Spin polarization in the Coulomb ionization of optically active molecules

V. A. Onishchuk

Institute of Chemical Physics, Academy of Sciences of the USSR

It is shown that the electrons released by Coulomb ionization of optically active molecules should be polarized parallel (or antiparallel) to the direction of motion of the exciting charged particles, the polarization changing sign on passing from the L form of the material to the D form. For incident charged particle velocities $v \gg ac$, a polarization of the order of $\lambda ac(Z\alpha)^2/v$ is to be expected, where Z is the charge of the heaviest nucleus in the asymmetric center of the molecule, λ is a quantity that characterizes the asymmetry of that center, and α is the fine structure constant. A similar phenomenon should accompany photoionization, but in that case the polarization should be of the order of $\lambda a(Z\alpha)^2$.

PACS numbers: 34.50.Hc

1. An asymmetry in the interaction of a polarized charged-particle beam with optically active antipodes (enantiomers) has recently been predicted,[1,2] the degree of the asymmetry being found to be of the order of α^3 in Ref. 1 and the order of α^4 in Ref. 2 ($\alpha \approx 1/37$ is the fine-structure constant). There are effects, however, that also change sign on passing from the L form to the D form of the medium but do not depend on the polarization of the particle beam. For example, a magnetic field with a nonvanishing component in the direction of the beam should arise in an optically active medium.[3,4]

In this paper we discuss a new effect of this type and estimate its order of magnitude: the longitudinal (in the beam direction) polarization of electrons released in the ionization of optically active molecules by charged particles. The effect is as follows. In optically active molecules, the imaginary part of the product $\langle 0|\mathbf{d}|n\rangle\langle n|\boldsymbol{\mu}|0\rangle$, where $\mathbf{d}$ and $\boldsymbol{\mu}$ are the electric and magnetic dipole-moment operators, differs from zero for some of the electron transitions. In order of magnitude, we have

$$\mathrm{Im}(\langle 0|\mathbf{d}|n\rangle\langle n|\boldsymbol{\mu}|0\rangle) = \lambda e^2 a^2 \alpha. \tag{1}$$

Here e is the electron charge, a is the size of the chiral center of the molecule, and λ is the degree of its asymmetry. In the case of ionization by fast charged particles, as well as in the case of photoionization, the electrons of the molecules that undergo transitions are shifted on the average in the direction of the momentum of the exciting particle (or photon). In view of Eq. (1), therefore, the projection in that direction of the orbital angular momentum of the ejected electron (and thanks to the spin-orbit coupling, the corresponding projection of its spin) will differ from zero during the transition. When the L form of the material is replaced by the D form, the product on the left in Eq. (1) changes sign, so the polarization of the electrons must also change sign.

An optically active molecule has neither a plane of symmetry nor a center of symmetry and transform into its antipode under coordinate inversion. Since the effect under discussion changes sign on going from the L form of the material to the D form, it must also be odd in the coordinates of the ejected electron. Effects associated with the asymmetry of the molecule will manifest themselves most strongly in the electrons to which the energy transfer is smaller than or of the order of the ionization energy I. At such energies we may expand the ionization cross section in the parameter $qa \ll 1$, where q is the momentum transfer in units of $\hbar$. The spin-independent part of the cross section will be of the second order in qa, while the part that is linear in the spin will be of the third order. Hence the degree of polarization

$$\eta = \frac{\sigma(+)-\sigma(-)}{\sigma(+)+\sigma(-)}, \tag{2}$$

where $\sigma(\pm)$ is the cross section for ionization with the electron spin parallel (antiparallel) to the momentum of the perturbing particle, must be given by the formula

$$\eta \approx \frac{|\langle 0|\mathbf{d}|n\rangle\langle n|\boldsymbol{\mu}|0\rangle|qaB}{|\langle 0|\mathbf{d}|n\rangle|^2\alpha} \approx \lambda qa(Z\alpha)^2. \tag{3}$$

Here B is a quantity characterizing the spin-orbit coupling $[B \approx (Z\alpha)^2$, where Z is the charge of the heaviest nuclei in the chiral center of the molecule][6] and λqa is the projection of the orbital angular momentum of the electron, in units of $\hbar$, onto the direction of the momentum of the perturbing particle, averaged over the time of the transition.

For zero-angle scattering (we consider the projection of the spin onto the direction of the incident beam) and energy transfers of the order of I, we have $qa \approx v_0/v \approx \alpha c/v$, where v is the velocity of the perturbing particle and v_0 is (in order of magnitude) the velocity of the valence electrons. This is the value of qa for the case of Coulomb excitation; in the case of photoionization we have $qa \approx \alpha$. In view of what was said above,

$$\eta \approx \lambda ac(Z\alpha^2)/v \tag{4}$$

for Coulomb ionization, and

$$\eta \approx \lambda a(Z\alpha)^2 \tag{5}$$

for photoionization.

