightarrow 3\sigma^*_u$ excited states, respectively[5].

In the case of the $1s \rightarrow 1\pi^*_g$ state, spectral shape of the anisotropy parameter traces the C-H stretching modes profile, which is in qualitative agreement with one obtained in the experiment. The angle-resolved ion yield spectra are strongly dependent on the lifetime of the excited state: decrease of lifetime suppresses the I_0 spectrum. It was shown[5] that weak coordinate dependence of the dipole moment of $1s \rightarrow 1\pi^*_g$ transition results in similar shape of the I_0 and I_{90} spectral profiles. In the case of the $1s \rightarrow 3\sigma^*_u$ state, on the contrary, the sufficient difference of the I_0 and I_{90} spectral shapes was explained due to strong coordinate dependence of the dipole matrix elements. The stretching modes play an important role in formation of the $1s \rightarrow 3\sigma^*_u$ spectra.
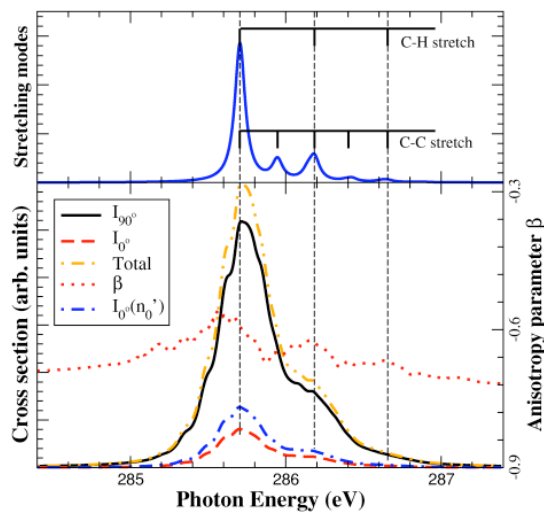

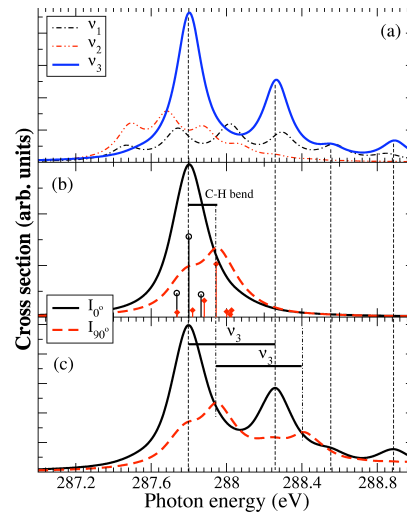Fig 2. ARPIS near C_2H_2 C1s$\rightarrow\pi^*$ resonance.

Fig 3. ARPIS near C_2H_2 C1s$\rightarrow\sigma^*$ resonance.

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