

Photon energy dependence of the vibrational fine structure in the C1s line of c(2x2)CO/Ni(100) in the threshold region

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Core-level ionization in molecules leads to an electronic redistribution which modifies the molecular potentials, thus leading to vibrational excitation [1]. The vibrational progressions found in free molecules exhibit a strong photon energy dependence. At the shape resonance this energy dependence is due to the temporary trapping of the photoelectron in the effective molecular potential. The shape resonance is known to be sensitive to both the overall bond length and also to detailed modifications of the molecular potential [2,3]. The photon energy dependence of the vibrational progression in the photoelectron C1s line has been studied in the free CO molecules where strong variations are observed [4]. For the study of adsorbates the occurrence of the shape resonance has been a valuable tool to determine i.e. molecular order and orientation in x-ray absorption spectroscopy [3]. Recently we have resolved vibrational fine structure in the C1s and O1s core level lines on CO chemisorbed on Ni(100) with x-ray photoemission (XP) spectroscopy. This opens up the possibility to study the photon energy dependence of the vibrational progression on a chemisorbed molecule.

The XP measurements were performed at the Advanced Light Source, Lawrence Berkeley National Laboratory, by combining highly monochromatic soft x-rays from beamline 8.0 with a Scienta SES 200 electron analyzer [5]. The overall resolution $\frac{\lambda}{\Delta\lambda}$ was approx. 12000 between 300 eV and 450 eV photon energy. All spectra were recorded at 80 K in normal emission in such a way that the electric field vector of the synchrotron radiation was normal to the crystal surface. We prepared the CO/Ni(100) phase as described elsewhere [6]. CO adsorbes on Ni(100) in a c(2x2) superstructure, where the molecule occupies in an upright position top sites with the carbon end down [7,8]. A XPS spectrum of the clean Ni(100) surface was measured for each excitation energy and subtracted from the adsorbate covered one. For the least squares fits we employed Doniach-Sunjic line profiles [9] convoluted with Gaussian functions. For each vibrational progression the same line profile was used for all components.

In Figure 1 we show the vibrationally resolved C1s line of c(2x2)CO/Ni(100) as a function of photon energy. We clearly observe different vibrational progressions for different photon energies. The higher vibrational components are enhanced between 310 eV and 320 eV photon energy, slightly above the known shape resonance position. At photon energies just above threshold (i.e. 299.2 eV) the higher vibrational components are very weak and the C1s line is dominated completely by the adiabatic transition.

We have quantified this description with a numerical fit. The vibrational progression is summarized in Table I and is found to follow to be evenly spaced. In Figure 2 the relative intensities $\nu_i / \sum \nu_i$ of each vibrational component ν_i and the branching ratio $\frac{\nu_i}{\nu_0}$ is shown as a function of photon energy.

The observed behaviour is not explainable within the Franck-Condon picture [10], where

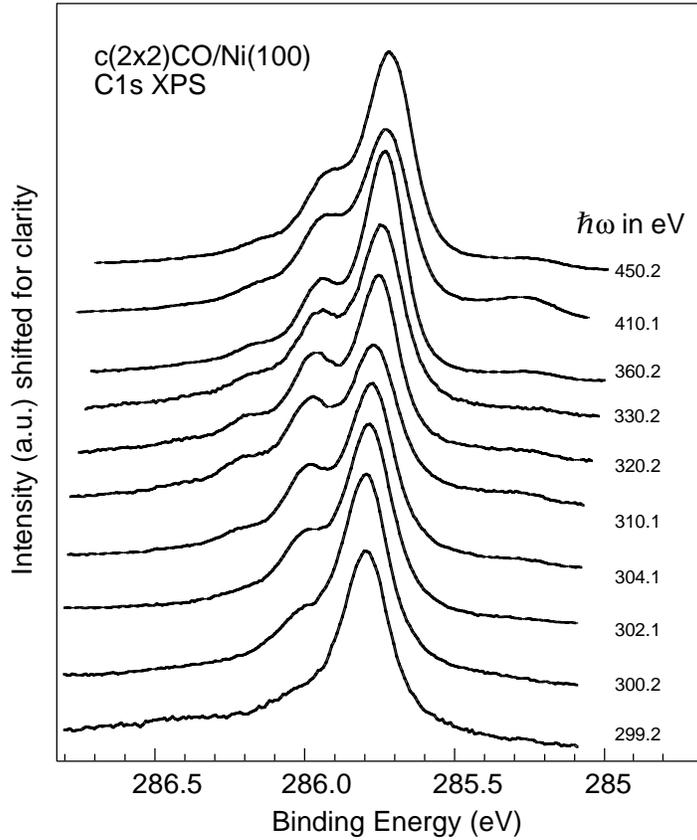


FIG. 1. Vibrational fine structure in the C1s line of $c(2 \times 2)\text{CO}/\text{Ni}(100)$ as a function of photon energy. Normal emission geometry.

the electronic transition moments are independent of the nuclear coordinates. We observe modifications of the Franck-Condon intensities with photon energy at the shape resonance. The shape resonance is known to depend on the nuclear coordinates [3]. So does the electronic wave-function of the system. If the Franck-Condon approximation does not hold, depend the electronic transition elements on the nuclear coordinates. Since different vibrational final states sample different internuclear geometries in the real space, will each vibrational state be associated with a different electronic transition element, leading to a modification of the Franck-Condon intensities. As a matter of fact is the excited and trapped electron part of the electronic wave function describing the molecular potentials. Changing

TABLE I. Vibrational Progression: Splitting between adiabatic transition and vibrationally higher excited states.