If the ionization is produced by a beam of heavy particles (much more massive than electrons), then

$\eta \approx \lambda (Z\alpha)^2$ provided that $v \sim v_0$. Then if we choose a material[7] for which $\lambda \sim 1$ that has a nucleus with $Z \gtrsim 50$ at or near the chiral center of the molecule we should obtain a polarization of the order of ten percent.

Actually, expressions (4) and (5) should also contain the ratio of the number of valence electrons in the chiral center to the total number of valence electrons, and as a result the effect will be several times smaller. Nevertheless the effect should be observable, at least in the case of Coulomb ionization.

In Sec. 2 below, the estimates obtained for the case of Coulomb ionization are confirmed by a more rigorous quantum mechanical treatment. It will be shown that the degree of polarization of the electrons may be expressed in terms of quantities that occur in the theory of optical activity. In the concluding stage it is shown, within the framework of the Condon model of optical activity,[8] that the expressions obtained actually do not vanish.

2. Let us show that the quantity η given by Eq. (2) actually differs from zero in the Born approximation. To do this we first replace all the cross sections in the expression for η by the total cross sections for one-electron inelastic excitation and then show that ionization makes the main contribution to difference between these cross sections.

The differential cross section for the transition from the ground state $|0\rangle$ to the state $|n\rangle$ has the form[6]

$$d\sigma_n = \frac{M^2 k'}{4\pi^2 \hbar^4 k} |\langle n|U(q)|0\rangle|^2 dO_n, \tag{6}$$

where

$$U(q) = \frac{4\pi e Q}{q^2} \sum \exp i\mathbf{q}\mathbf{r}_i. \tag{7}$$

in the case of electron transitions incident to Coulomb excitation. Here $\mathbf{q} = \mathbf{k} - \mathbf{k}'$, $\mathbf{r}_i$ is the radius vector of the i-th electron, M is the reduced mass of the system, and Q is the charge of the particle. The moduli of the wave vectors for the initial and final states (k and k', respectively) are related by the formula

$$k' = [k^2 - (2M/\hbar^2)(E_n - E_0)]^{1/2} = (k^2 - \varepsilon_{n0})^{1/2}. \tag{8}$$

At small scattering angles θ ($\theta \ll 1$) we have

$$q \approx [((E_n - E_0)/\hbar v)^2 + (k\theta)^2]^{1/2} \approx k[(v_0/v)^4 (m/M)^2 + \theta^2]^{1/2} \tag{9}$$

(m is the electron mass), from which it follows that the dependence of q on the energy E_n of the state $|n\rangle$ may be neglected when $\theta \gg m v_0^2 / M v^2$.

Let us take the spin-orbit coupling into account in Eq. (6). For simplicity we shall consider the spin-orbit coupling only in the ground state of the molecule, since it is strongest in that state. Retaining in Eq. (6) the part that is linear in the spin, we obtain

$$d\sigma_n' = \frac{2M^2}{(2\pi\hbar^2)^2} \frac{k'}{k} \mathrm{Re} \left(\langle 0|U^+(q)|n\rangle\langle n|U(q)\frac{1}{E_0 - H} V_{oL}|0\rangle \right) dO_n, \tag{10}$$

where $V_{oL} = A \sum L_i \sigma_i$ is the operator for the spin-orbit interaction, the coupling constant being given by $A = (Z\alpha)^2 R$, in which R denotes the atomic frequency unit.

Let us first consider scattering angles $\theta \gg m v_0^2 / M v^2$. Replacing dO_n by $q \, dq \, d\varphi / kk'$ in (10) and summing over n (using the fact that q is independent of E_n), we obtain

$$d\sigma' \sim \langle 0||U(q)|^2 \frac{1}{E_0 - H} \hat{V}_{oL}|0\rangle. \tag{11}$$

Since neither $|U(q)|^2$ nor $\hat{V}_{oL}$ contains odd terms in the coordinates, the contribution to the longitudinal polarization of the excited electrons from scattering at the angles being considered is negligibly small.[1]

