

Site-resolved recoil-induced asymmetry of nondipole molecular-frame photoelectron angular distributions in inner-shell photoionization of CO by 20 keV photons

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Angular distributions of *K*-shell photoelectrons from CO molecules ionized by 20 keV photons are studied experimentally and theoretically in the molecular frame of reference. At this high photon energy, nondipole contributions to the light-matter interaction induce a strong forward-directed emission of the photoelectrons, which is only slightly modulated by scattering from the molecular potential. In addition, we observe a recently predicted asymmetry in the photoelectron emission distributions with respect to the polarization direction [Phys. Rev. Lett. **123**, 243201 (2019)], which is caused by a rotational recoil of the nuclei imposed by the fast photoelectrons and high-energy photons. By addressing the C and O atoms separately in CO, we are able to resolve the molecular site that experiences this rotational kick, which was not possible in the previous study of N₂ molecules. Our experimental results are explained by *ab initio* electronic structure calculations augmented by a semiclassical modeling of the rotational-recoil effect.

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I. INTRODUCTION

Nowadays, modern synchrotron radiation facilities enable state-of-the-art investigation of light-matter interactions in the hard x-ray domain [1], even well beyond photon energies of 100 keV [2]. In addition, x-ray free-electron lasers that are currently in operation access photon energies of up to about 25 keV [3]. A number of fundamental phenomena emerge when such short-wavelength radiation interacts with atoms and molecules. First and foremost, the commonly applied electric-dipole approximation, which neglects the spatial dependence of the electromagnetic-radiation plane wave by approximating $e^{i\mathbf{k}_\gamma \cdot \mathbf{r}}$ by unity (where $\mathbf{k}_\gamma$ is the photon linear momentum), breaks down. This approximation thus starts to be inaccurate as soon as the wavelength of the ionizing radiation becomes comparable to the spatial extent of the orbital under consideration. As a consequence, higher-order terms in the expansion of the plane wave (known as the nondipole contributions) become significant and alter the dipolar photoelectron

angular emission distributions [4,5]. In particular, these nondipole contributions cause a notable forward-backward asymmetry in the photoemission, with typically more high-energy photoelectrons being emitted along the light propagation direction (i.e., along $\mathbf{k}_\gamma$) [6–8].

Similarly important, when a very fast photoelectron is emitted, it naturally imparts recoil momentum to the nuclei [9], causing, for example in molecules, significant rotational [10–13] and vibrational [12–16] excitations, even up to selective bond breaking [17]. For photon energies of a few tens of keV, even the transfer of the photon momentum $\mathbf{k}_\gamma$ to the nuclei becomes notable [18]. Both the nondipole and recoil effects increase with the photon energy, and their synergy may lead to nontrivial consequences. As demonstrated in our recent study of N₂ photoionization with 40 keV photons [19], the nondipole-induced forward-backward asymmetry of the molecular-frame photoelectron angular distributions can be modified by a substantial recoil effect, resulting in an additional asymmetry with respect to the light polarization axis. The extended calculations suggest that the rotational recoil induced by the fast photoelectron and high-energy photons leads to a breakdown of the axial-recoil approximation [20]. As a consequence, the recoil-induced molecular rotations deplete the observation of breakup directions perpendicular to the recoil momentum, thereby enhancing photoemission along the forward-pointing nitrogen atom [19].

In the aforementioned study of the homonuclear N₂ molecule, the atomic site that receives the recoil is unknown.

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As a consequence, the electron emission distributions, calculated assuming that the recoil was imparted separately to the two nitrogen atoms, were added together to model the experimental observation. These contributions are, obviously, rather different, since the recoil effect induces rotations of the molecule in two opposite directions, depending on which atomic site receives the kick. In the case of N_2 , it is also an open question whether the momentum kicks due to the ionization of the gerade or ungerade K -shell orbitals should instead be deposited coherently to the nuclei, thereby exciting a superposition of clockwise and counterclockwise rotating ensembles [21]. In the present work, we study experimentally and theoretically inner-shell photoionization of heteronuclear CO molecules by 20 keV photons in order to resolve the molecular site that experiences the recoil kick. Our experimental and theoretical approaches are outlined in Secs. II and III, respectively, while the obtained results are compared and discussed in Sec. IV. We conclude in Sec. V with a brief summary.

