Asymmetry in Photoelectron Emission from Chiral Molecules Induced by Circularly Polarized Light

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In photoionization of free, unoriented chiral molecules with circularly polarized radiation, a significant circular dichroism, i.e., an asymmetry in the forward-backward electron emission, has been observed in the photoelectron angular distribution. This leads also to an asymmetry in the momentum transfer to the photoions. The spectra for the left- and right-handed enantiomers of bromocamphor exhibit asymmetries up to several percent which vary as a function of orbital binding energy. This enantioselective effect can similarly occur for biomolecules with handedness, like amino acids, and may thus be a contributing factor related to the origin of the terrestrial biomolecular homochirality.

Nature is dissymmetric on the macroscopic and microscopic scale. Processes with chiral molecules exhibiting strong enantiomeric selectivity and the unresolved origin of the homochirality of terrestrial life, i.e., the predominance of one handedness for all biomolecules, have received special attention [1]. Asymmetries in the interaction of polarized light with chiral molecules have been studied since Pasteur's pioneering experiments on optical activity [2]. While optical techniques with visible light are routinely used in this context, only a few studies of chirality were performed with ionizing radiation. Very recently, it was found that aerosol particles of chiral molecules exhibit in the total photoelectron yield a circular dichroism which increases with particle size and crystallite order [3]. However, up to now, no experimental observations were reported on the intrinsic effects of the molecular chirality in photoelectron spectroscopy. Here we show that ionization with circularly polarized radiation leads to a significant circular dichroism in the photoelectron angular distribution of free, unoriented $(1R)$-$(+)$ bromocamphor ($C_{10}H_{15}BrO$) molecules. Our findings confirm general predictions [4,5] for the angular dependence and demonstrate that sizable dichroic effects exist for isolated, randomly oriented gas-phase molecules with definite handedness.

Because of its "handed" structure, a chiral molecule has no symmetry plane and also no center of inversion. The two enantiomers of a chiral molecule are mirror images of each other and cannot be superimposed; however, on the basis of electromagnetic interaction theory they have *identical* electronic structure. As was first pointed out by Ritchie [4] and later discussed in detail by Cherepkov [5,6], this lack of symmetry should lead to an optical activity, i.e., helicity-dependent effects, in photoemission, even if the molecules are randomly oriented. In contrast to the circular dichroism (CD) of the total (angle-integrated) photoelectron yield, the circular dichroism parameter of the angular distribution (CDAD) should be larger since it occurs already in pure electric dipole approximation. Very

recently, Powis has obtained pronounced effects in numerical CDAD calculations for chiral molecules [7]. For atoms and unoriented (nonchiral) molecules the dependence of the photoelectron intensity $I(\theta)$ on the emission angle θ is given in terms of the cross section $\sigma(\omega)$, the β parameter, and the second Legendre polynomial $(\frac{3}{2}\cos^2\theta - \frac{1}{2})$. As described in the theory papers [4,5], for the case of *chiral* molecules ionized with circularly polarized light, due to the reduced symmetry an additional contribution arises which contains a $\cos\theta$ dependence, a coefficient D, and the light helicity $m = \pm 1$:

$$I(\theta) = \frac{\sigma(\omega)}{4\pi}\left[1 - \frac{\beta}{2}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) + mD\cos\theta\right]. \tag{1}$$

Thus, for photons with one helicity interacting with molecules with one handedness the angular distribution should become asymmetric; i.e., the photoelectron emission should be different with respect to the forward and backward directions of the photon beam. In principle, this asymmetry arising from the last term of Eq. (1) is experimentally accessible by a reversal of the light helicity, the molecular chirality, or the emission direction.

In contrast to the naturally occurring intrinsic dichroism of chiral substances discussed here, a CDAD effect was observed for *nonchiral* compounds by Schönhense and co-workers, when the target was oriented and a chirality was *induced* by the geometry of the experiment [8]. Electron dichroism (ED), a related electron-scattering effect in the spin-dependent attenuation of polarized electrons by chiral molecules was recently observed: A small asymmetry on the order of 10^{-4} was found for vapors of bromocamphor and also for large handed molecules containing rare earth atoms by Kessler and co-workers [9]. In contrast, Ray *et al.* [10] have measured a fairly large electron dichroism for pure Langmuir-Blodgett films of oriented chiral molecules. The corresponding theoretical developments were reviewed recently [11].