When $\theta \ll m v_0 / M v$ (in this case we may have $\theta \gtrsim m v_0^2 / M v^2$) the condition $qa \ll 1$ is satisfied, where a is a quantity of the order of the size of the chiral center, so the exponentials in the expression for $U(q)$ may be expanded in series. On performing the expansion and assuming for simplicity that there is only one chromophoric electron in the chiral center, we obtain the following expression in the lowest order in the parameter qa:

$$d\sigma_n' = \frac{4}{q^3} \left(\frac{eQ}{hv} \right)^2 A \, \mathrm{Im} \left\{ \langle 0|(\mathbf{q}\mathbf{r})^2|n\rangle\langle n|(\mathbf{q}\mathbf{r})\frac{1}{E_0 - H} \mathbf{L}\boldsymbol{\sigma}|0\rangle \right.$$
$$\left. - \langle 0|\mathbf{q}\mathbf{r}|n\rangle\langle n|(\mathbf{q}\mathbf{r})^2 \frac{1}{E_0 - H} \mathbf{L}\boldsymbol{\sigma}|0\rangle \right\} dq \, d\varphi. \tag{12}$$

We take the z axis in the direction of $\mathbf{k}$, integrate Eq. (12) over φ from 0 to 2π and over q from $k - k' \approx \varepsilon_{n0}/2k$ to γ/a, where γ is a constant ≤ 1, and retain only the principal terms in v_0/v. As a result, we obtain

$$\sigma_n' \approx 2\pi \left(\frac{eQ}{hv} \right)^2 \frac{\varepsilon_{n0}}{k} A \ln \frac{2\gamma k}{a\varepsilon_{n0}} \mathrm{Im} \left\{ \langle 0|r^2 - z^2|n\rangle \right.$$
$$\left. \times \langle n|z\frac{1}{E_0 - H} L_z|0\rangle - \langle 0|z|n\rangle\langle n|(r^2 - z^2)\frac{1}{E_0 - H} L_z|0\rangle \right\} \sigma_z. \tag{13}$$

Terms containing the products $L_x \sigma_x$ and $L_y \sigma_y$ have been dropped since they vanish on averaging over the orientations of the molecules. Now we neglect the dependence on E_n of the argument of the logarithm, sum over n, and, after averaging over the orientations of the molecules, replace $r^2 - z^2$ by its approximate value $2r^2/3$; this yields

$$\sigma_{in}' = \frac{\sigma_{in}(+) - \sigma_{in}(-)}{2} = \frac{8\pi}{9} \left(\frac{eQ}{hv} \right)^2 \frac{A}{mv} \ln \frac{2\gamma k}{a\varepsilon}$$
$$\times \mathrm{Re} \left\{ \langle 0|(r^2\mathbf{p} - \mathbf{r}(\mathbf{pr} + \mathbf{rp})) \cdot \frac{1}{H - E_0} \mathbf{L}|0\rangle \right\}, \tag{14}$$

in which ε is an average excitation energy of the order of the ionization energy and m is the electron mass.

If we rewrite the product $-\mathbf{r}(\mathbf{p} \cdot \mathbf{r})$ in the form $3i\hbar\mathbf{r} - \mathbf{r}(\mathbf{r} \cdot \mathbf{p})$ we find that there arises in the expression for σ_{in}' an additive term containing a matrix element that may be expressed in terms of a quantity that occurs in the theory of optical activity:

$$3\hbar \, \mathrm{Im}\langle 0|\mathbf{r}\frac{1}{E_0 - H} \mathbf{L}|0\rangle = \frac{3mc}{e^2} \sum_{n \neq 0} \frac{\mathrm{Im}\{\langle 0|\mathbf{d}|n\rangle\langle n|\boldsymbol{\mu}|0\rangle\}}{E_0 - E_n}. \tag{15}$$

In order to find out how much the matrix element in curly brackets in Eq. (14) (which we denote by I_1) differs from the left hand side of Eq. (15) (I_2) we use the Condon model of optical activity[8] to estimate their magnitudes. In that model, the chromophoric electron is treated as an asymmetric oscillator moving in the field

$$V = (k_1 x^2 + k_2 y^2 + k_3 z^2)/2 + Axyz \tag{16}$$

with $k_1 \neq k_2 \neq k_3$. The term $Axyz$ is treated as a perturbation.

