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Effects of molecular potential and geometry on atomic core-level photoemission over an extended energy range – the case study of CO molecule

E. Kukk^{1*}, D. Ayuso², T.D. Thomas³, P. Decleva⁴, M. Patanen⁵, L. Argenti², E. Plésiat², A. Palacios², K. Kooser¹, O. Travnikova⁵, S. Mondal⁶, M. Kimura⁶, K. Sakai⁶, C. Miron⁵, F. Martín^{3,7}, and K. Ueda^{6§}

¹ Department of Physics and Astronomy, University of Turku, 20014 Turku, Finland

² Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, Cantoblanco 28049 Madrid, Spain

³ Department of Chemistry, Oregon State University, Corvallis, Oregon 97330, USA

⁴ Dipartimento di Scienze Chimiche, Università di Trieste, 34127, and CNR-IOM, Trieste, Italy

⁵ Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France

⁶ Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

⁷ Instituto Madrileño de Estudios Avanzados en Nanociencia, Cantoblanco, 28049 Madrid, Spain

Synopsis We report an experimental and theoretical study of single-molecule inner-shell photoemission over an extended range of photon energies. The vibrational ratios $v=1/v=0$ from the C 1s photoelectron spectra, although mostly determined by the bond length change, are shown to be affected also by photoelectron recoil and scattering on the neighboring oxygen atom. Density functional theory is used to encompass all these effect in unified treatment. It is also demonstrated that the DFT calculations can be used as a means to extract dynamic and static molecular geometry values.

Diatomic molecules in the gas phase have long been of fundamental scientific interest as the simplest quantum mechanical systems combining fast (electronic) and slow (nuclear) dynamics. In this study, we present an analysis of inner-shell photoemission spectra of carbon monoxide, covering an extended photon energy range. The focus is on the ratio of vibrational intensities (the 'v-ratio') in the C 1s photoemission, $v=1/v=0$, as obtained from the experiment and by static-exchange density functional theory (DFT) [1].

The v-ratios are primarily determined by a dynamic structural parameter – the change ΔR of the internuclear equilibrium distance R_0 – and are calculated by means of the Franck-Condon factors. But there are several effects modifying these v-ratios even far above the ionization threshold: in the case of CO, both photoelectron recoil [2] and intramolecular photoelectron scattering must be taken into account for accurate description of the v-ratios and of their dependence on the photoelectron momentum. The former effect induces an increase in the v-ratios as the electron momentum increases and the latter causes an oscillatory behavior with a period approximately inversely proportional to the internuclear distance R_0 .

The v-ratios were determined from a combined experimental dataset based on several experiments at the SPring-8 (beamline BL27SU [3]) and SOLEIL (beamline PLEIADES [4])

*E-mail: edwin.kukk@utu.fi

§E-mail: ueda@tagen.tohoku.ac.jp

synchrotron radiation facilities. The theoretical DFT results include the conventional Franck-Condon excitations, photoelectron recoil and intramolecular scattering on the neighboring oxygen atom.

First, we have demonstrated by a set of theoretical v-ratio curves (as a function of the electron's momentum k), that the v-ratios are potentially a very sensitive means of determining both the static (R_0) and dynamic (ΔR) geometrical parameters simultaneously. Second, the full static exchange DFT calculation have been used as a tool to determine the structural parameters of the molecule, by performing a least-squares fit of the theoretical curve to experimental v-ratio data points. The parameters optimized in this case were R_0 and ΔR . From the fit, we extracted the values $R_0=2.071$ a.u. and $\Delta R=-0.0944$ a.u., and demonstrated the feasibility of using the static exchange DFT calculations for geometry determination in molecules. The special feature of the approach described here is its ability to determine the static and dynamic geometry values simultaneously, which is a pre-requisite for accurate determination of the Franck-Condon factors and ΔR derived from these.

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