Asymmetric molecular-frame photoelectron angular distributions for C 1s photoejection from CO$_2$; a theoretical study

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Abstract. We report the results of ab initio calculations of cross sections and molecular-frame photoelectron angular distributions for C 1s ionization of CO$_2$, and propose a mechanism for the recently observed asymmetry of those angular distributions with respect to the CO$^+$ and O$^+$ ions produced by subsequent Auger decay. The fixed-nuclei, photoionization amplitudes were constructed using variationally obtained electron-molecular ion scattering wave functions. We have also carried out electronic structure calculations which identified a dissociative state of the CO$_2^+$ dication that is likely populated following Auger decay. We show that a proper accounting of vibrational motion in the computation of the photoelectron angular distributions, along with reasonable assumptions about the nuclear dissociation dynamics, gives results in good agreement with recent experimental observations.

1. Introduction
Liu et al [1] showed that molecular-frame photoelectron angular distributions (MFPAD) for C 1s ionization of CO$_2$ are asymmetric with respect to CO$^+$ + O$^+$ fragment ions for certain photon energies. The authors argued that the asymmetry is due to an interference between the gerade and ungegadregue intermediate states, implying a partial breakdown of the two-step model for core-level photoionization and subsequent Auger decay. Here we show that a proper treatment of asymmetric vibrational motion in the target molecule, along with reasonable assumptions about the dissociation dynamics following Auger decay, can account for the observed angular distributions without invoking a breakdown of the two-step model.

2. A mechanism for asymmetric body-frame photoelectron angular distributions
There are three conditions under which C 1s MFPADs of CO$_2$ can be asymmetric:
1) the fixed-nuclei carbon K-shell photoionization cross section must show a measurable asymmetry at geometries sampled by asymmetric stretch vibrational motion
2) the time for Auger decay must be shorter than the period for asymmetric vibrational motion
3) there must be a singlet electronic state of CO$_2^+$ that promptly fragments to O$^+$+CO$^+$.

The fixed-nuclei MFPAD of CO$_2$ in its asymmetric geometry must be asymmetric. C 1s electrons in CO$_2$ are tightly confined about the carbon atom and it requires photon energies greater than 297.6 eV [2] to ionize one of them. Once ionized, the interaction potential
experienced by the ejected photoelectron is determined by the target electron charge distribution, which in turn is sensitive to the instantaneous positions of the nuclei at the moment the photon is absorbed. As the photoelectron exits the target molecule, the nuclei, on a time scale determined by the fundamental frequencies of the molecule, vibrate about their equilibrium positions. To obtain an asymmetric MFPAD, we can calculate the fixed-nuclei photoionization cross section at an asymmetric geometry and multiply by the square of the corresponding vibrational wavefunction. However, asymmetry in the fixed-nuclei cross section for certain geometries is not sufficient to produce an observable effect, since the asymmetry vanishes when it is averaged over an ensemble of molecules. What is needed is another measurable process that can be recorded in coincidence with the photoelectron ejection and that can retain the memory of any initial asymmetry in the target. Asymmetric ion fragmentation can be such a process.

The core-hole state produced by photoionization is not stable and promptly decays by Auger emission to produce a CO$_2^{++}$. If there is a dissociative dication state(s) that leads directly to O$^+$ + CO$^+$ fragments, then any initial asymmetry in the CO bond lengths at the time the photon is absorbed will be reflected in the dissociation products provided that the dissociative state(s) is created by the Auger process before significant vibrational or rotational motion can occur. Since the time for Auger decay is shorter than the period of CO$_2$ asymmetric vibrational motion, coincident measurements of photoelectron and fragment ion momenta can lead to the observation of an asymmetric angular distribution.