Choosing the $|000\rangle$ oscillator state as the ground state and performing some cumbersome calculations, we can show that the main contribution to I_1 comes only from the intermediate states for which n_i $(i = 1, 2, 3)$ is either zero or unity. In view of this, we have

$$I_1 \approx \frac{A(2+\sqrt{2})\hbar(\omega_1-\omega_2)(\omega_2-\omega_3)(\omega_3-\omega_1)}{16m^2(\omega_1+\omega_2+\omega_3)\omega_1^2\omega_2^2\omega_3^2}, \qquad (17)$$

whereas the exact model expression for I_2 has the form

$$I_2 = \frac{3A\hbar(\omega_1-\omega_2)(\omega_2-\omega_3)(\omega_3-\omega_1)}{4m^2(\omega_1+\omega_2+\omega_3)\omega_1\omega_2\omega_3(\omega_1+\omega_2)(\omega_2+\omega_3)(\omega_3+\omega_1)}. \qquad (18)$$

Since $\omega_1 \approx \omega_2 \approx \omega_3$, we have $I_1/I_2 \approx 2$. In other words, I_1 and I_2 are quantities of the same order, so we may write

$$\sigma_{1n}' \approx \frac{8\pi}{3mv}\left(\frac{eQ}{\hbar v}\right)^2 A \ln\frac{2\gamma k}{\varepsilon a}\sum_{n\neq 0}\frac{\mathrm{Im}\langle 0|\bar{r}|n\rangle\langle n|\mathbf{L}|0\rangle}{E_n-E_0}. \qquad (19)$$

For the total inelastic cross section $\sigma_{1n} = [\sigma_{1n}(+) + \sigma_{1n}(-)]/2$ we have the expression[6]

$$\sigma_{1n} = \frac{8\pi}{3}\left(\frac{eQ}{\hbar v}\right)^2 \ln\frac{\beta k}{\varepsilon a}\langle 0|r^2|0\rangle, \qquad (20)$$

where again β is a dimensionless constant $\leqslant 1$. Assuming that $\beta = 2\gamma$ and substituting $(Z\alpha)^2 R$ for A, we find that

$$\sigma_{1n}'/\sigma_{1n} \approx \lambda(Z\alpha)^2 v_0/v \approx \lambda(Z\alpha)^2\alpha c/v, \qquad (21)$$
$$\lambda = \mathrm{Im}\,(\langle 0|d|n\rangle\langle n|\mu|0\rangle)/\langle 0|d^2|0\rangle\alpha.$$

Here the state $|n\rangle$ is selected so that the electron transition $|0\rangle \rightarrow |n\rangle$ will be the one that has the greatest optical rotatory power.

Estimate (21) is also valid for the polarization of electrons ejected by Coulomb ionization. This can be most easily seen as follows. We introduce the factor ε_{n0}, in the form of a commutator with the "shortened" (i.e., not containing the spin-orbit interaction operator) Hamiltonian, into Eq. (13) under the sign of the matrix elements that do not contain the orbital angular momentum operator. Then we replace the states $|n\rangle$ by plane waves and integrate formally over the entire momentum space, making the same assumptions as we did in passing from Eq. (13) to Eq. (14). This leads us again to Eq. (14). It follows from this that the main contribution to σ_{1n}' comes from ionization. Thus, $\eta \approx \sigma_{1n}'/\sigma_{1n}$.

We have assumed that the chiral center has only one chromophoric electron. In the general case σ_{1n}' will be proportional to the number of valence electrons in the chiral center, while σ_{1n} will be proportional to the number of valence electrons in the entire molecule. This can reduce the estimate (21) of η by only a moderate factor and will not substantially alter the order of magnitude of the polarization.

---

[1] These angles contribute somewhat to the part of the differential cross section that is linear in the spin. At these angles, however, the cross section itself is small. The polarization of the electrons emitted at such angles may therefore turn out to be substantial, but it may be difficult to measure because the cross section is small.

[1] Ya. B. Zel'dovich and D. B. Saakyan, Zh. Eksp. Teor. Fiz. 78, 2233 (1980) [Sov. Phys. JETP 51, 118 (1980)].

[2] V. A. Onishchuk, Zh. Eksp. Teor. Fiz. 81, 59 (1981) [Sov. Phys. JETP 54, 25 (1981)].

[3] A. G. Sitenko and A. A. Kolomenskiĭ, Zh. Eksp. Teor. Fiz. 30, 511 (1956) [Sov. Phys. JETP 3, 410 (1956)].

[4] V. G. Baryshevskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. 20, 423 (1974), erratum, 21, 9 (1975) [JETP Lett. 20, 190 (1974), erratum, 21, 264 (1975)].

[5] M. V. Vol'kenshteĭn, Molekulyarnaya optika (Molecular optics), Gostekhizdat, M.-L., 1951, p. 670.

[6] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum mechanics), Fizmatgiz., M., 1963, pp. 297, 658 [Pergamon, 1968].

[7] U. Kozman, Introduction to Quantum Chemistry, (cited in Russ. Transl., IIL, M., 1960, p. 542).

[8] E. U. Condon, William Altar, and Henry Eyring, J. Chem. Phys. 5, 753 (1937).

Translated by E. Brunner