Spin-Polarized Photoelectrons from Randomly Oriented Halogen Molecules by Unpolarized Radiation

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Molecular photoelectrons have been observed to be spin polarized even if ejected from a beam of randomly oriented molecules by unpolarized radiation. The polarization and the asymmetry parameter β for Br_2, I_2, CH_3Br, and CH_3I are compared with general predictions of a nonrelativistic model. While all available data of the differential cross section agree with this prediction, spin-polarization results partly disagree, manifesting the influence of the spin-orbit interaction upon the phases of molecular continuum wave functions.

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Recent theoretical[1-3] and experimental[4] investigations have shown that photoelectrons from unpolarized atoms can be highly spin polarized even if unpolarized or linearly polarized radiation is used. This effect of spin-orbit coupling prompted strong interest in the question whether molecules yield polarized photoelectrons. In atomic photoionization the direction of the polarization vector is given by the normal to the photoionization reaction plane as shown in Fig. 1. The photoelectron-emission experiment has to be performed energy and angle resolved in order to separate the fine-structure components and to meet the fact that the polarization is emission-angle dependent, showing different signs in the four quadrants.

In molecular photoionization one has to take into account that the intramolecular Coulomb interaction is usually much stronger than the spin-orbit interaction. Therefore, it was believed over a period of several years that an electron polarization cannot occur in the photoionization of a randomly oriented molecular beam, if one assumes a stronger influence of the intramolecular axis than of the geometry shown in Fig. 1 upon the direction of the spin-polarization vector. It is the purpose of this Letter to present experimental results of spin polarization in molecular photoionization. The data shown for different orbitals of four halogen compounds indicate that the existence of polarized molecular photoelectrons seems to be not exceptional. Furthermore, these polarization data as well as the results of the asymmetry parameter β also measured are compared with a theoretical prediction.

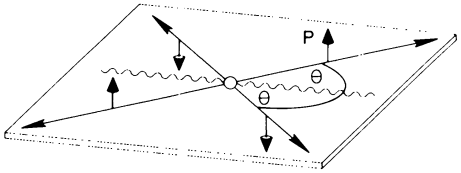

FIG. 1. Photoionization reaction plane. The spin-polarization vector of the photoelectrons $P(\theta)$ shows π periodicity, i.e., the results do not depend on whether the unpolarized radiation (wavy line) is incident from the left or from the right.

The photoionization experiments have been performed as in the atomic case, with unpolarized line radiation (Ar I 11.83 eV, Ne I 16.85 eV, and He I 21.22 eV) for the measurement of the spin polarization[4] and linearly polarized radiation for the study of the photoelectron angular distribution.[5] The spin polarization defined with respect to the reaction plane in Fig. 1 is given by

$$P(\theta)=\frac{N_\uparrow-N_\downarrow}{N_\uparrow+N_\downarrow}=\frac{\xi\sin 2\theta}{1-\frac{1}{2}\beta P_2(\cos\theta)},$$

where $N_\uparrow$ and $N_\downarrow$ are the numbers of photoelectrons with spin up and spin down; the denominator is the angular part of the differential cross section with the asymmetry parameter β and the second Legendre polynomial P_2. The spin parameter ξ is directly determined from the measured polarization at the magic angle $\theta_m=54°44'$ [i.e., $\xi=1.06\times P(\theta_m)$].

Figure 2 shows a typical photoelectron spectrum obtained for I_2 with He I radiation and a new gridless cylindrical-mirror–analyzer electron spectrometer designed chiefly for investigations of chemically aggressive vapors that sublimate as insulators. Photoelectron peaks originating from the three outer molecular orbitals[7] $p\pi_g$ (antibonding), $p\pi_u$ (bonding), and $p\sigma_g$ (bonding) have been resolved. The $^2\Pi$ peaks show a spin-orbit fine-structure splitting corresponding to the ionic states with $\Omega=\Lambda\pm\frac{1}{2}$, whereas there is no spin-orbit (i.e., spin-axis) interaction in the $^2\Sigma_g^+$ ionic state.

