Shape-Resonance-Enhanced Vibrational Effects in the Angular Distributions of C 1*s* Photoelectrons from Fixed-in-Space CO Molecules

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Angular distributions of C 1*s* photoelectrons from fixed-in-space CO molecules have been measured with vibrational resolution. A strong dependence of the angular distributions on the vibrational states of the residual molecular ion has been found for the first time in the region of the shape resonance. Calculations in the relaxed core Hartree-Fock approximation have reproduced the angular distributions fairly well in the general shapes of the angular distributions due to the correct description of nuclear motion as an average of the internuclear-distance-dependent dipole amplitudes.

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Vibrationally resolved photoelectron spectra are essential ingredients for probing the photoionization dynamics of molecules (see Refs. [1–4], and references therein). Recent improvements of synchrotron radiation sources and experimental techniques have enabled measurements of the partial photoionization cross sections and angular distributions of photoelectrons for several vibrational levels over the wide energy range from valence to core shells. Vibrationally resolved photoelectron spectroscopy is especially powerful for the investigation of molecular shape resonances, because photoelectron peaks for different vibrational final states preferentially sample different internuclear distance on photoionization [4]. The first investigation of a molecular shape resonance by vibrationally resolved photoelectron spectroscopy was carried out by Stockbauer *et al.* in 1979 [5]. They observed non-Franck-Condon vibrational intensity distributions in the 5σ photoionization of the CO molecule. Dehmer *et al.* [6] demonstrated theoretically using the example of $3\sigma_g$ photoionization of N_2 molecules that the position and width of the σ shape resonance strongly depends on the internuclear distance. This explained the striking breakdown of the Franck-Condon approximation observed in [5] by the influence of the nuclear motion on the photoionization process, especially in the vicinity of the shape resonance. After these pioneering works, studies of molecular shape resonances in the valence shells have been further extended [3,7]. Since in valence photoionization many autoionizing states overlap with the shape resonance, it is, however, more favorable to study core-level photoionization, which is free from this complexity except for some double excitations. Recently, vibrational effects in the shape resonance region of the C 1*s* photoionization of CO molecules have been experimentally demonstrated [8–10]. Figure 1 shows the vibrationally resolved C $1s^{-1}$ partial cross sections of Ref. [9], together with the present calculations (see below for details). The maxima of the resonance peaks for different vibrational final states shown in Fig. 1 move substantially to lower energies with increasing vibrational quantum number v_f of the ionized state. The purpose of the present work is to obtain more direct information on the influence of the vibrational motion on the photoionization process and to account for it.

In this Letter, we present vibrationally resolved molecular-frame C 1*s* photoelectron angular distributions (MF-PAD) for the CO molecule which have been measured by an angle-resolved photoion-photoelectron coincidence technique [11]. Also presented are theoretical

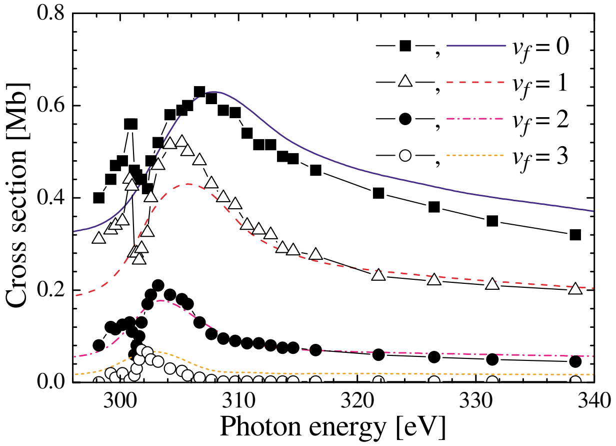

FIG. 1 (color online). The C $1s^{-1}$ partial photoionization cross sections of the CO molecule for different final vibrational states. The present theoretical results (curves) and the experimental data of Köppe *et al.* [9] (points) are shown. All theoretical curves are shifted by 2 eV to lower energies to adjust the peak positions of the shape resonance in the calculation to those of the experiment.