Our angle-resolved photoemission experiments on the natural dichroism were carried out with unoriented bromo-camphor molecules and with vacuum ultraviolet (VUV) radiation at the Berlin storage ring for synchrotron radiation (BESSY) using the 6.5 m normal-incidence monochromator and the circularly polarized σ^+ and σ^- light emitted above and below the storage ring plane; see [12]. Rather than deriving the asymmetry A_{CDAD} from sequential intensity measurements with σ^+ and σ^- light [8], we have chosen to determine A_{CDAD} from simultaneous measurements at two opposite emission directions (see Fig. 1) according to

$$A_{\text{CDAD}}(\theta) = \frac{I(\theta) - I(\theta + 180°)}{I(\theta) + I(\theta + 180°)}. \qquad (2)$$

The experimental precision increases by this recording technique with two detectors since only the intensity *ratio* is needed, and vapor pressure fluctuations as well as light intensity changes cancel. The photoelectrons were recorded at variable polar emission angle θ by means of two identically built hemispherical spectrometers (ca. $\pm 5°$ acceptance angle), mounted opposite to each other and equipped with channeltron detectors. The whole two-spectrometer unit was rotatable around a common axis oriented at an angle of 45° relative to the storage ring plane and of 90° relative to the photon beam. In order to obtain high count rates, the spectrometers were operated at 20 eV pass energy resulting in a resolution of ~ 0.4 eV. The vapors of 98% pure samples of ($[1R]$-endo)-(+)-3 bromocamphor or ($[1S]$-endo)-(−)-3 bromocamphor were admitted through heated valves to the ionization region via a heated gas pipe and nozzle (1 mm diam) from two reservoirs each kept at $\sim 70\,°C$. The background pressure inside the differentially pumped vacuum chamber was on the order of 10^{-4} mbar or less. Magnetic fields were compensated to $\leq 1\ \mu T$. The photon bandwidth was ~ 0.2 eV, and the degree of circular polarization was set to 0.92 ± 0.03. Even when aligned carefully, the two
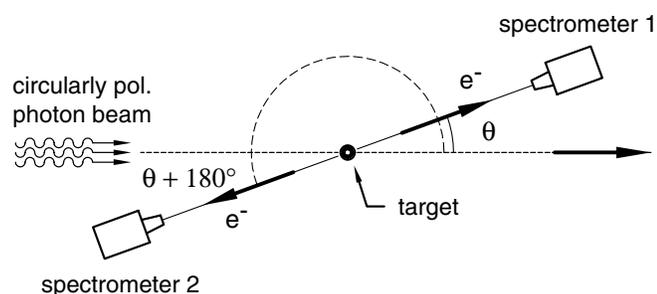

FIG. 1. Scheme of the experimental setup for the angle-resolved investigation of the circular dichroism in photoemission using circularly polarized synchrotron radiation at BESSY. For the simultaneous detection of the emission asymmetry at the angles θ and $\theta + 180°$ two electron spectrometers are mounted opposite to each other and rotated together in the detection plane.

detection systems do not have identical collection angle, transmission, and detection efficiency. Consequently, a second measurement is required to determine A_{CDAD} with all apparatus asymmetries eliminated. Reversal of the light helicity leads to small changes of the focal position of the radiation in the ionization region which in turn changes the electron collection geometry. Interchange of the two spectrometers by a rotation by 180° also did not eliminate all systematic errors; therefore, the vapor sample was switched sequentially between (R) and (S) enantiomers *without* any other changes in order to derive the asymmetry A_{CDAD}.

A typical photoelectron spectrum obtained for $(1R)$-(+) bromocamphor molecules with σ^+ light at a photon energy of 16.2 eV is plotted in Fig. 2(a) as a function of binding energy. The data were recorded at the so-called magic angle θ_m, where the second Legendre polynomial and thus the dependence of the intensity on the β parameter vanishes, leaving only the dependence on the cross section and on the light helicity [see Eq. (1)]. The highest occupied molecular orbital at a binding energy of 9.0 eV corresponds to electron emission from the oxygen nonbonding orbital localized mainly near the carbonyl C—O double bond, this represents the most weakly bound electron state in many camphor derivatives. Comparison with previous He I photoelectron studies [13,14] of camphor and bromocamphor reveals that the peak at binding energies of 10–11 eV is related to the electron emission from the lone-pair orbitals localized at the Br atom, whereas the structures at higher energy are due to various σ bonds within the molecule.