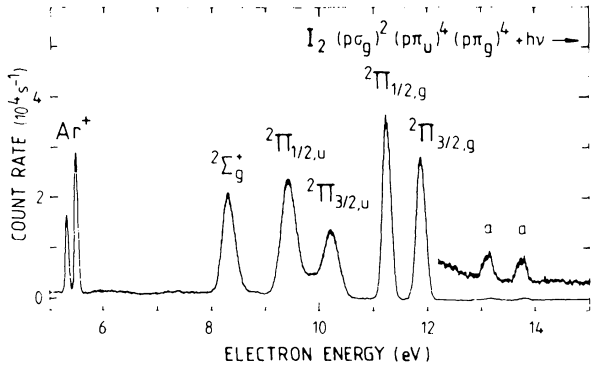

FIG. 2. He I (21.22 eV) photoelectron spectrum of I_2 at the magic angle; on the left are calibration peaks of argon ($Ar^+\ ^2P_{1/2,3/2}$), on the right the two small peaks denoted "*a*" correspond to ionization with He Iα light (Ref. 6) (23.07 eV).

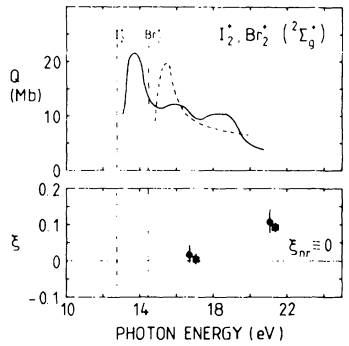

FIG. 3. Experimental results of the spin parameter ξ for photoelectrons leaving Br_2^+ (squares) and I_2^+ (circles) in their $^2\Sigma_g^+$ states in comparison with the corresponding partial cross sections Q of Ref. 7 (Br_2 dashed, I_2 solid). The vertical lines indicate the adiabatic ionization thresholds.

For diatomic molecules a general theoretical treatment of photoelectron spin orientation has been recently carried out by Cherepkov,[8] including spin-orbit effects in the final ionic states and in the electronic continuum. He also gives general predictions of the photoelectron polarization obtained neglecting the influences of the spin-orbit interaction in the partial waves of the continuum states as well as autoionization effects. This nonrelativistic model predicts a vanishing spin polarization for Σ peaks (no spin-orbit splitting) and for the case where the $^2\Pi_{1/2,3/2}$ peaks would not be resolved in the experiment. Since nonrelativistic theory yields the statistical value of $Q_{\Lambda+1/2}/Q_{\Lambda-1/2}=1$ for the branching ratio of the intensities (given by the areas of the peaks) the resulting ratio of the corresponding photoelectron polarizations simply is $\xi_{\Lambda+1/2}/\xi_{\Lambda-1/2}=-1$. For the angular asymmetry parameters the corresponding relation reads $\beta_{\Lambda+1/2}/\beta_{\Lambda-1/2}=1$.

Figure 3 (lower part) shows the measured values of ξ for the $^2\Sigma_g^+$ peaks of I_2 and Br_2. While at 16.8-eV photon energy the experiment yielded the nonrelativistic value of $\xi_{nr}=0$, there is a clear deviation from nonrelativistic theory at 21.2 eV. Although there was no fine-structure splitting in the photoelectron spectrum as shown in Fig. 2, the spin polarization was found to be different from zero for I_2 as well as for Br_2. The corresponding partial photoionization cross sections measured by Ref. 7 (bandwidth 0.8 nm), shown in the upper part of Fig. 3, are decreasing when going from 16.8 eV towards higher energies. This behavior for σ orbitals is in strong analogy to the well-known Fano effect[9] in *s*-subshell ionization of atoms, where a polarization of photoelectrons occurs, which is direct evidence of spin-orbit interaction in the continuous spectrum, leading to a phase-shift difference between the $\epsilon p_{1/2}$ and $\epsilon p_{3/2}$ outgoing partial waves. Being usually rather small, this difference can be strongly enhanced near the Cooper minimum of the cross section[10] or in autoionization regions.[11] The results of Fig. 3 appear to be an evidence for such a phase-shift effect in the continuum.

Figure 4 shows the results of the partial cross section[7] Q, the spin parameters $\xi_{3/2}$, $\xi_{1/2}$, and their ratio, as well as $\beta_{3/2}$ and $\beta_{1/2}$ for [Fig. 4(a)] the π_u orbital of Br_2 and I_2, and for the π_g orbital of [Fig. 4(b)] Br_2 and [Fig. 4(c)] I_2. In Figs. 4(a) and 4(b) $\xi_{3/2}$ and $\xi_{1/2}$ are different from zero and show opposite signs, whereas $\beta_{3/2}=\beta_{1/2}$ within the error limits. As expected, β is increasing with energy due to the variation of the well-known Coulomb-phase shift. The situation in Fig. 4(c) for $I_2(\pi_g)$ is very similar regarding the behavior of β, but quite different for the spin parameter ξ. While $\xi_{1/2}$ is 0.2 and 0.1 for 16.8 and 21.2 eV, respectively, $\xi_{3/2}$ vanishes for both energies, so that the ratio $\xi_{3/2}/\xi_{1/2}$ deviates considerably from the nonrelativistic prediction (chain line). The same behavior occurs for $Br_2(\pi_g)$ in the region between $^2\Pi_g$ and $^2\Pi_u$ thresholds [see Fig. 4(b)], most likely because—similar to the atomic case[11] —spin-orbit effects are "amplified" by autoionization resonances. It is worth noting that the measured points above the $^2\Sigma_g^+$ threshold could in principle also be influenced by autoionization, although the cross sections[7] do not show clear evidence of such features. In addition, we have also performed spin-polarization measurements yielding ξ for the outermost (lone pair) $2e$ orbitals of CH_2Br and CH_3I.

