Polarization of Atomic Fluorescence Excited by Molecular Dissociation*

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Fluorescence from excited atomic fragments which arises from molecular dissociative processes can be shown in general to be polarized. The degree of polarization is related to the form of the anistropy in the angular distribution of dissociation products.

INTRODUCTION

Consider a molecule undergoing a dissociative process such that one of the fragments is left in an excited state from which it radiates. It is assumed in this particular case that dissociation occurs when the target molecule is subjected to impacts by projectiles having a preferred direction of incidence. For example, we might imagine the molecule being bombarded by a beam of photons, electrons, or heavy particles. We shall assume for simplicity that the excited fragment is an atom, although the following discussion could conceivably be modified to apply to cases where more complex excited fragments are involved. We then ask, under what conditions might the atomic emission of the excited fragment be polarized?

It will be shown here that two necessary conditions for polarization are: (a) an anisotropic spatial distribution of dissociation products, and (b) a preferential population of the magnetic sublevels of the excited fragments. Both of these conditions will be satisfied in many cases where dissociation proceeds via a single, well-defined repulsive molecular state.

Whenever preferred orientations for dissociation of the target molecule exist with respect to the incident beam direction, the angular distribution of fragments may be expected to be anisotropic. Simple symmetry arguments show that this will be the case for dissociation by photon and electron impact.1,2 Experimental confirmation of this effect has been obtained in a variety of photodissociation and electron impact dissociation studies of different diatomic molecules.3-7

Dissociation by heavy-particle impact in many cases might also be expected to result in anisotropic fragment distributions. This has been borne out in several recent experimental studies of molecular dissociation by fast ion- and neutral-particle impact.8-10 In general, the case of heavy-particle bombardment leading to dissociative excitation or chemiluminescent reactive scattering is expected to have associated with it complex angular distributions of products. However, the arguments presented here will still apply provided the fragments can be described as originating from repulsive molecular states of well-defined symmetry.

The second condition for polarization of atomic fluorescence is that the constituent atoms into which the molecule dissociates have selective M-state excitation. This condition will be fulfilled in many different dissociative processes. When two atoms are placed near each other, an inhomogeneous electric field arises in the direction of the line joining their nuclei, producing a space quantization of the angular momenta of the separated atoms. Thus, when two atoms are brought together to form a manifold of electronic molecular states, each molecular state is built up from atoms having well-defined projections of their angular momenta on the internuclear axis. Conversely, when two atoms separate from a repulsive molecular state, they depart from each other in well-defined M states with respect to the internuclear axis.

Rules for determining what types of molecular states result from given states of the separated atoms, and vice versa, have been worked out for diatomic molecules by Wigner and Witmer11 and by Mulliken.12 Generalization of these rules to the correlation between the electronic states of a polyatomic molecule and states of its separated atoms or groups of atoms has been discussed at length by Mulliken.13 Shuler14 has applied these correlation rules to the chemiluminescent processes

\[ \text{H} + \text{O}_2 \rightarrow \text{OH}^* + \text{O} \quad \text{and} \quad \text{O} + \text{H}_2 \rightarrow \text{OH}^* + \text{H} \]

in a particularly illuminating treatment. A general review of the derivation of molecular electronic states from those of other molecules is given by Mulliken.15

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7 J. Solomon, J. Chem. Phys. 47, 889 (1967). Anisotropic angular distributions have been detected by this method of "photolysis mapping" for various aliphatic carbonyl compounds as well as diatomic halogens, R. Berchoff (private communication, Chemistry Department, Columbia University, New York, N.Y.).
the separated atoms can be found in the comprehensive works of Herzberg.\textsuperscript{16}

For simplicity, we will concentrate our attention on diatomic molecules. We will assume that Russell-Saunders coupling is valid for the separated atoms as well as for the molecule. Different correlation rules apply for other coupling cases; these have been worked out by Wigner and Witmer and by others. Suppose two atoms A and B with L and S values equal to \( L_A \) and \( S_A \) and \( L_B \), \( S_B \) come together to form the diatomic molecule \( AB \), producing a space quantization of \( L_A \) and \( L_B \) with components \( M_{LA} \) and \( M_{LB} \) upon the AB internuclear axis. The resultant orbital angular momentum about the internuclear axis is given by

\[
\Lambda = |M_{LA} + M_{LB}|. \tag{1}
\]

Molecular states which differ only in the sign of both \( M_{LA} \) and \( M_{LB} \) have equal energies, provided \( M_{LA} \) and \( M_{LB} \) are nonzero. Such states correspond to degenerate \( \Lambda \)-doubling components. For \( \Lambda = 0 \) (\( \Sigma \) states) each combination, however, corresponds to a different molecular state.