II. EXPERIMENT

The experiment was performed using a Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) setup [22–24] at beamline ID31 [2] of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Photons with an energy of 20 keV and a bandwidth of approximately 2% were selected from the undulator beam with the help of a pinhole monochromator [25] and intersected at right angles with a supersonic gas jet of CO molecules, expanded through a 30- μ m nozzle with a backing pressure of 9.5 bars. The vacuum pressure in the main chamber, where the photoreaction takes place, was in the range of 8×10^{-9} mbar. The full acquisition time of our dataset was approximately 100 h. The electrons and ions created in the photoreaction were guided from the reaction volume onto two time- and position-sensitive detectors with hexagonal delay-line position readout [26]. The ion arm of the spectrometer had a length of 840.4 mm, and we achieved an ion-momentum resolution of around 0.7 a.u. by incorporating an electrostatic lens for focusing [27]. The electron arm of the spectrometer had a length of 32.5 cm. The employed parallel 55 V/cm electric and 31 G magnetic fields enabled a 4π solid angle acceptance for the coincident detection of all relevant Auger electrons and the Coulomb-exploding $C^+ + O^+$ fragments. We obtained the initial momenta of all detected particles by measuring their times of flight and impact positions on the detectors.

The high-energy photoelectrons (with relativistic momenta of around 38 a.u.) cannot be detected directly, and their momenta were therefore calculated according to momentum conservation from the momenta of the other particles. The energy distribution of the measured electrons, which includes contributions from Compton and Auger processes, shows two prominent peaks at about 255 and 500 eV. These represent $C\ 1s^{-1}$ and $O\ 1s^{-1}$ Auger electrons, respectively, which allow identification of the atomic site of photoionization in our experiment. For photoionization by 20 keV photons, the ions acquire a large photoelectron recoil of about 38 a.u., while in the case of Compton ionization, the relatively small momentum of the emitted electron (here below 11 a.u. [28,29]) is

not compensated by the nuclei but originates from the photon momentum transfer. Thus, by excluding small sum momenta $\mathbf{p}_{\text{sum}} = \mathbf{p}(C^+) + \mathbf{p}(O^+)$, we separate photoionization events from those where Compton ionization occurred [7]. Under the assumption of the axial-recoil approximation [20], the relative momentum of the ions $\mathbf{p}_{\text{rel}} = \mathbf{p}(C^+) - \mathbf{p}(O^+)$ would represent the orientation of the molecular axis with respect to the light polarization direction. From the measured laboratory-frame photoelectron momentum $\mathbf{k}_e$ we obtain the relative emission angle with respect to $\mathbf{p}_{\text{rel}}$ in our offline analysis.

III. THEORY

We performed our electronic-structure calculations within the frozen-core Hartree-Fock approximation using the stationary single-center method [30–32], similarly to our previous studies of the nondipole photoelectron emission distributions in N_2 [19] and CO [33] molecules. The bound molecular orbitals of neutral CO were (i) generated at the fixed equilibrium internuclear distance of $r_e = 2.132$ a.u. [34] by the PC GAMESS (US) [35] quantum chemistry package in the triple-zeta valence basis set [36], (ii) decomposed over spherical harmonics with $\ell_b \leq 99$ and $|m_b| \leq 1$ with respect to the geometrical molecular center, and (iii) further used to generate the direct and exchange Coulomb potentials for the photoelectron. In order to properly describe such high-energy photoelectrons and transitions induced by nondipole effects, the respective single-center expansion included partial electron waves with angular momentum quantum numbers $\ell_c \leq 69$ and $|m_c| \leq 4$. The respective nondipole photoionization amplitudes were computed in the velocity gauge by explicitly including the plane wave $e^{i\mathbf{k}_\gamma \cdot \mathbf{r}}$ in the transition matrix element.