The behavior of spin polarizations and photoelec-

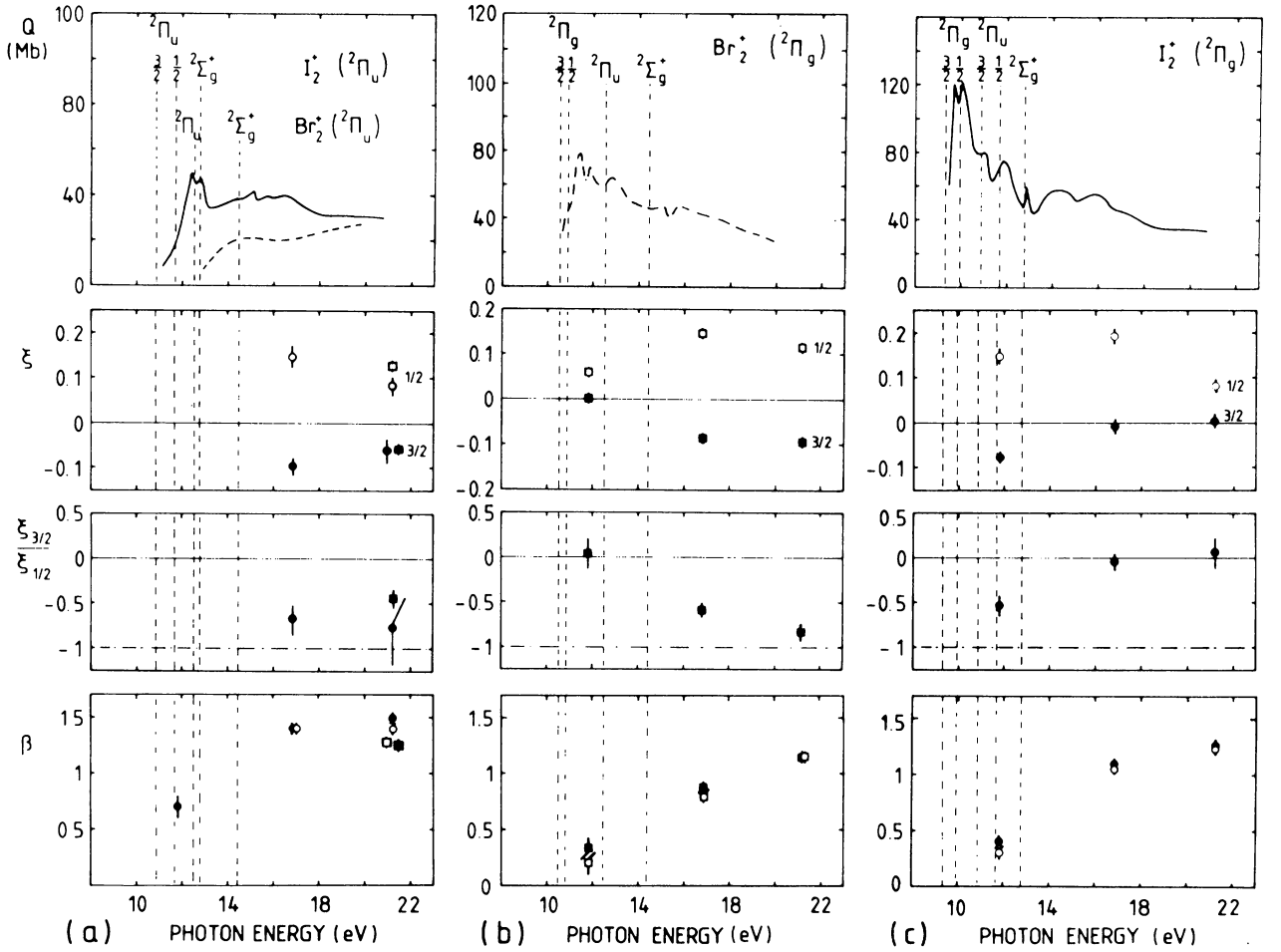

FIG. 4. Partial photoionization cross section Q (Ref. 7), spin parameter ξ, ratio of ξ, and asymmetry parameter β (a) for the Π_u peaks in the photoelectron spectrum of I_2 and Br_2, (b) for the Π_g peaks of Br_2, and (c) for the Π_g peaks of I_2 (Br_2, dashed curve, solid squares and open squares; I_2, solid curve, solid circles and open circles for $\frac{3}{2}$ and $\frac{1}{2}$, respectively). The vertical lines indicate the corresponding adiabatic ionization thresholds.

tron intensities for the outermost orbitals of Br_2, I_2, CH_3Br, and CH_3I is the most striking example studied in atomic and molecular photoionization with respect to the fact that photoelectron intensity data follow a certian theoretical prediction—in our case the nonrelativistic model—whereas spin polarizations do not. In order to demonstrate this, we have summarized in Fig. 5 all experimental ratios of the spin parameter ξ, the asymmetry parameter β, and the partial cross section Q for the spin-orbit components of these lone-pair orbitals. In all cases the ratio of β agrees with the theoretical prediction of $+1$ and the branching ratio $Q_{3/2}/Q_{1/2}$ (for I_2 only) is also identical to the statistical value over the energy range outside the threshold region. In contrast to this behavior of the differential cross section, the ratios of the spin parameters show a significant systematic deviation. While $\xi_{3/2}/\xi_{1/2}$ is close to -1 for CH_3Br (triangles) and not far from -1 for Br_2 (squares), it is zero for I_2 (circles), and tends to -2 for CH_3I (diamonds). Thus there is an increasing trend in the absolute value of this ratio when going from the heavier halogen to the heavier methyl halide. The extreme effects for I_2 and CH_3I most likely result from the high weight of the iodine atom, where the influence of spin-orbit interaction is more pronounced than at the lighter bromine atom. It