Figure 2(b) shows the corresponding asymmetry $A_{\text{CDAD}}(\theta_m)$ obtained for ionization with either σ^+ or with σ^- light. Sampling at intervals of 0.5 eV, several spectral scans were averaged, yielding total count rates of up to 10^6 s^{-1}. The data of Fig. 2(b) demonstrate that for the chiral molecules examined here an energy-dependent asymmetry of up to $\pm 3\%$ exists and that the sign of A_{CDAD} changes when the light helicity is reversed. Taking this sign change into account, a combined asymmetry $A_{\text{CDAD}}^{\pm}(\theta) = \frac{1}{2}[A_{\text{CDAD}}^{+}(\theta) - A_{\text{CDAD}}^{-}(\theta)]$ can be formed. These average values, obtained at three different emission angles, are plotted in Fig. 2(c). Because of the dependence on $\cos\theta$ [see Eq. (1)] the asymmetry disappears for $\theta = 90°$ within experimental uncertainty and reverses its sign, when going from $\theta_m = 55°$ to $\theta_m' = 125°$ (i.e., $180° - \theta_m$), in agreement with Eq. (1). The zero result at emission angle $\theta = 90°$ and consistent results at θ_m and θ_m' obtained with interchanged positions of spectrometers 1 and 2 show that any remaining systematic apparatus-related asymmetries are small compared to the detected A_{CDAD} signal. At the magic angles $\cos\theta$ is equal to $\pm 1/\sqrt{3}$; thus, the asymmetry and the D parameter are directly related, *independent* of the β parameter: $D = \sqrt{3} A_{\text{CDAD}}(\theta_m)$. Consequently, the combined CDAD-parameter D {with the sign referring to the
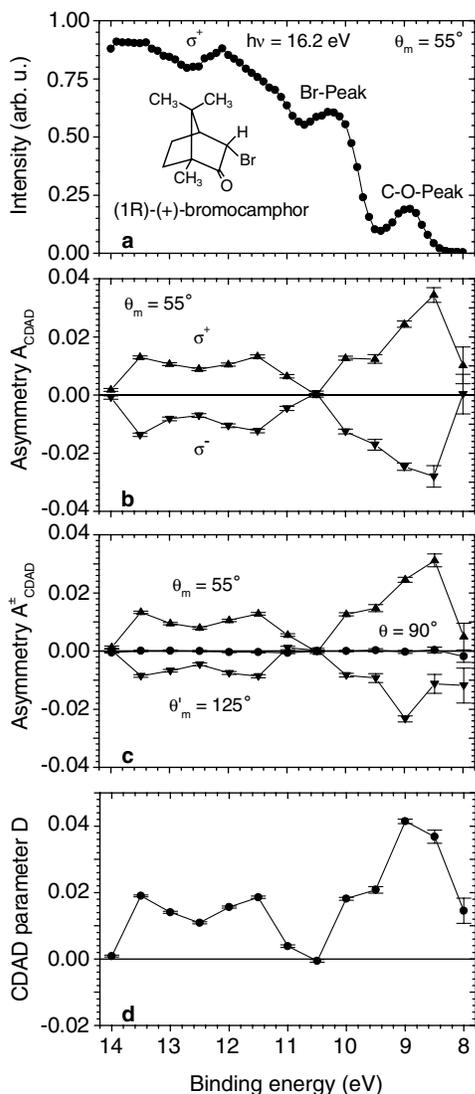
FIG. 2. Circular dichroism in the angular distribution for bromocamphor molecules. (a) Photoelectron intensity spectrum for the $[1R]$-$(+)$ enantiomers obtained at a photon energy of 16.2 eV at the magic angle θ_m. The inset shows the structural formula of $([1R]$-endo$)$-$(+)$-3-bromocamphor. (b) Corresponding asymmetry A_{CDAD} obtained from sequential measurements with $R(+)$ and $S(-)$ enantiomers with either σ^+ or with σ^- light, respectively. (c) Asymmetry $A_{\text{CDAD}}^{\pm}$ at three different angles as determined for $R(+)$ and $S(-)$ enantiomers with σ^+ and with σ^- light. (d) CDAD parameter D as derived by averaging the results obtained with σ^+ and with σ^- light at both magic angles.