If we assume the coupling of orbital angular moments of the atoms to the field between the nuclei is strong compared to the coupling between \( L \) and \( S \) (spin–orbit coupling), then the spin of each atom is uninfluenced by the presence of the other atom, and the two spin vectors \( S_A \) and \( S_B \) add to form a resultant spin \( S \), which determines the possible multiplicities of the molecular states. If the coupling between \( L \) and \( S \) in the separated atoms is strong compared to the coupling of \( L \) to the internuclear axis, a space quantization of \( J \) (which is the vectorial sum of \( L \) and \( S \)) rather than \( L \) results. We must then replace Eq. (1) by

\[
\Omega = |M_{J_A} + M_{J_B}|. \tag{2}
\]

where \( \Omega \) represents the electronic angular momentum along the internuclear axis (including spin).

To each molecular state of the \( AB \) molecule there corresponds a state or pair of states of the separated atoms A and B having fixed values of \( M_{LA} \) and \( M_{LB} \) with respect to the internuclear axis. In particular, only one of the following pairs of \( M_L \), values \( (0, \pm 1, \pm 2, \cdots, \pm L) \) for each atom can result from a given (repulsive) state of the \( AB \) molecule.\textsuperscript{18} This is a consequence of the fact that \( \Omega (\Omega) \) retains its meaning as a function of internuclear separation, even at close distances where the \( L \) and \( M_L \) values of the individual atoms are no longer defined. Thus molecular dissociation can be viewed as a highly efficient atomic M-state selector. This last statement, of course, should be qualified to apply to those dissociative processes in which one or a limited number of repulsive molecular states contribute to fragment production. We also note that the correlation rules we have been discussing are derived under the assumption of adiabatic motion of the nuclei, i.e., the nuclei are assumed to move in the electronic potential states of the molecule defined in the Born-Oppenheimer approximation. If the dissociation process cannot be regarded as adiabatic, the fragments may still separate in selectively excited \( M \) states, but our discussion is no longer valid.

**CALCULATION OF ATOMIC FLUORESCENCE POLARIZATION**

Let us now turn to the question of how polarization of the atomic radiation is quantitatively related to \( M \)-state selection and spatial anisotropies in the dissociation process. Let the beam direction be defined along the \( Z \) axis and the atomic emission be observed along the \( Y \) axis (see Fig. 1). The molecules are assumed to be randomly oriented, and the direction of the molecular axis is specified by the polar angles \( \theta \) and \( \phi \) shown in Fig. 1. It is important to distinguish the two axes present in this problem: the molecular axis, which serves as the quantization axis for defining the \( M \)-state projections of the separating atoms; and the beam axis, which serves as a laboratory reference axis for describing the angular distribution of products. Let an observer along the \( Y \) axis measure the components of the atomic emission polarized parallel and perpendicular to the beam direction, \( I^{||} \) and \( I^\perp \), along the \( Z \) and \( X \) axes, respectively. We then define the degree of polarization \( P \) in the usual manner,\textsuperscript{17}

\[
P = (I^{||} - I^\perp)/(I^{||} + I^\perp). \tag{3}
\]


\textsuperscript{18} When two separated atoms are brought together more than one \( \Sigma, \Pi, \Delta, \cdots \) state may be formed. However, when any one particular \( \Sigma, \Pi, \Delta, \cdots \) state of a diatomic molecule is separated into its two constituent atoms, each one of these atoms will have a projection of \( \pm M_{LA}, \pm M_{LB} \) upon the line of separation so that the absolute value of the sum of the projections will equal \( \Lambda(\Omega) \). See Eqs. (1) and (2).