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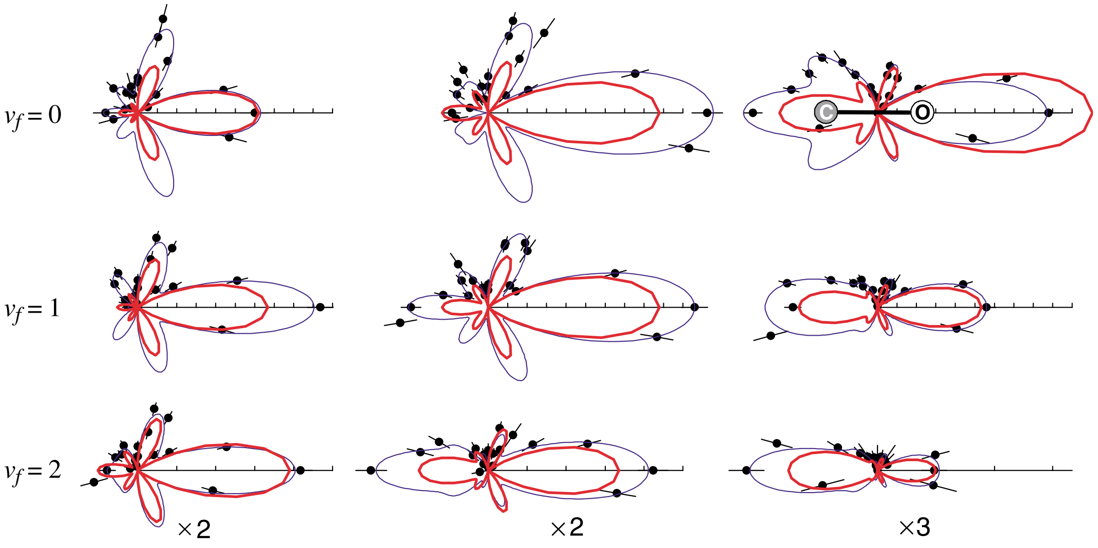
calculations in the relaxed core Hartree-Fock approximation.

The experiment was performed on the soft x-ray undulator beam line BL-2C [12] at the Photon Factory 2.5 GeV storage ring. The description of the experimental apparatus and the procedure has been reported elsewhere in detail [13]. Only the essential improvements are mentioned here. The three-cylinder zoom lens of the parallel-plate electron energy analyzer, placed in the dipole plane, was replaced with an afocal zoom lens of five cylindrical elements [14]. Furthermore, the exit slit of the electron analyzer was removed, and a two-dimensional position sensitive detector [15] was incorporated. Using this improved apparatus and a new data processing system [16], we can record the whole vibrationally resolved C $1s^{-1}$ main band at once. We can also record the time correlation between photoelectron and fragment ion signals for C^+ and O^+. The fragment ions were detected with two parallel-plate ion energy analyzers placed in the parallel and perpendicular directions to the electric vector of the incoming light. The photoelectron spectrum in true coincidence with the fragment ions was then obtained by subtracting the spectrum including only the accidental coincidences from the spectrum including both the true and accidental coincidences. To evaluate the coincidence intensities of the vibrational peaks in the C $1s^{-1}$ main band, we have used an analytical post-collision-interaction line profile [17], which has been convoluted by a Gaussian function to account for experimental broadenings. All the true coincidence spectra measured at every angle have been analyzed using a least squares fitting routine.

The vibrationally resolved MF-PAD's have been scaled to their absolute values in Mb · sr^{-1} as follows. First we have assumed that the vibrational branching ratios in the C $1s \rightarrow \varepsilon\ell\sigma$ channels are equal to those in the C $1s \rightarrow \varepsilon\ell\pi$ channels. Based on this assumption, we have evaluated the vibrationally resolved partial cross sections for the C $1s \rightarrow \varepsilon\ell\sigma$ transitions using the symmetry-unresolved and vibrationally resolved partial photoionization cross sections of Köppe *et al.* [9,10] and the symmetry-resolved photoion yields of Shigemasa *et al.* [18]. Finally, the vibrationally resolved MF-PAD was integrated over the whole solid angle, and the integrated value was normalized to the vibrationally resolved partial cross sections for C$1s \rightarrow \varepsilon\ell\sigma$. In the present work, we focus our discussion on the MF-PAD for the parallel transitions, because the σ shape resonance appears in these transitions.