Vibrational transition $\nu \rightarrow \nu'$	Splitting to adiabatic peak (meV)
0 \rightarrow 1	217.7 \pm 2.2
0 \rightarrow 2	440.3 \pm 3.1
0 \rightarrow 2	655.1 \pm 8.9

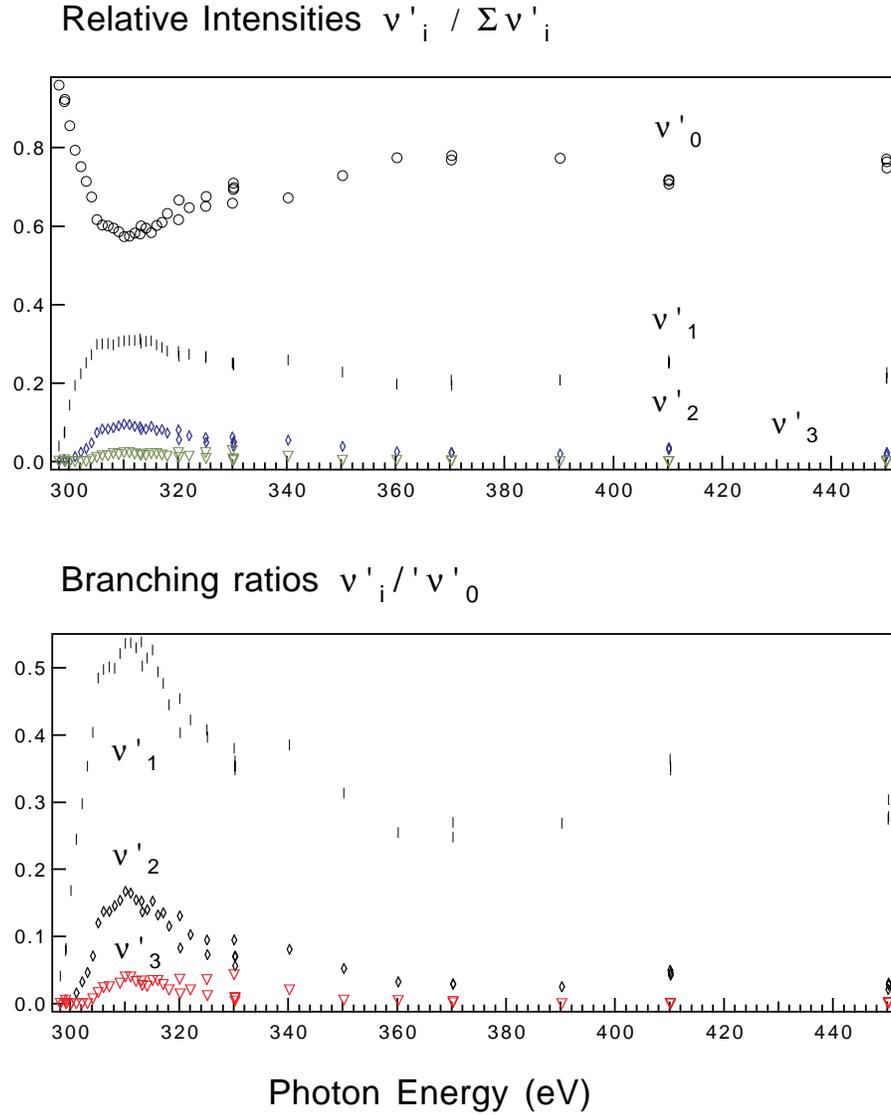


FIG. 2. Relative Intensities and Branching ratio of the vibrational components in the C1s lines of $c(2 \times 2)\text{CO}/\text{Ni}(100)$ as a function of photon energy, from Fig. 1.

the photon energy alters the excitation and trapping process. Consequently are the molecular potentials influenced by the photon energy and a photon energy dependence of the vibrational progression is found around an electronic resonance.

Viewing the shape resonance as a temporary trapping of the photoelectron implies, that the width of the shape-resonance is related to the trapping time according to the Heisenberg principle of uncertainty. We see from Figure 2 that the shape-resonance spans at least 5 eV to 6 eV associated with a trapping time shorter than 0.1 fs. The time-scale of trapping is rather short in comparison to the nuclear motion. This indicates that the observed vibrational fine structure is mostly due to vertical transitions, where the nuclear coordinates are unchanged on the time-scale of the photoemission process. The energy dependent modifications in the vibrational progression are within this reasoning due to the dependence of the electronic transition element on nuclear coordinates, as discussed above. However, the idea

of vertical transitions is based on the validity of the Born-Oppenheimer approximation. It is not certain, as a matter of fact, that this approximation is still valid in our case.

So far discussed effects were concerned with the molecular nature of CO adsorbed on Ni(100). In the case of adsorbed molecules one also has to consider substrate-dependent contributions. It has been established previously, that charge transfer screening plays an important role in photoemission on adsorbates. On a qualitative level it is clear that the extend of charge transfer should depend on the distance between the CO molecule and the substrate. This CO-substrate distance is then again related to the intermolecular distance. Consequently could the selection of different vibrational final states with different internuclear distances also modify the screening probability through charge transfer from the metallic substrate. An other substrate-dependent contribution could be effects related to the spatial order of the adsorbate system. Photo-electron diffraction in the back-scattering regime are energy dependent phenomena and can also be seen as a temporary trapping of the out-going photoelectron. Some deviations between the behaviour in the free molecule and the adsorbed molecule could be ascribed to this additional process.

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