Dependence of Molecular Shape Resonance Energy on Inter-nuclear Distance Probed by High-resolution Core-level Photoelectron Spectroscopy

The advent of third generation synchrotron radiation facilities has provided a wealth of information about inner shell photoionization processes because they offer a combination of high-resolution and high-intensity beams.

Shape resonances are one of the most interesting features observed in core-level molecular photoionization. By definition, shape resonances arise from the temporal trapping of a photoelectron in the intermediate states by a centrifugal barrier. The resonance can be viewed as a broad enhancement in the ionization cross section where the photoelectron is resonantly scattered. As illustrated in Fig. 1, one can infer that the shape resonance positions should be sensitive to the intramolecular distances [1].

Köppe *et al*. [2] showed that the C $1s^{-1}\sigma^*$ shape resonance in CO that appears at the photon energy $h\nu \approx 305$ eV in the photoabsorption spectrum is not only present in the C $1s^{-1}$ single-hole ionization (SHI) partial cross sections for the individual vibrational components v', but also that the energies of the shape resonances decrease with increasing vibrational quantum number, i.e., from ~307 eV for $v' = 0$ to ~302 eV for $v' = 2$.

In this work carried out on the C branch of the soft X-ray photochemistry beamline **BL27SU**, the CO O 1*s* photoelectron spectra were recorded at photon energies across the σ* shape resonance region [3]. The O $1s^{-1}$ SHI cross sections for the vibrational components $v' = 0$, 1 and 2 are shown together with the C $1s^{-1}$ SHI cross sections from Köppe *et al*. [2] in Fig. 2. It is clear that the O $1s^{-1}\sigma^*$ shape resonance energies increase with increase in v', i.e., opposite to the C $1s^{-1}\sigma^*$ shape resonance. The corresponding displacements of the nuclear separation from the equilibrium distance R_e of the ionic states were determined to be + 0.025, + 0.068 and + 0.111 Å for C 1*s* and - 0.020, - 0.074 and - 0.109 Å for O 1*s* for

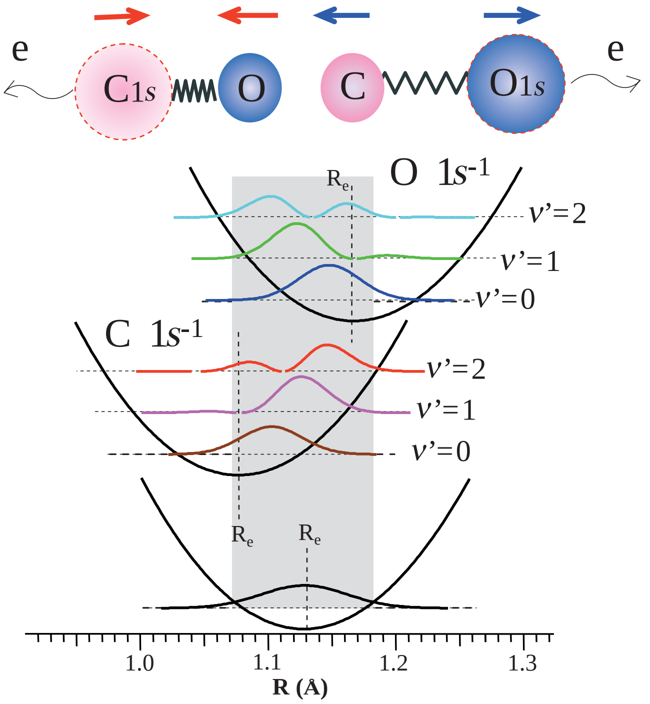

Fig. 1. Schematic diagram of nuclear motion upon photoionization-induced vibrational excitation showing potential curves for the ground and core-ionized C $1s^{-1}$ and O $1s^{-1}$ in CO, respectively. R_e is the equilibrium internuclear distances: R_e = 1.128 Å, 1.167 Å and 1.079 Å for the ground and core-ionized C $1s^{-1}$ and O $1s^{-1}$ states, respectively.

v' = 0, 1 and 2, respectively. This indicates that the photoelectron is trapped by a compressed ion and the compression increases with increasing *v*' for O 1*s* in contrast with an elongation that increases with n' in the case of C 1*s* [3] (see Fig. 1).

