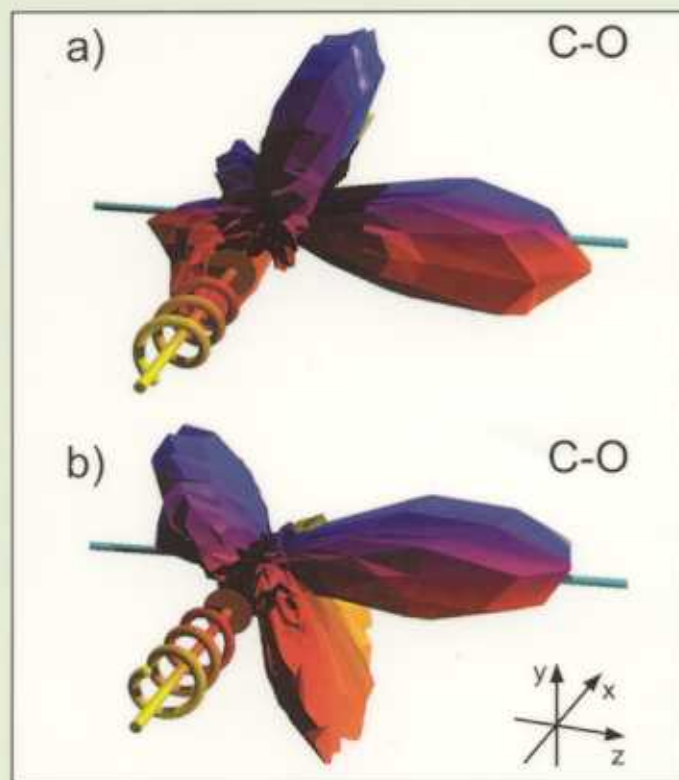


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Circular Dichroism in K -Shell Ionization from Fixed-in-Space CO and N₂ Molecules

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We have measured the angular distributions of $1s$ photoelectrons excited by circularly and linearly polarized light from fixed-in-space CO and N₂ molecules, in the vicinity of their shape resonances. A strong circular dichroism, i.e., a strong dependence on the sense of rotation of the polarization vector of the photons, is found for both molecules. State-of-the-art one-electron multiple scattering and partially correlated random phase approximation calculations are in good agreement with many, but not all, aspects of the experimental data.

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The interaction of light with matter depends on the polarization properties of the photons. Optically active media, for example, can show different absorption for left and right circularly polarized light, a much-studied effect. Much more recently, the angular distributions of photoelectrons from molecular adsorbates and solids have been found to show the effect of (nonmagnetic) circular dichroism in their angular distributions (CDAD), i.e., a modification with changing helicity of the light (see, e.g., [1] and references therein). A sufficient requirement to observe CDAD is an experimental system which defines three non-coplanar vectors (see, e.g., [2]). An exemplary system for which CDAD has been predicted is the emission of one photoelectron from an oriented diatomic molecule such as CO [3,4]. In this case, the three vectors are given by the angular momentum vector of photons, the molecular axis, and the photoelectron momentum. Pioneering experiments have been performed on photoelectrons emitted from the 4σ and 5σ orbitals [5] and the carbon K -shell [6] of CO, oriented by adsorption on a Pd surface. However, by orienting the molecules via adsorption not all emission angles of the photoelectron are accessible and the influence of the surface cannot be neglected.

In this Letter we present a detailed measurement of CDAD of K -shell photoelectrons emitted from molecules with definite orientations ("fixed-in-space") in the gas phase. The experimental method permits covering all angles and several photon energies in the vicinity of the K -shell shape resonances. We show that CDAD is prominent not only for oriented fixed-in-space molecules such as CO but also for emission from N₂ which has an alignment but no orientation. The molecule axis at the instant of photoabsorption has been measured by detecting

the direction of molecule fragmentation. The creation of the K hole is, in most cases, followed by the emission of at least one Auger electron. The resulting doubly (or highly) charged molecular ion breaks apart on a time scale which, for high enough fragmentation energies, is fast compared to typical rotation times (the axial recoil approximation is known to be valid for CO and N₂ under the conditions of our measurements [7]). This method of measuring the angular distribution of photoelectrons from fixed-in-space gas phase molecules by coincident detection of molecule fragments and the electron was pioneered by Shigemasa and co-workers (see [8] for N₂). More recently three groups have reported angular distributions of carbon- K photoelectrons from CO emitted by linearly polarized light [7,9–12].

