Symmetry-dependent Vibrational Excitation in Core-level Photoionization of Small Molecules: Experiment and Theory

Electronically excited states often have individual stable geometries that are different from the ground state. Photoexcitation causes a sudden redistribution of electric charges. Nuclei cannot adapt to this on the same time scale and are considered stationary during electronic transition. As a consequence, the final state is often left vibrationally excited. One can obtain information on the stable geometry of the electronically excited state by analyzing the distribution of the population of vibrational components on the basis of the Franck-Condon (FC) principle [1].

A high photon flux at very narrow photon bandwidths available using high-resolution soft X-ray monochromators installed at high-brilliance third generation synchrotron radiation light sources has stimulated renewed interest in core-level photoelectron spectroscopy [2,3]: one can observe vibrational structures in the core-level photoelectron mainline spectra of various molecules and thereby discuss the stable geometries of core-hole states [3,4]. In the present work, we demonstrate that one can observe vibrational structures even in the core-level photoelectron satellite spectra and thereby can discuss potential energy surfaces of the shake-up satellite states based on the FC principle [5,6].

Photoelectron satellites are classified into two groups, direct shake-up and conjugate shake-up. The conjugate shake-up contribution is significant near the ionization threshold and decreases rapidly with increasing energy. At high energies, the direct shake-up contribution becomes dominant and the asymmetry parameter approaches two. Thus, recording photoelectron satellite spectrum as a function of photon energy, in the direction both parallel and perpendicular to the polarization axis, one can separate the direct and conjugate shake-up contributions and therefore the symmetries of the shake-up satellite states.

Symmetry-resolved C $1s$ photoelectron satellite spectra of CO were obtained by angle-resolved photoelectron spectroscopy carried out on the c-branch of the soft X-ray photochemistry beamline **BL27SU**. The results are compared in Fig. 1 with those of *ab initio* calculations employing symmetry-adapted cluster-expansion configuration-interaction (SAC-CI) general-R methods, where vibrational

intensity ratios were determined by FC factors [5]. Very reasonable agreements of the vibrational distributions between the experimental and theoretical spectra confirm not only the assignments of these satellite states to $2\sigma^{-1}1\pi^{-1}2\pi^* {}^2\Sigma^+$ dominated by the direct shake-up and $2\sigma^{-1}5\sigma^{-1}2\pi^* {}^2\Pi$ attributed to the conjugate shake-up, but also the validity of the present *ab initio* potential curves of these shake-up satellite states. The activation of the high vibrational states in the ${}^2\Sigma^+$ band is due to the large relaxation with
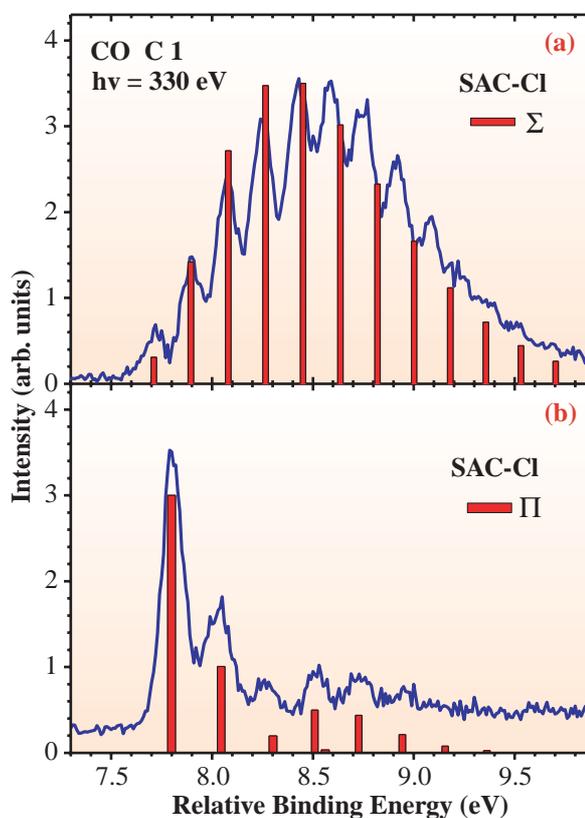

Fig. 1. C 1s satellite bands of CO for transitions to $2\sigma^{-1}1\pi^{-1}2\pi^* {}^2\Sigma^+$ **(a)** and $2\sigma^{-1}5\sigma^{-1}2\pi^* {}^2\Pi$ **(b)**: comparison between experimental (blue solid line) and theoretical (red vertical bars) results. The binding energy scale is relative to the C 1s binding energy.

elongation of the bond length by 0.17 Å relative to the neutral ground state. The spectra for both $^2\Pi$ bands have a maximum intensity at v = 0 as a result of the small relaxation with bond elongation of less than 0.1 Å.