3. Theory and Computation

3.1. Electronic structure calculations (fragmentation of singlet CO$_2^{++}$)

The electronic structure calculations for this study were carried out using a multireference configuration-interaction approach. We employed Dunning’s double-zeta plus polarization basis of contracted Gaussian functions for carbon and oxygen [3], augmented with two additional p-type functions on each atom. The calculations were carried out in linear geometry for the OC–O coordinate, with one CO distance fixed at the equilibrium geometry of the neutral molecule (2.20 bohr). The OC–O potential energy curves are shown in Fig. 2 for the $1\Sigma^+$ state(s) is created by the Auger process before significant vibrational or rotational motion can occur. Since the time for Auger decay is shorter than the period of CO$_2$ asymmetric vibrational motion, coincident measurements of photoelectron and fragment ion momenta can lead to the observation of an asymmetric angular distribution.

3.2. Computation of molecular-frame photoionization cross sections

Fixed-nuclei photoionization amplitudes were computed using the complex Kohn variational method [4]. Here we give a brief summary.

The final-state wave function for production of photoions in a specific state $\Gamma_0$ is written as

$$\Psi_{\Gamma_0} = \sum_{\Gamma} A(\chi_{\Gamma} F_{\Gamma \Gamma_0})$$

where $\Gamma$ labels the final ionic target states $\chi_{\Gamma}$ included, $F_{\Gamma \Gamma_0}$ are channel functions that describe the photoionized electron, and $A$ is the antisymmetrization operator. Note that we are using $\Gamma_0$ as a combined index to denote the target ion electronic state and the angular momentum quantum numbers $l_0, m_0$ of the ejected photoelectron.

In the Kohn method, the channel functions are further expanded, in the molecular frame, as

$$F_{\Gamma \Gamma_0}(r) = \sum_i c_i^{\Gamma \Gamma_0} \varphi_i(r) + \sum_{lm} \left[ f_{lm}(k_\Gamma, r) \delta_{l_00} \delta_{m_00} \delta_{\Gamma \Gamma_0} + T_{ll_0mm_0}^{\Gamma \Gamma_0} h_{lm}^{-}(k_\Gamma, r) Y_{lm}(\hat{r})/r^{\frac{3}{2}} \right],$$

where the $\varphi_i(r)$ are a set of square-integrable (Cartesian Gaussian) functions, $Y_{lm}$ is a normalized spherical harmonic, $k_\Gamma$ are channel momenta, and the $f_{lm}(k_\Gamma, r)$ and $h_{lm}^{-}(k_\Gamma, r)$ are numerical.
continuum functions that behave asymptotically as regular and incoming partial-wave Coulomb functions, respectively [5]. The coefficients $T_{\Gamma_0}^{\Gamma}$ are the T-matrix elements.

Photoionization cross sections in the molecular frame can be constructed from the matrix elements

$$I_{\Gamma_0}^\mu = \langle \Psi_{-\Gamma_0} | r^\mu | \Psi_0 \rangle,$$

where $r^\mu$ is a component of the dipole operator, which we evaluate here in the length form,

$$r^\mu = \{ z, \mu = 0 \pm (x \pm iy) / \sqrt{2}, \mu = \pm 1 \}$$

and $\Psi_0$ is the initial state wave function of the neutral $N$ electron target. In order to construct an amplitude that represents a photoelectron with momentum $k_{\Gamma_0}$ ejected by absorption of a photon with polarization direction $\hat{\epsilon}$, measured relative to the molecular body-frame, the matrix elements $I_{\Gamma_0}^\mu$ must be combined in a partial wave series

$$I_{k_{\Gamma_0},\hat{\epsilon}} = \sqrt{\frac{4\pi}{3}} \sum_{\mu_0 m_0} i^{\mu_0} e^{i\delta_{\mu_0}} I_{\Gamma_0}^\mu Y_{\mu_0}(\hat{\epsilon}) Y_{\mu_0 m_0}(k_{\Gamma_0}),$$

where $\delta_{\mu_0}$ is a Coulomb phase shift. The cross section, differential in the angle of photoejection and photon polarization relative to the fixed body-frame of the molecule, is then given by

$$\frac{d^2 \sigma}{d\Omega_{k_{\Gamma_0}} d\Omega_{\hat{\epsilon}}} = \frac{8\pi \omega}{3c} |I_{k_{\Gamma_0},\hat{\epsilon}}|^2,$$

where $\omega$ is the photon energy and $c$ is the speed of light.