The effect of the rotational recoil induced by the fast photoelectron and high-energy photon on the computed photoelectron emission distributions was simulated with a semiclassical model developed in our previous work [19]. With the present photon energy of $\omega = 20$ keV and ionization potentials of 296.2 eV for $C\ 1s$ [37] or 542.5 eV for $O\ 1s$ [38] of the CO molecule, we obtain the following relativistic photoelectron momenta $|\mathbf{k}_e| = 38.42$ or 38.18 a.u. and the photon linear momentum $|\mathbf{k}_\gamma| = \omega/c \approx 5.36$ a.u. Being imparted perpendicularly to the molecular axis on the emitting C or O atom with masses M_C and M_O , the maximal recoil momentum of $|\mathbf{k}_\gamma - \mathbf{k}_e| = 43.78$ or 43.54 a.u. transfers to the molecule an angular momentum $L_{C/O} = \frac{M_{O/C}}{M_C + M_O} |\mathbf{k}_\gamma - \mathbf{k}_e| r_e$ of about $53\hbar$ or $40\hbar$. These maximal angular momenta correspond to maximal angular frequencies $\omega_{C/O} = \frac{|\mathbf{k}_\gamma - \mathbf{k}_e|}{r_e M_{C/O}}$ of about 0.00093 or 0.00070 a.u. (radian per atomic unit of time) and to maximal rotation angles of about 18° or 7° during the respective Auger decay lifetimes τ_A of about 8.2 or 4.2 fs (corresponding to decay rates Γ_A of about 80 or 157 meV [39]). The employed model includes a recoil-induced rotation of the molecule with a constant angular frequency $\omega_{C/O}$ before it undergoes Auger decay and starts to fragment via Coulomb explosion. Furthermore, for this particular case of maximal recoil momentum imparted perpendicularly to the molecular axis, a part of it $P_{C/O} = \frac{M_{O/C}}{M_C + M_O} |\mathbf{k}_\gamma - \mathbf{k}_e|$ with a value of about 25.0 or 18.6 a.u. is present in the experimentally measured ionic momenta $\mathbf{p}(C^+)$ and $\mathbf{p}(O^+)$, and thus in $\mathbf{p}_{\text{sum}}$ and $\mathbf{p}_{\text{rel}}$.

For the average value of the measured kinetic energy release (KER) of 13 eV, this results in a maximal error $\Delta\phi_{C/O}$ in the determination of the spatial orientation of the molecular axis via $\mathbf{p}_{\text{rel}}$ of about 13° or 10° , respectively for the C or O atom ionization cases. Of course, the true values of the estimated quantities depend on the relative orientation of the recoil momentum and the molecular axis. This can be estimated with the help of the photoelectron emission angle ϕ in the molecular frame of reference by scaling the maximal recoil momentum (and thus the estimated maximal values of $\omega_{C/O}$ and $\Delta\phi_{C/O}$) with a factor of $\sin\phi$.

Our rotational-recoil model [19] accounts for the fact that the true electron emission angle ϕ , defined relative to the molecular axis at the emission instant t , is not the angle $\tilde{\phi}$ measured with respect to the relative momentum $\mathbf{p}_{\text{rel}}$ in the experiment. Therefore, (i) the emission angle ϕ in the computed nondipolar emission distributions $W(\phi)$ needs to be corrected as $\tilde{\phi} = \phi \pm [\omega t + \Delta\phi] \sin\phi$, depending on the direction of the recoil-induced rotations, (ii) the respective contributions should be weighted by the exponential distribution $e^{-\Gamma_A t}$ of the Auger decay times, and (iii) the respective contributions are integrated over all emission angles ϕ and sufficiently large times t , which yields

$$\tilde{W}(\tilde{\phi}) = \int e^{-\Gamma_A t} dt \int W(\tilde{\phi} \mp [\omega t + \Delta\phi] \sin\phi) d\phi,$$

with the parameters Γ_A , ω , and $\Delta\phi$ discussed above for the emitting carbon or oxygen atoms.