The present experiment was performed using COLTRIMS (cold target recoil ion momentum spectroscopy; see [13] for a recent review) at elliptically polarized undulator beam line 4.0.2 of the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory. The Stokes parameter S_3 of the light from this beam line was measured to be $|S_3| > 0.98$ for the photon energies used in this work. The photon beam was focused onto a supersonic molecular gas jet. The ion fragments were collected with 4π efficiency by an electric field (20 V/cm) which directs them to a position sensitive channel plate detector with delay line multihit readout [14]. From the position of impact and time of flight, the charge state and momentum vector of each fragment is determined. In a similar manner, the electric field and a superimposed homogeneous magnetic field guide the photoelectron to a second position and time sensitive detector from which its momentum is determined [15].

Only those events in which two positive ions are detected in coincidence with the photoelectron are recorded. The resolution for the photoelectron ranges from 1–3 eV depending upon its energy; this is sufficient to discriminate the direct K -shell photoelectron from the Auger and satellite shakeup electrons. For CO we have used only the $C^+ + O^+$ decay channel with a kinetic energy release $KER > 10.2$ eV [7] and for N_2 all ions from the $N^+ + N^+$ decay channel for the analysis.

Figure 1 shows the measured angular distributions of K -shell ($1s$) photoelectrons from CO and N_2 on the peaks of their σ shape resonances. For CO, the effect of circular dichroism becomes obvious by comparing the distributions for right-hand circular polarization (RCP) [Fig. 1(a)] and left-hand circular polarization (LHC) [Fig. 1(b)]. The

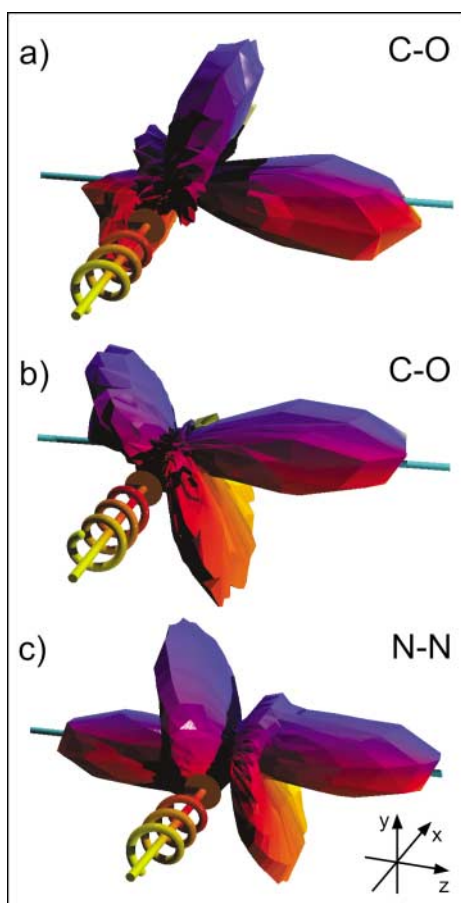


FIG. 1 (color). (a),(b) Angular distributions of $C(1s)$ photoelectrons (10 eV kinetic energy, on shape resonance) emitted from a CO molecule by absorption of left and right circularly polarized photons. The sense of rotation of the polarization vector is indicated by the spiral, where the photon propagation vector lies along the $+x$ axis (i.e., into the page) in all cases. The molecule is aligned along the z axis, with the carbon atom at negative z in (a) and (b). Each vertex of the three-dimensional shape represents one data point. The data have not been smoothed, with the maximum corresponding to about 1000 counts. (c) Analogous distribution of $N(1s)$ photoelectrons (9 eV, on resonance) from N_2 .

three-dimensional distributions in Fig. 1 are only a subset of the data since all other molecular orientations are collected simultaneously; marked dichroism is observed for most other orientations as well. For N_2 [Fig. 1(c)], the two ends of the molecule are equivalent, so its axis has no unique direction, and the geometry does not have a well-defined handedness. Nevertheless, the data show that CDAD is nonzero even in this situation, with a similar mirror image being observed for RCP excitation (not shown).