Figure 2 shows typical experimental results (on an absolute scale) of the vibrationally resolved MF-PAD's for C $1s$ photoionization of CO molecules together with the theoretical results described below. One can see a drastic variation of the MF-PAD with the vibrational quantum number v_f at each photon energy. Because the photoelectron kinetic energies for the different vibrational final states differ by the vibrational energy of ~0.3 eV, it may be possible to suppose that the variation of the MF-PAD with v_f appears due to the kinetic energy variation for different v_f. To rule out this supposition, we have measured the MF-PAD's at $h\nu = 306.1$ eV and $h\nu = 306.4$ eV, and we have not found any detectable difference between the MF-PAD's for the same v_f. So, the variation of MF-PAD with v_f is unquestionably due to



(a) h = 303.2 eV (b) h = 305.1 eV (c) h = 310.1 eV

FIG. 2 (color online). Polar plots of molecule-frame C $1s$ photoelectron angular distributions of the CO molecule for different vibrational final states at (a) 303.2 eV, (b) 305.1 eV, and (c) 310.1 eV. The light polarization is parallel to the molecular axis. Experimental data (full circles with error bars), fitting results (thin curves), and RCHF results (bold curves) are shown. One scale division represents 0.05 [Mb · sr^{-1}].

vibrational effects. It should be noted that the sum of all the vibrationally resolved MF-PAD's is in good agreement with the earlier vibrationally unresolved experimental data [13,19].

To understand the vibrational effects in the MF-PAD's in the shape resonance region, we have performed calculations using the relaxed core Hartree-Fock (RCHF) approximation as described in Ref. [20]. In this approximation, the initial state wave functions are taken from the self-consistent HF ground state of a neutral molecule. Then, the self-consistent HF molecular ion wave functions are calculated as a core-hole state, and the photoelectron wave functions are calculated in the frozen field of the molecular ion state. The role of many-electron correlations in the CO molecule, contrary to the N_2 molecule [20], is rather small due to the large energy separation of the C K-shell from all other shells of the molecule. Therefore we have restricted our calculations by the RCHF approximation. The MF-PAD's have been calculated by the method described in detail in Refs. [13,21]. Usually the wave functions and the dipole matrix elements are calculated at a fixed equilibrium internuclear distance R_e, however. To take into account the vibrational motion in an adiabatic approximation we have followed the procedure proposed in Ref. [6]. First, the RCHF calculations described above were performed at nine fixed internuclear distances. Then the dipole matrix elements corresponding to a definite transition between a given initial v_i and final v_f vibrational states were calculated as an average of the R-dependent dipole amplitudes $d(\omega, R)$ with ω being the photon energy, weighted by the product of the initial and final vibrational state wave functions, $\chi_{v_i}(R)$ and $\chi_{v_f}(R)$, at each R,

$$d_{v_i v_f}(\omega) = \int_0^\infty \chi_{v_f}(R) d(\omega, R) \chi_{v_i}(R)\, dR. \qquad (1)$$

Here we take $v_i = 0$, because $v_i = 1$ has only a very low population at room temperature. The vibrational wave functions were approximated by harmonic-oscillator functions. We used $R_e = 1.128$ Å and a vibrational energy of 269 meV [22] for the ground state, and $R_e = 1.080$ Å and a vibrational energy of 302 meV from Köppe *et al.* [9] for the core-hole state. We have approximated the integration over R in Eq. (1) by summation over nine points. As demonstrated in Fig. 1, the theoretical results show a good agreement with the corresponding experimental data by Köppe *et al.* [9]. The theoretical results for the MF-PAD's are shown in Fig. 2. The calculated MF-PAD's reproduce the experimental ones fairly well both in overall shape and in the absolute scale. This good agreement between theory and experiment implies that the adiabatic approximation is valid. The main contribution to the cross section in the region of the σ shape resonance is given by the $f\sigma$ partial wave. The next largest contribution to the cross section, that of $d\sigma$-partial wave, is about 3–4 times smaller than that of $f\sigma$ partial wave. The $p\sigma$ and $s\sigma$ partial wave contributions are smaller by an order of magnitude.