IV. RESULTS AND DISCUSSION

We first discuss theoretical results, obtained in the electric-dipole approximation and further including the nondipole contributions, but without simulating the rotational-recoil effect (see Fig. 1). Here, the molecule is oriented in the (picture) plane spanned by the light propagation (along $\mathbf{k}_y$) and polarization (along $\boldsymbol{\varepsilon}$) directions at angles $\pm\alpha$, as sketched in the insets and indicated in the legends. Within the electric-dipole approximation (left panels), the emission distributions follow the well-known cosine-squared envelope, which is independent of the molecular orientation angle. These distributions are modified by weak molecular-field (i.e., scattering) effects, which depend on the molecular orientation angle. In particular, the computed distributions exhibit forward-scattering lobes pointing from the emitter in the direction of the scatterer [40,41], whose nucleus acts as a lens for the outgoing electron wave. As one can see, for carbon ionization (upper panels), the lobes point upward. For the ionization of oxygen they face downward (lower panels). Furthermore, the directions of their appearance coincide with the orientation of the molecular axis. Including nondipole effects (right panels) results in a strong bending of the computed distributions in the forward emission direction along $\mathbf{k}_y$. The directions of the forward-scattering lobes caused by the molecular-field effects do not change, but they are now significantly enhanced or suppressed depending on whether they point in the forward or backward emission directions [33] (cf. distributions computed for similar molecular orientation angles in the left and right panels of Fig. 1).

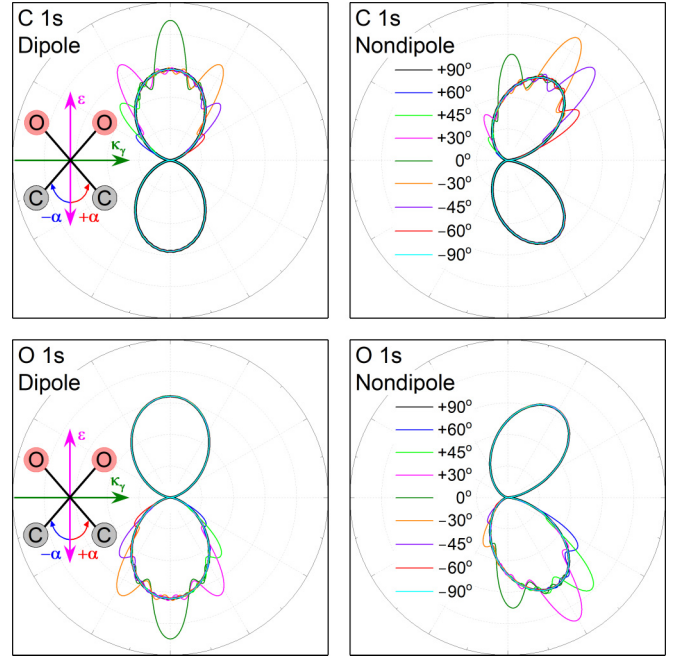


FIG. 1. Theoretical molecular-frame angular distributions of 1s photoelectrons of carbon (upper panels) and oxygen (lower panels) atoms of fixed-in-space CO molecules ionized by 20 keV photons, as computed in the electric-dipole approximation (left panels) and after including nondipole contributions (right panels). The light propagates from left to right (along $\mathbf{k}_y$, green arrow in the insets) and is linearly polarized in the vertical direction (along $\boldsymbol{\varepsilon}$, vertical magenta double arrows). The molecular axis lies in the picture plane, spanned by the $\mathbf{k}_y$ and $\boldsymbol{\varepsilon}$ vectors. Within this plane, it is oriented at angles $\pm\alpha$ (see legends) with respect to the polarization axis, such that the carbon (oxygen) atom points always downward (upward). The absolute scales of all panels are unrelated, while the distributions depicted within each panel are shown on the same relative scale.

We now turn to the discussion of the rotational recoil. We compare our experimental results with theoretical simulations covering this effect in Figs. 2 and 3, respectively, for the K-shell ionization of carbon and oxygen atoms in CO. We use a data representation similar to that in Fig. 1, but instead of showing the orientation of the molecular axis we indicate in each panel the experimentally determined orientation of the relative momentum of the ions $\mathbf{p}_{\text{rel}} = \mathbf{p}(\text{C}^+) - \mathbf{p}(\text{O}^+)$ (blue arrow in the insets pointing from oxygen to carbon), which coincides with the molecular axis only within the axial-recoil approximation. While the theoretical results (solid curves) represent slices of the emission distributions in the picture plane, the experimental results (symbols with error bars) include all photoelectrons emitted within an opening angle of $\pm 6^\circ$ out of the picture plane defined by $\mathbf{p}_{\text{rel}}$ and the light propagation direction. The error bars represent the absolute statistical uncertainties.