More quantitatively, Fig. 2 shows the photoelectron angular distribution from CO in the y - z -plane (perpendicular to the photon propagation) where CDAD is strongest. The molecule lies along the horizontal axis, as shown in the schematic, and the photon propagation vector is into the page. The electron energies are 1.6, 10.0, and 24.6 eV. The carbon- K σ shape resonance results in a maximum of the cross section at around 10 eV (306 eV photon energy). The right panels show the CDAD defined as

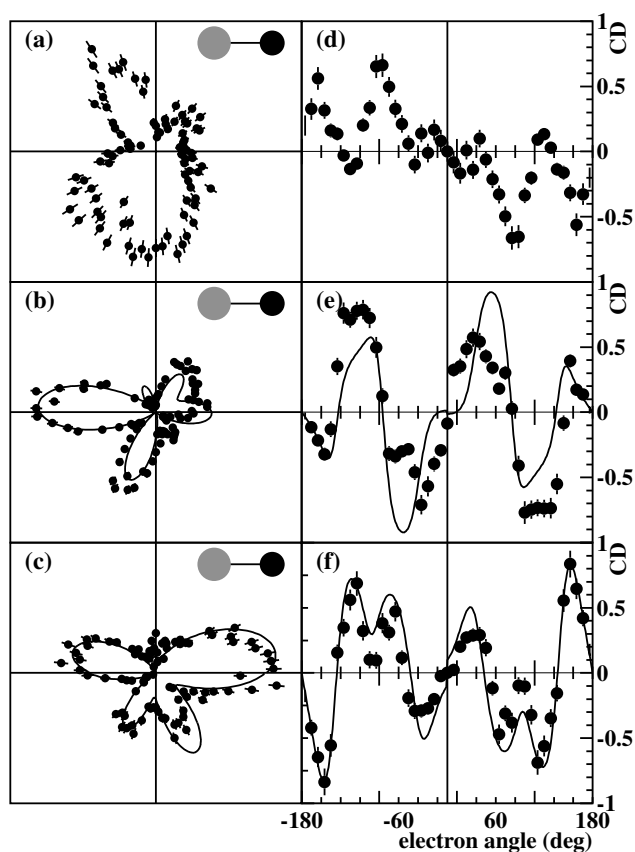


FIG. 2. (a)–(c) Angular distribution of $C(1s)$ photoelectrons emitted from a CO molecule by absorption of right circularly polarized photons where the propagation vector of the light is into the page. The molecule lies along the horizontal axis as indicated, and both electrons and molecules lie within 10° of the plane of the page. The electron energies are (a) 1.6, (b) 10.0, and (c) 24.6 eV. Panels (d)–(f) show the corresponding circular dichroism as defined in the text. Electron angle 0 corresponds to the direction of the carbon. Full lines: Theoretical multiple scattering calculations for the two higher energies, convoluted with the experimental resolution.

$$\text{CDAD} = (\sigma_{\text{LCP}} - \sigma_{\text{RCP}})/(\sigma_{\text{LCP}} + \sigma_{\text{RCP}}). \quad (1)$$