It is better to study the variation of MF-PAD's with photon energy for a given vibrational final state, because the MF-PAD's are related to the position and width of the σ shape resonance for each vibrational final state. The peak position of the resonance for the $v_f = 2$ occurs at a photon energy of 303.2 eV (see Fig. 1). Reflecting this, at 303.2 eV the MF-PAD pertaining to $v_f = 2$ shows the characteristic feature of the $f\sigma$ orbital, which is deformed by a strong forward-backward asymmetry due to the interference among partial waves. This characteristic feature disappears in the MF-PAD pertaining to $v_f = 2$ at 310.1 eV corresponding to the higher energy tail of the resonance for $v_f = 2$. The resonance peak for $v_f = 1$ occurs at a photon energy of 305.1 eV (see Fig. 1). At 305.1 eV the MF-PAD pertaining to $v_f = 1$ indicates the characteristic feature of the$f\sigma$ orbital. At 303.2 eV, only 2 eV lower than the resonance peak, the MF-PAD still indicates the $f\sigma$-orbital character. However, it is hard to see the characteristic feature of the $f\sigma$ orbital in the MF-PAD pertaining to $v_f = 1$ at 310.1 eV corresponding to the higher energy tail of the resonance. The broad shape resonance for $v_f = 0$ occurs around 307 eV (see Fig. 1). The experimentally examined photon energies are located in the peak region of the shape resonance, therefore at all three energies, 303.2, 305.1, and 310.1 eV, the characteristic feature of the $f\sigma$ orbital is seen in the MF-PAD's pertaining to $v_f = 0$. A quantitative discussion, involving experimentally determined dipole matrix elements, of the shape resonance for the different vibrational final states will be reported in a forthcoming paper [23].

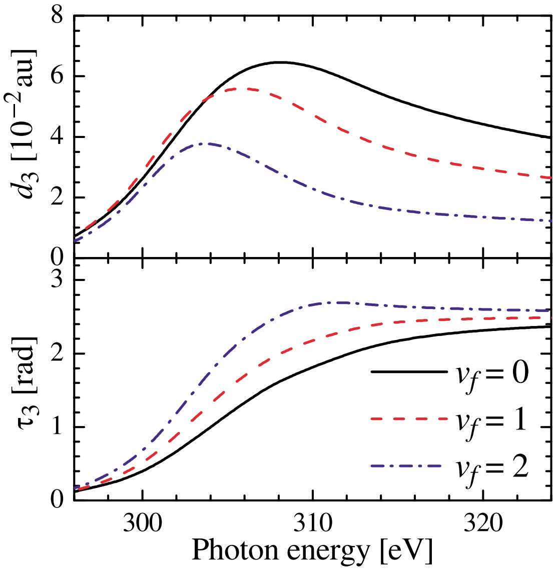


FIG. 3 (color online). Dipole matrix elements d_3 (a) and short range phase shifts τ_3 (b) for the$f\sigma$- partial wave of C K-shell photoionization of the CO molecule for different vibrational final states, calculated within the RCHF approximation.

In order to interpret the variations in the MF-PAD's, let us consider in more detail the behavior of the theoretical dipole matrix elements and phase shifts within the present approximated calculations. Figure 3 shows the matrix element d_3 and the short-range phase shift τ_3 (without the Coulomb phase shift, see Ref. [21] for details) of the $f\sigma$ partial wave as a function of photon energy for different vibrational final states. This matrix element shows a typical resonant behavior, that is, a well-defined maximum of the matrix element is accompanied by an increase of the phase shift by about π radians within the width of the shape resonance(the next largest $d\sigma$ dipole matrix element has a similar behavior, though the phase shift τ_2 does not increase by π within the shape resonance). We can deduce that the shape-resonance-enhanced vibrational effects in the MF-PAD's for C 1s photoionization predominantly result from the different resonance-behavior of the $f\sigma$-partial wave for different v_f.

Dehmer *et al.* have shown in fixed-R calculations for the $3\sigma_g$-shell ionization of N_2 that the peak of the shape resonance shifts to lower energies with increasing of R [6]. In the present case of the CO molecule, the peak of the calculated shape resonances shifts to lower energies by about 2 eV with the increase of the vibrational quantum number v_f by 1, in agreement with the experimental results (see Fig. 1). Since $R_e = 1.128$ Å in the ground state of the CO molecule is larger than $R_e = 1.080$ Å in the C 1s ionized state, the R giving the maximum value to the product $\chi_{v_f}(R)\chi_{v_i}(R)$ becomes larger with increasing vibrational quantum number v_f. Therefore, one can deduce that the peak of the calculated shape resonance shifts to low energies with the increase of R, which is consistent with the results of the R-fixed calculations by Dehmer *et al.* [6].

In conclusion, we have demonstrated for the first time, both experimentally and theoretically, the existence of a strong variation of the MF-PAD's with the vibrational quantum number v_f of the C 1s ionized state of the CO molecule in the region of the σ shape resonance. This variation is induced by the influence of the vibrational motion on the photoionization process. Namely, for different final vibrational states, different internuclear distances give the main contribution to the photoionization process. This phenomenon is quite general and must exist in other molecules. The study of this effect will shed new light on the shape resonance dynamics of molecules.

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