As can be seen from Figs. 2 and 3, the effect of rotational recoil on the computed and measured photoelectron emission distributions is very strong. In particular, the distributions differ strongly from those theoretical distributions that include only nondipole contributions but neglect recoil (depicted in the right-hand-side panels of Fig. 1). As demonstrated in

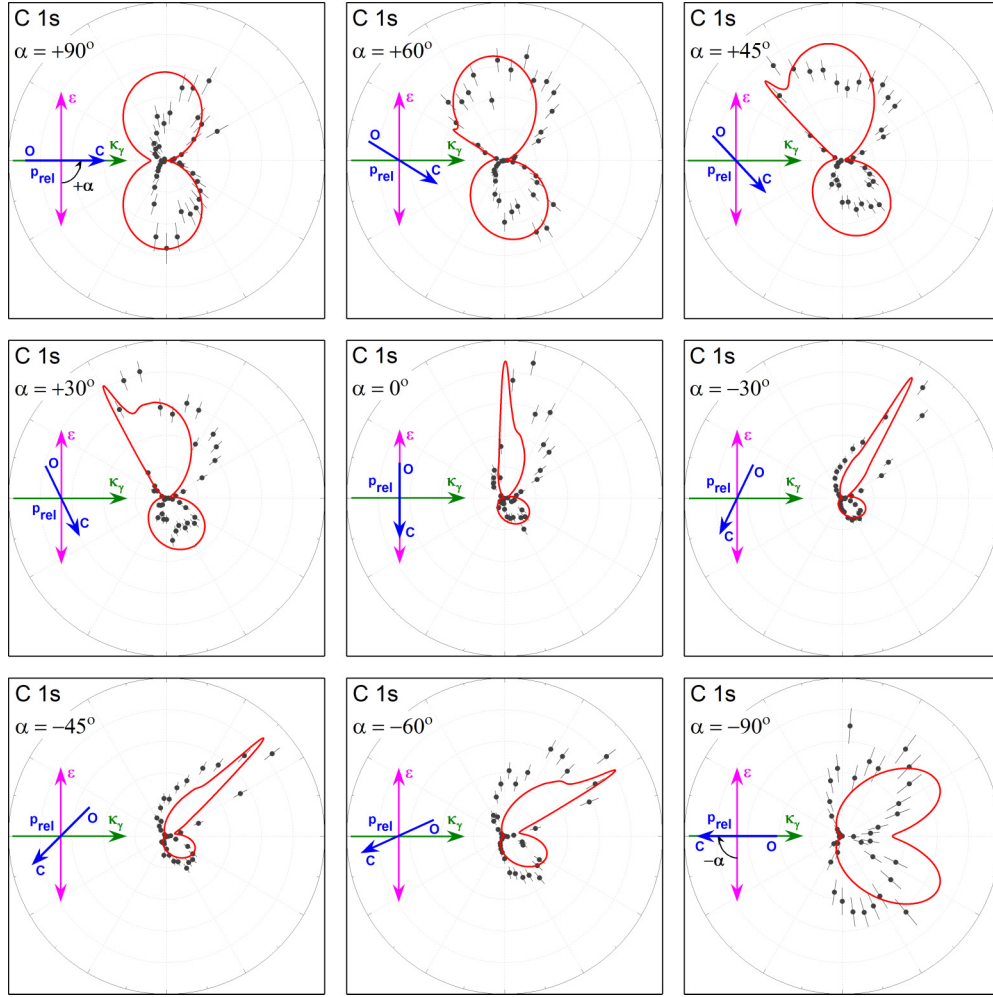


FIG. 2. Angular emission distributions of the C 1s photoelectrons of CO molecules ionized by 20 keV photons. The light propagates from left to right (green horizontal arrow) and is linearly polarized in the vertical direction (vertical magenta double arrows). The relative momentum of the ions $\mathbf{p}_{\text{rel}} = \mathbf{p}(\text{C}^+) - \mathbf{p}(\text{O}^+)$ is oriented in the picture plane at angles $\pm\alpha$ (indicated in each panel) with respect to the polarization axis and always points downward from the oxygen to the carbon atom (blue arrow). Symbols with error bars: measured data for different orientations of $\mathbf{p}_{\text{rel}}$ (see insets in each panel). Solid curves: simulations including the rotational recoil induced by the fast photoelectrons and high-energy photons. The absolute scales of all panels are unrelated, while the experimental distributions in each panel are normalized to the theoretical ones.