The CDAD defined above can be viewed in a simple physical picture as being proportional to the sine of the phase difference between the continuum photoelectron wave created by linearly polarized light parallel and perpendicular to the molecular axis (σ and π transitions) (see, e.g., [2,4]). More generally, the differential cross sections for linearly (σ_{lin}) and circularly polarized light ($\sigma_{\text{LCP,RCP}}$) in the molecule fixed frame are given by

$$\begin{aligned} \sigma_{\text{lin}} = & |T_z \cos \vartheta_\epsilon|^2 + |T_y \sin \vartheta_\epsilon|^2 \\ & + 2|T_z \cos \vartheta_\epsilon| |T_y \sin \vartheta_\epsilon| \cos \delta, \end{aligned} \quad (2)$$

$$\sigma_{\text{LCP,RCP}} = |(T_z \pm iT_y)|^2, \quad (3)$$

where ϑ_ϵ is the angle between the molecular axis and the linear polarization axis. In Eq. (3), the molecule axis (z axis) is perpendicular to the photon propagation, $T_{y,z}$ are the transition matrix elements for linearly polarized light along y, z , δ is the phase difference between T_z and T_y , and the $+$ sign gives σ_{LCP} . From this we obtain

$$\text{CDAD} \propto |T_z| |T_y| \sin \delta. \quad (4)$$

Circular dichroism thus gives direct access to the sine of the relative phase between the σ and π photoelectron waves excited by z and y polarized light, respectively. Because the sine and cosine are double valued, δ cannot be unambiguously determined from an experiment with only linearly or circularly polarized light; one must do both or a measurement with elliptically polarized light. The usefulness of CDAD measurements in testing theory becomes obvious in the comparison of the experimental data to the theoretical calculations shown in Fig. 2 by the solid lines. These calculations are performed in a one-electron model using multiple scattering theory in nonspherical self-consistent potentials (MSNSP) [16] using the experimental values of the electron energy. The molecular ionic potential is split into two touching roughly hemispherical cells in which the full self-consistent potential is present. This allows us to include regions of space neglected by standard multiple scattering theory, and to avoid the usual spherical symmetrization of the potentials around each atomic scattering center. The inclusion of nonspherical effects has been found to be crucial in the calculation of the photoelectron angular distributions for kinetic energies of the electron lower than approximately 30 eV [16]. The experimental angular distributions at the two highest energies are very well reproduced by these calculations, with only slight differences seen just on resonance [Fig. 2(e)]. For the lowest electron kinetic energy (1.6 eV), the electron scattering is too sensitive to the potential cutoff at long distances, and MSNSP theory does not provide reliable results.

For a homonuclear diatomic such as N_2 , the separation in energy between the two K -shells with g and u symmetry is too small (97 meV for N_2 [17]) to be resolved,

so all our experiments on angular distributions represent the sum of both components. In Fig. 3, we compare our data to another set of theoretical calculations, in which many-electron correlations have been taken into account in the random phase approximation (RPA) (see [18,19] for detail). In this approach the nonspherical relaxed core Hartree-Fock potential is used as the zero order approximation for the photoelectron wave functions, and the