The work has been extended to N_2 [6]. Compared with CO, N_2 has an additional complication: each of its mainline and satellite states splits into closely-separated gerade (g) and ungerade (u) states. FC analysis of the g and u individual mainlines, whose separation is ~100 meV, indicates that bond length shrinks by 0.018 and 0.023 Å for the g and u core-hole states, respectively. SAC-CI calculations for the potential energy curves successfully confirmed the observed difference in stable geometry between the g and u core-hole states. The g-u separations for the satellite states estimated by the SAC-CI calculations are ~40 meV, much smaller than the lifetime width of ~120 meV, and thus cannot be resolved experimentally. As shown in Fig. 2, SAC-CI satellite spectra agree well with experimental ones, confirming the assignments to $1\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1$ $^2\Sigma_g^+$, $1\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1$ $^2\Sigma_u^+$, $1\sigma_u^{-1}3\sigma_g^{-1}1\pi_g^1$ $^2\Pi_u$, and $1\sigma_g^{-1}3\sigma_g^{-1}1\pi_g^1$ $^2\Pi_g$. SAC-CI calculations predict large elongation of the bond length by 0.164 Å for the $^2\Sigma_{g,u}^+$ states and 0.062-0.091 Å for the $^2\Pi_{g,u}$ states. This explains that the high vibrational states are activated in the $^2\Sigma_{g,u}^+$ band and that the vibrational states are less excited in the $^2\Pi_{g,u}$ band.
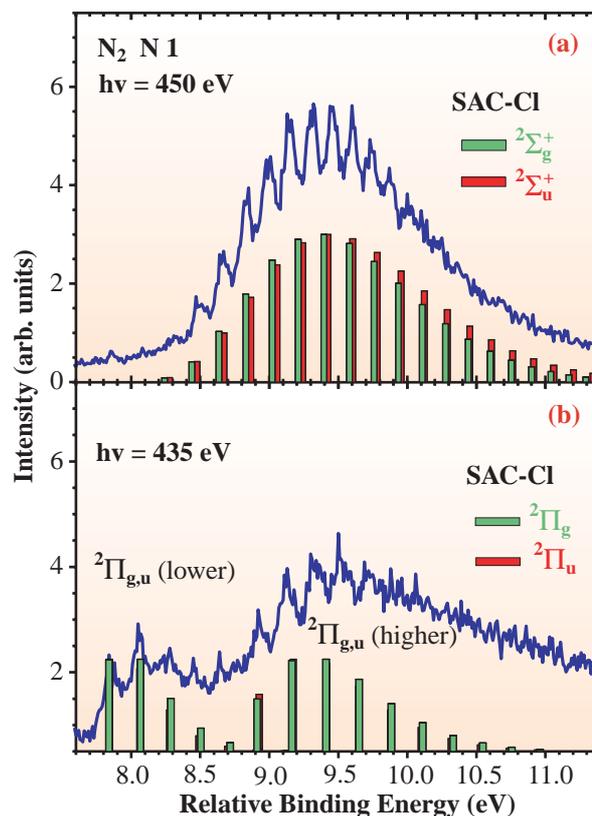

Fig. 2. N 1s satellite bands of N_2 for the transitions to $1\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1$ $^2\Sigma_g^+$ and $1\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1$ $^2\Sigma_u^+$ **(a)** and $1\sigma_u^{-1}3\sigma_g^{-1}1\pi_g^1$ $^2\Pi_u$ and $1\sigma_g^{-1}3\sigma_g^{-1}1\pi_g^1$ $^2\Pi_g$ **(b)**: comparison between experimental (blue solid line) and theoretical (green and red vertical bars for g and u, respectively) results. The binding energy scale is relative to the N 1s 1σ_g binding energy.

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