$[1R]$-$(+)$ isomer$\}$ of endo-(3)-bromocamphor molecules resulting from *all* our measurements at both magic angles is given in Fig. 2(d). The magnitude of D is largest near the oxygen orbital at $E_{\text{bin}} = 9.0$ eV and is close to zero at the Br peak. It may be noted that the dichroism observed at 16.2 eV does not vanish when integrated over all binding energies examined. Similar measurements at higher photon energies (up to 23 eV) showed also some

negative values of D for some regions of E_{bin}; however, the integrated value remained always positive.

The physical origin of the CDAD for chiral molecules has been described before [4]; its principle dynamical dependence for the example of a carbonyl group was also discussed [5]. The D parameter depends on transition matrix elements and phase shift differences of two-center wave functions. Quite generally, the dichroism depends on the handedness of the initial and of the final states. In analogy to optical activity, a "screw sense" of the electron charge cloud from the respective molecular orbital considered can thus lead to a CDAD effect. In principle, by electron spectroscopy each initial state orbital can be analyzed separately to extract dynamical information on the ionization process. However, for the case examined here, because of the σ onset for binding energies above ca. 10 eV overlapped bands from many different bromocamphor orbitals are expected to contribute to the photoionization intensity displayed in Fig. 2(a). The corresponding dichroism [Fig. 2(d)] thus has to be viewed as the net result of several orbitals with fairly delocalized electron density spread out over large regions of the molecule. In contrast, the peak at 9.0 eV originates from a single orbital with a chiral electron distribution localized at several atoms in the vicinity of the carbonyl group. It is thus concluded that the chirality of the electron charge distribution in this fairly localized region leads to the observed strong CDAD asymmetry. On the other hand, the next peak due to emission from the lone-pair orbital near the Br atom (with unresolved spin-orbit splitting) results from a very strongly localized orbital, with electron density predominantly at the heavy bromium atom and the adjacent carbon atom. Therefore, it can be expected that this electron charge distribution has no strong chirality and, consequently, it is quite reasonable that there is no strong contribution to the dichroism from this electron orbital. This is consistent with the observed small D parameter in the energy region of the Br peak. This view on the handedness of the electron distributions involved is supported by molecular orbital calculations on camphor and bromocamphor using quantum chemistry computer codes [15,16]. In general, these calculations confirm the expectations outlined above on the shape and chirality of the outer electron orbitals.

The fairly large size of the observed dichroic effects can be explained by the fact that natural CDAD occurs already in electric dipole interactions [4–6], in contrast to natural CD which is due to electric dipole–magnetic dipole [3–6] or electric dipole–electric quadrupole [17] interference terms and typically distinctly smaller than 10^{-3} for VUV absorption spectra of free molecules [18,19]. Similarly, the gas-phase CDAD effects have been predicted [5] to be larger than the ED effects in elastic electron scattering. It may be expected that other chiral molecules, including amino acids, exhibit CDAD effects of similar magnitude as detected here for bromocamphor. This leads to important implications of our findings. Asymmetrically

distributed circularly polarized radiation which has been observed for the daylight variation on Earth [20] and for star formation regions in Space [21] might have played a major role in inducing a chiral asymmetry in terrestrial or, especially, in interstellar organic molecules relevant for the origin of life. In particular, asymmetric interactions in photon energy bands matching outer valence levels of chiral centers within the molecules can cause enantiomeric selection. Circular dichroism is an enantioselective effect of the kind required for the initiation of biomolecular processes which might ultimately have led to terrestrial homochirality — either in Space, with subsequent particle delivery to Earth, or in an Earth-based mechanism.

Our results show that already free, noninteracting unoriented molecules give rise to sizable dichroic effects in the VUV range, in contrast to other cases [3] where the dichroism is enhanced by crystalline order. Angle-resolved photoelectron spectroscopy of free chiral molecules with circularly polarized light can thus be regarded as a fundamental experiment in noncoincidence, spin-unresolved photoionization. Moreover, it represents a case of "true chirality" in Barron's terminology [22]. Because of the absence of mirror symmetry, when averaged over all molecular orientations, the dichroic effects do not cancel. This is reflected in the forward-backward asymmetry of the photoelectron angular distribution which gives rise to an asymmetric momentum distribution of the recoil ions. Therefore, when the handedness of the molecules is changed, the contribution to the momentum transfer to the ions reverses its sign due to the photoelectron asymmetry. Thus, even though there is no dichroism for the angle-integrated photoelectron current, this can lead to a separation of chiral molecules by photoionization for light incident from one direction.

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