3.3. Inclusion of vibrational motion

To account for the target vibrational motion, we make the Born-Oppenheimer approximation for the initial state and the final scattering states, writing them as products of electronic functions.
times vibrational functions. We can then rewrite the amplitude (defined in Eq. ??) for a particular \( \nu \rightarrow \nu' \) transition as

\[
I_{k_{\Gamma_0}^{\nu,\nu'}} = \sqrt{\frac{4\pi}{3}} \sum_{\mu l_{\Gamma_0} m_0} i^{-l_0} e^{i\delta_0} Y_{1\mu}(\hat{\epsilon}) Y_{l_0 m_0}(\hat{k_{\Gamma_0}}) \times \int I_{\nu}^\mu(s) \eta_\nu(s) \eta_{\nu'}(s) ds,
\]

(7)

where we have used \( s \) to denote the internal coordinates and \( \eta_\nu \) and \( \eta_{\nu'} \) are the initial (neutral) and final (ion) vibrational wave functions, respectively. Note that we have ignored the dependence of the photoelectron wave vector \( k_{\Gamma_0} \) on the final vibrational state, which is a good approximation except very close to thresholds. If we are not interested in the excitation of individual vibrational levels, then we can sum over final \( \nu' \) in computing the body-frame cross section, using the closure relation,

\[
\sum_{\nu'} \eta_{\nu'}(s) \eta_{\nu'}(s') = \delta(s - s')
\]

(8)

to obtain the differential body-frame photoionization cross section for a target molecule in initial vibrational state \( \nu \)

\[
\frac{d^2\sigma_\nu}{d\Omega_{k_{\Gamma_0}} d\Omega_\hat{\epsilon}} = \int \eta_\nu(s)^2 \frac{d^2\sigma}{d\Omega_{k_{\Gamma_0}} d\Omega_\hat{\epsilon}}(s) ds.
\]

(9)

We approximate the initial vibrational wave function as a product of harmonic oscillator functions in the asymmetric-stretch and bending normal coordinates using force constants derived from our SCF calculations. In the experiment, the body-frame photoelectron angular distributions were measured in coincidence with the asymmetric O\(^+\)+CO\(^+\) ion fragmentation channel. We propose that for the combined photo- and Auger ionization process, the memory of the instantaneous position of the nuclei at the time of photoionization is imprinted on the final dication state, provided the Auger decay occurs before the memory is washed away by the vibrational motion of the ion. For the asymmetric stretch of CO\(_2\) the time scale for one complete vibration is approximately 14.2 fsec. This means that the Auger decay time (\( \sim 6 \) fsec [6]) must be less than or equal to half the period of asymmetric mode, 7.2 fsec, assuming that the asymmetric stretch frequencies for the neutral and core-hole surfaces are comparable. We therefore incorporate the asymmetric stretch motion of the neutral target into the observed MFPAD by confining the average to half of the allowed range of nuclear geometries. This treatment would be exact if the Auger decay were instantaneous.

4. Results

The square-integrable portion of the basis for the complex Kohn calculations consisted of Dunning’s double-zeta basis [3], augmented with two p-type, two d-type and three f-type functions on the carbon atom, along with two p-type, two d-type and one f-type function on the oxygen atoms. We also included numerical continuum functions up to \( l=7 \). To avoid working with non-orthogonal orbitals, we use a single set of molecular orbitals to construct both the initial neutral and final ion states. In order to generate these orbitals, we start with a reference ion configuration with a single vacancy in the carbon 1s orbital. We then perform an all-singles configuration-interaction calculation, keeping the carbon 1s occupancy either one or zero. The natural orbitals from that calculation are then used in the photoionization calculations.