This work on CO has been extended to other molecules (H_2CO [4], CO_2, N_2O, C_2H_2, C_2H_4 and C_2H_6), which offers an interesting systematic study of these effects. The g-u symmetry-resolved C 1*s* σ_g and $1\sigma_u$ SHI partial cross sections of C_2H_2 are shown in Fig. 3 for *v*' = 0, 1 and 2 vibrational components. The shape resonance appears only in the C 1*s* σ_g photoionization and can be assigned to σ_g^*. The energy of the C 1*s* σ_g^{-1} σ_u^* shape resonance decreases with the increase in the vibrational quantum number ν', i.e., in a way similar to the result of CO C 1*s*$^{-1}\sigma^*$ shape resonance discussed above. This is the first observation of the vibrational effects on shape resonance energy in the g-u symmetry-resolved SHI cross sections [5].

The analysis of the results for the other molecules is still in progress.

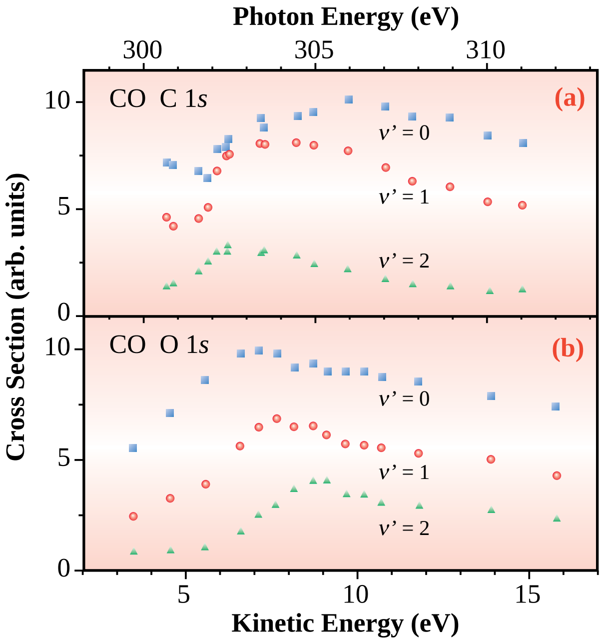

Fig. 2. SHI cross sections for vibrational components *v*' = 0, 1 and 2 for **(a)** C 1*s*$^{-1}\sigma^*$ from Köppe *et al.* [2] and, **(b)** current results for O 1*s*$^{-1}$ $1\sigma^*$. The photon energy scale above the top panel applies only to the CO C 1*s* data, whereas the kinetic energy scale applies to both panels.

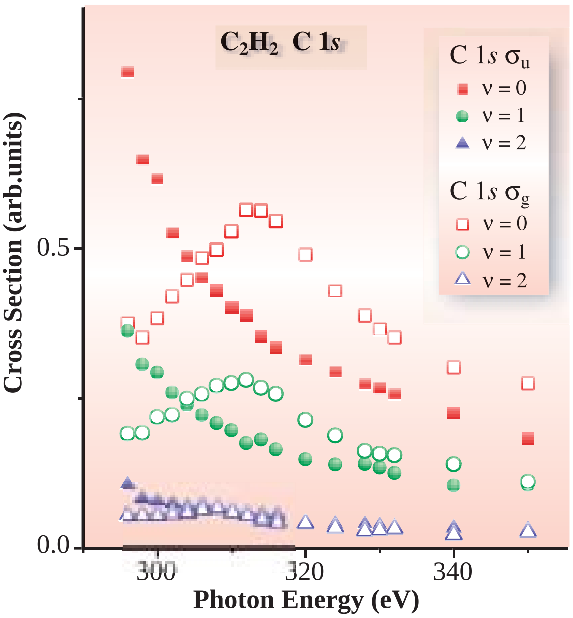

Fig. 3. g-u symmetry-resolved C 1*s* σ_g and $1\sigma_u$ SHI partial cross sections of C_2H_2 for ν' = 0, 1 and 2 vibrational components.

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