does not seem to be surprising that these differences occur mainly at the outermost orbitals, because there are the nonbonding lone-pair orbitals, localized essentially at the (heavy) halogen atom. Consequently they are rather atomlike, whereas the inner bonding orbitals would not be expected to reflect the behavior of the single halogen atom in the molecule so strongly.

In summary, our results have shown that in

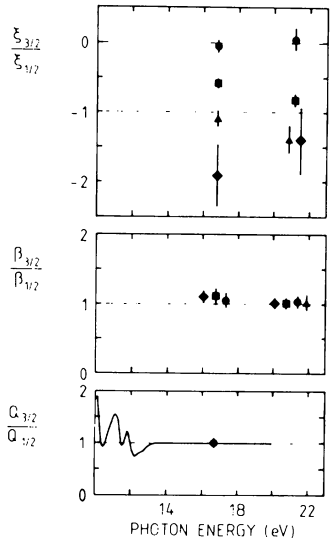

FIG. 5. Comparison of the ratios of spin parameter ξ, asymmetry parameter β, and partial photoionization cross section Q (Ref. 7, for I_2 only) with the nonrelativistic predictions of Ref. 8 (chain lines) for photoelectrons from the outermost orbitals of Br_2, I_2, CH_3Br, and CH_3I (squares, circles, triangles, and diamonds, respectively). The results correspond to photon energies of 16.85 and 21.22 eV.

molecular photoionization it does not suffice to compare measured and calculated differential cross sections in order to check the validity of a theory; this Letter indicates the necessity of performing spin-polarization experiments. In contrast to the cross sections, the spin polarizations are very sensitive to any phase shift of the continuum wave functions induced by the weak spin-orbit interaction.[12] Last, but not least, the results demonstrate that for future investigations in molecular photoionization one has to take into account that molecular photoelectrons may be polarized even in the photoeffect from a randomly oriented beam of unpolarized radiation.

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[12]The extreme sensitivity of ξ upon continuum spin-orbit interaction is a consequence of its quantum-mechanical nature, resting purely on interference of different partial continuum waves, i.e., on terms like $|d_i||d_j|\sin(\delta_i-\delta_j)$ with dipole matrix elements $d_{i,j}$ and corresponding phase-shift differences $\delta_i-\delta_j$ of continuum wave functions (cf. Refs. 1–4, 8, 10, and 11).