our previous study on N_2 [19], rotational recoil results in a propensity for the ions to break up along the axis of the imparted recoil momentum. This, in turn, significantly enhances photoemission along the forward-pointing scatterer atom (see, e.g., distributions for the orientation angles $\alpha = 0^\circ$, -30° , -45° , and -60° in Fig. 2, or $\alpha = +60^\circ$, $+45^\circ$, $+30^\circ$, and $+0^\circ$ in Fig. 3), thereby causing a strong asymmetry of the distributions with respect to the light polarization direction.

Our observations, resolving the photoemission site in the molecule, can be understood by inspecting two extreme cases in which $\mathbf{p}_{\text{rel}}$ is parallel or antiparallel to the light propagation direction $\mathbf{k}_y$ (i.e., the upper-left and lower-right panels in Figs. 2 and 3 with $\alpha = \pm 90^\circ$). Let us first consider the case in which the emitting atom is located on the left (corresponding to the panels for $\alpha = -90^\circ$ in Fig. 2 and $+90^\circ$ in Fig. 3) and focus on the upper lobe in the distributions, which on average causes a recoil-induced molecular rotation in the counterclockwise direction. As a consequence of such rotation, the photoelectron emission angle $\tilde{\phi}$ measured relative

to $\mathbf{p}_{\text{rel}}$ becomes smaller than the emission angle ϕ determined with respect to the real molecular axis. Such a smaller angle $\tilde{\phi}$ results in a stronger bending of the respective lobe in the forward direction. Note that the respective distributions for these extreme cases are up-down symmetric, and similar conclusions therefore apply to the lower emission lobes. In contrast, if the emitting atom is located on the right-hand side of the molecule ($\alpha = +90^\circ$ in Fig. 2 and -90° in Fig. 3), the upper photoemission lobe induces on average a clockwise molecular rotation. Since the molecule now rotates in the opposite direction, the measured angle $\tilde{\phi}$ becomes larger than the real emission angle ϕ . The respective lobe is therefore bent in the backward direction, i.e., the recoil-induced rotations compensate for the nondipole-induced bending of the distributions.

Figures 2 and 3 illustrate an overall agreement between the measured results and theoretical emission distributions obtained by incorporating rotational recoil effects. The agreement is better for the case of oxygen ionization shown in