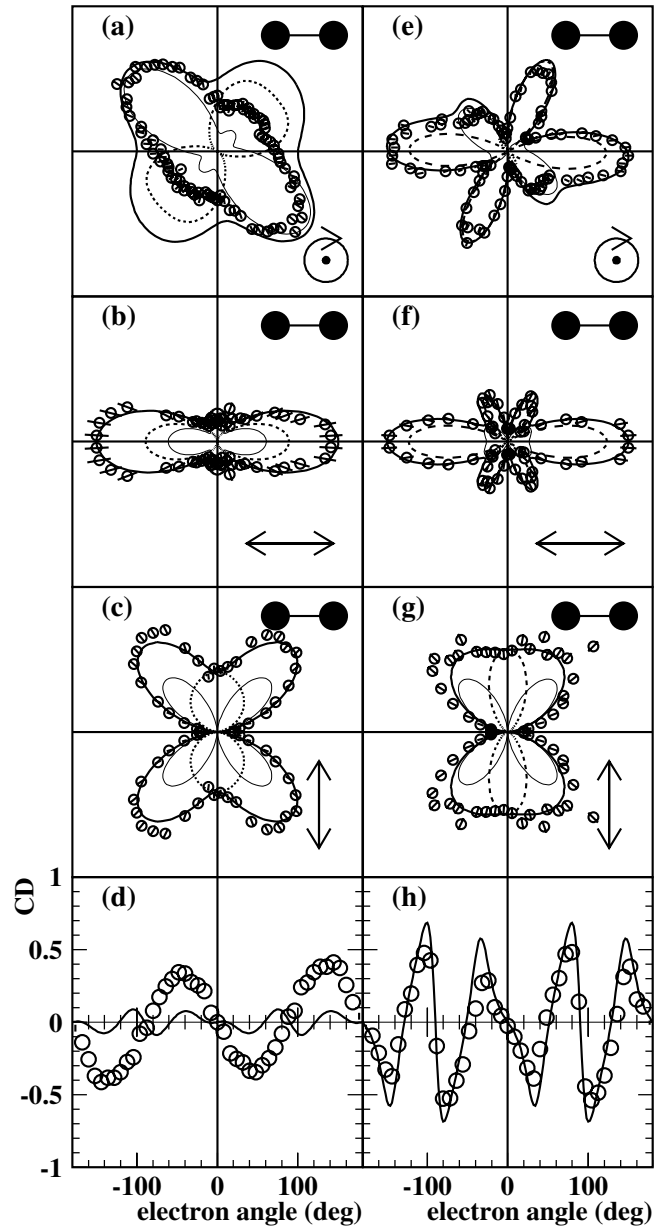


FIG. 3. K -shell ionization of N_2 . The alignment of the molecule is horizontal. Electron energy 2 eV (a)–(d) and 9 eV (e)–(h). (a) and (e) left-hand circularly polarized light, geometry as in (d) and (h) corresponding circular dichroism (see text), (b) and (f) linearly polarized light, molecule parallel to polarization, (c) and (g) linearly polarized light, molecule perpendicular to polarization. Lines show RPA calculations: thin lines, contribution from g initial state; dashed lines, contribution from u initial state; thick lines, incoherent sum of g and u .

coupling between the 1σ - g and 1σ - u channels is included within the RPA method.

In these experimental and calculated angular distributions for circularly polarized light [see Figs. 3(a) and 3(e)], the g and u contributions are shown separately, and they can be almost directly associated with particular lobes observed also in the experiment. Thus the angular distribution for circular light can provide a sensitive test not only of the phase shift but also (predictions) of the ratio of the g and u channel contributions. Figure 3(e) suggests that the RPA calculation overestimates the u contribution to the shape resonance by about 30%, as it follows more directly from comparison with the partial cross sections measured in [17]. This is also confirmed by a zoomed inspection of Fig. 3(f) where the minimum at around 30° from the polarization direction is much deeper in the experiment than in theory, where it is filled by the u contributions. We attribute the deeper minimum in our data, as compared to those in [19], to the better angular resolution in the present experiment. We note also that the data in Figs. 3(e)–3(h) are recorded at a photoelectron energy of 9 eV on the observed maximum of the shape resonance, whereas the calculations are for 11 eV (where RPA predicts the maximum of the shape resonance). The agreement between RPA theory and experiment for the CDAD is good at this electron energy. Much closer to threshold at 2 eV electron energy [Fig. 3(a)–3(d)], RPA still gives good agreement with the distributions for the parallel and perpendicular transition; however, it fails for circularly polarized light. Calculations at the N_2 resonance (not shown here) based on the MSNSP, which do not include g - u coupling agree well with the data for linear polarized light. This also supports that interchannel coupling plays a less important role. The MSNSP calculations, however, fail in the present stage to reproduce the phase between the σ and π channel in N_2 and hence fail on reproducing the data for circular polarized light.

In conclusion, we have presented experimental and theoretical angular distributions of K photoelectrons from CO and N_2 emitted by circularly polarized light in the region of the σ shape resonance. We observe a strong circular dichroism for both molecules which implies significant phase shifts between the σ and π photoelectron waves. Theoretical calculations of two types are found to reproduce many features of the observations, but the dichroism measurements stand as a new level of challenge to the theory of electron emission from molecules. Our measurements thus provide benchmark tests of theoretical methods which are indispensable, for example, in the interpretation of photoemission and photoelectron diffraction data from solids.

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Note added.—Closely related work on circular dichroism in $2\sigma_g$ shell ionization has been reported by Motoki *et al.* [20].

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