Fig. 2a shows our calculated molecular-frame angular distributions for several photon energies for the case where the photon polarization lies along the molecular axis. The top row is MFPADs calculated with the nuclei fixed at the equilibrium geometry. The striking feature here is that the relatively simple two-lobed patterns seen at low and high photoelectron energies become highly structured over a narrow range of energies near 20 eV, where they show an almost complete extinction of probability for electron ejection along the molecular axis.
Figure 2. a. Fixed-nuclei molecular-frame phototelectron angular distributions (MFPAD), in units of Mb/steradian, for polarization parallel to molecular axis. $E_e$ is the photoelectron energy. Top: equilibrium geometry; bottom: asymmetric geometry (CO distances are 2.146 and 2.254 bohr). b. $\Sigma_u$ partial-wave contributions to the total cross section

The origin of the aforementioned pattern becomes clear when we examine the partial wave contributions to the total cross section in $\Sigma_u$ symmetry, which are shown in Fig. 2b. It is seen that at photoelectron energy of 21.7 eV, the magnitudes of the $l = 1$ and $l = 5$ partial cross sections become equal. Moreover, at this energy, the $l = 3$ partial cross section is almost an order of magnitude smaller. The rapid change in the observed MFPADs is evidently the result of a destructive "interference" between the $l = 1$ and $l = 5$ amplitudes, which have the same magnitude at an energy where the $l = 3$ contribution is small.

To see the effect of asymmetric stretch displacement of the nuclei from their equilibrium positions on the angular distributions, we show another set of MFPADs in the bottom row of Fig. 2a. The results shown here were computed with the nuclei at their root mean square (RMS) displacements in the harmonic asymmetric-stretch potential and are plotted at the same energies as the equilibrium geometry case. The RMS values were derived from a normal mode analysis of the ground-state CO$_2$ potential calculated at the MP2 level with a triple-zeta plus polarization basis. Asymmetry in the angular distributions is clearly evident in the calculated MFPADs. It is worth noting that there is a shift in the asymmetry pattern as the energy passes through the region where the rapid changes in the MFPADs occur: below this "interference" region, ejection toward the CO$^+$ end of the asymmetrically stretched molecule is favored, while at higher energies, the probability of ejection shifts toward the O$^+$ side. For the comparison between measured and calculated MFPADs, we evaluated the differential photoionization cross section using Eq. ??, including the asymmetric-stretch and bending vibrational functions as outlined above. Our calculation places the $\Sigma_u$ shape resonance $\sim$3 eV higher than experiment [7]. To account for this difference when comparing theory with the experimental MFPADs of Liu et al [1], we subtracted 3 eV from the theoretical value of the photon energy associated with a particular photoelectron energy, so that we are comparing cross sections measured at the same energy relative to the resonance peak. Fig. 3 shows the results at two photon energies, one below and one above the "interference" region. The experimental photoelectron energies and the energies at which the calculations were performed are both indicated in the figure. We see that the shapes of the calculated and measured distributions, including the magnitudes of the asymmetry, are in good mutual agreement. (For comparison, the completely symmetric fixed-nuclei results calculated at the equilibrium geometry are also plotted.) Furthermore, the
asymmetry shift from left to right is clearly seen in both the calculated and measured data.

5. Discussion
We have carried out theoretical calculations of molecular-frame photoelectron angular distributions for C 1s ionization in CO\(_2\) with a view towards explaining the weak but definite asymmetry seen when the photoelectrons are measured in coincidence with asymmetric ion fragmentation. The asymmetry seen in the fixed-nuclei angular distributions with the nuclei displaced from their equilibrium positions by the root-mean square values of the asymmetric-stretch normal coordinate is well correlated with the observed MFPADs. We have proposed a mechanism to explain how the memory of these photoelectron distributions produced from asymmetric geometries is imprinted on the nuclear dynamics following Auger decay. Since the Auger lifetime is shorter than the asymmetric stretch vibrational period, population of an electronically excited dication state that produces CO\(^+\) + O\(^+\) fragment ions by direct dissociation can be used to monitor any asymmetry in the photoelectron angular distribution when measured in coincidence with the latter. Our electronic structure calculations on CO\(_2^{++}\) have identified such a state. This mechanism explains how asymmetric angular distributions can be produced without invoking a breakdown of the two-step mechanism or the existence of a post-collision interaction between photo- and Auger electrons.

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Acknowledgement
This work was performed under the auspices of the US Department of Energy and was supported by the USDOE Office of Basic Energy Science, Division of Chemical Sciences.