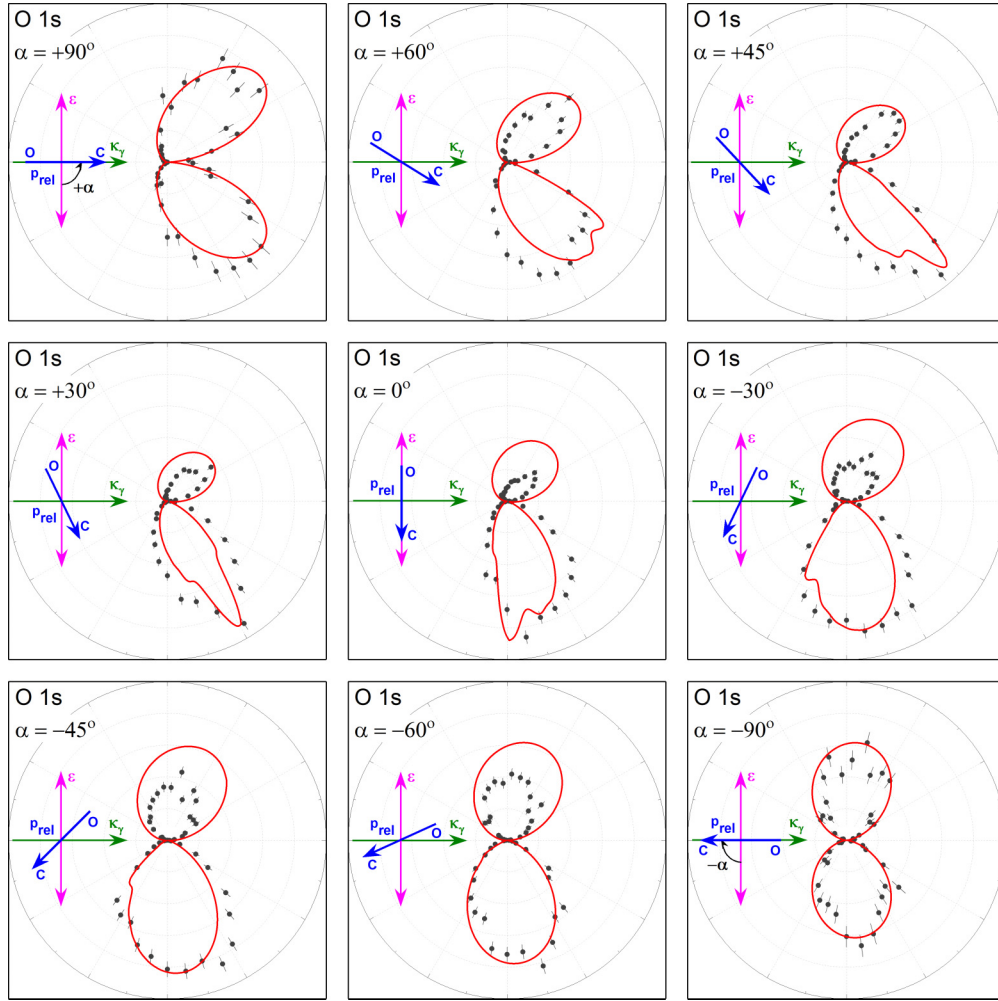


FIG. 3. Same as Fig. 2, but for the O 1s photoionization of CO (see also its caption for details of the data representation).

Fig. 3. The remaining quantitative disagreement can be attributed to several limitations. To gather sufficient statistics, it is necessary to average over finite angular intervals in the experiment. As a consequence, on the one hand, some details and sharp features present in the computed distributions are washed out in the measured ones. On the other hand, experimental distributions include out-of-plane contributions from the photoelectrons. Including such contributions in the theory would require going beyond the two-dimensional rotational-recoil model and accounting for three-dimensional molecular rotations. In addition, the theoretical model includes an average KER value to estimate the error $\Delta\phi$ in determining the spatial orientation of the molecular axis via $\mathbf{p}_{\text{rel}}$, whereas the experimental data are integrated over a large KER interval from 11 to 20 eV. Moreover, the model neglects additional contributions to the rotational recoil imparted on the opposite side of the molecule via scattering of fast photoelectrons on the neighboring atom. This scattering is not negligible, as its impact is visible in the computed distributions as forward-scattering lobes in Fig. 1. Finally, Auger electrons impart an average recoil momentum of $|\mathbf{k}_A| = 4.3$ or 6.1 a.u., corresponding to average Auger electron energies of 255 and 500 eV for the C $1s^{-1}$ and O $1s^{-1}$ states, respectively, and this effect is neglected in the theoretical model. This additional

rotational recoil influences the molecular orientation retrieved in the experiment via the relative momentum $\mathbf{p}_{\text{rel}}$, resulting in an isotropic smoothing of the experimentally observed asymmetry.

V. CONCLUSIONS

We report a continuation of our systematic study of the interplay between the nondipole and rotational-recoil effects in core-shell photoemission from diatomic molecules ionized by hard x-ray photons. The former induce a strong forward-backward asymmetry in the angular emission distribution along the light propagation direction, while the latter create a significant up-down asymmetry along the light polarization axis. By experimentally investigating *K*-shell photoionization of the heteronuclear CO molecule with 20 keV photons, we were able to observe asymmetries in the photoelectron emission distributions induced by the rotational recoil imparted on a well-defined molecular site, i.e., the carbon or the oxygen atom. Our semiclassical modeling of the rotational-recoil effect on the *ab initio* computed nondipole molecular-frame photoelectron angular distributions reproduces the experimental observations fairly well.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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