The calculation of the degree of polarization is performed by: (a) evaluating the parallel and perpendicular polarization intensities for each possible orientation of the molecule and (b) averaging this over the distribution of quantization axes occurring in the dissociation process. The atomic transitions can be divided into two types: \( \Delta M = 0 \), where the transition-dipole moment lies along the quantization axis of the separating fragments; and \( \Delta M = \pm 1 \), where the transition dipole moment is located in a plane perpendicular to the quantization axis. For a selected \( M \) state of the atom, the relative probabilities for these two types of transitions are proportional to the square of the Clebsch-Gordan coefficients, \( \left| C(J'1J;M'm) \right|^2 \), where \( J' \) is the total angular momentum of the upper state; \( J \) refers to the lower state; and \( m \) is 0 or \( \pm 1 \) for the two different types of transitions, respectively. Let the probability for dissociating a molecule whose axis points into the infinitesimal solid angle element \( d\Omega = \sin\theta d\theta d\phi \) be given by \( f(\theta, \phi) d\Omega \). The intensity components for \( \Delta M = 0 \) and \( \Delta M = \pm 1 \) atomic transition types can be shown to be proportional to

\[
I^{(\Delta M = 0)} = \sum_{M't,-M't} \left| C(J'1J;M'0) \right|^2 \times \int_0^{2\pi} \int_0^\pi f(\theta, \phi) \cos^2 \theta d\Omega, \tag{4a}
\]

\[
I^{(\Delta M = 0)} = \sum_{M't,-M't} \left| C(J'1J;M'0) \right|^2 \times \int_0^{2\pi} \int_0^\pi f(\theta, \phi) \sin^2 \theta \cos^2 \phi d\Omega, \tag{4b}
\]

and

\[
I^{(\Delta M = \pm 1)} = \sum_{M't,-M't} \sum_{m=-1,1} \left| C(J'1J;M'm) \right|^2 \times \int_0^{2\pi} \int_0^\pi f(\theta, \phi) \sin^2 \theta \cos^2 \phi d\Omega, \tag{4c}
\]

\[
I^{(\Delta M = \pm 1)} = \sum_{M't,-M't} \sum_{m=-1,1} \left| C(J'1J;M'm) \right|^2 \times \int_0^{2\pi} \int_0^\pi f(\theta, \phi) (1 - \sin^2 \theta \cos^2 \phi) d\Omega. \tag{4d}
\]

Here we have summed over the \( \pm M' \) pairs of the excited atom selected by the dissociative process. The form of Eqs. (4a)-(4d) holds for whatever correlation rules apply between the molecular state and its separated atoms in a given dissociative process.

The distribution of quantization axes \( f(\theta, \phi) d\Omega \) can be shown\(^{18}\) to be nearly the same as the angular distribution of the products, provided the recoil energy of separating atoms is much larger than their rotational energy. This assumption, the case of axial recoil, is normally well satisfied since the rotational energy of diatomic molecules is on the order of 0.01 eV, whereas dissociation often proceeds to a sloping portion of the repulsive-potential curve which lies 0.1 eV or more above the infinite separation energy of the recoil partners. Henceforth, we will assume the angular distribution of products is equivalent to the distribution of quantization axes. Deviations from axial recoil behavior tend to blur the form of the angular distribution of products, and its effects have been considered in detail elsewhere.\(^{1,19}\)

The differential cross section \( f(\theta, \phi) \) may be readily expanded in terms of spherical harmonics:

\[
f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm} Y_{lm}(\theta, \phi). \tag{5}
\]

For molecular photodissociation the angular distribution has in general a dipolar form; the differential cross section may then be written

\[
f(\theta) = (\sigma/4\pi) \left[ 1 + \beta P_2(\cos\theta) \right], \tag{6}
\]

where \( \sigma \) is the total cross section;

\[
P_2(\cos\theta) = \frac{1}{2} (3 \cos^2 \theta - 1)
\]

is the Legendre polynomial of second order; and \( \beta \) is an asymmetry parameter. For linearly polarized light Eq. (6) holds if \( \theta \) is measured from the polarization vector of the light. Then \( \beta \) ranges in value from \( \beta = 2 \), where \( f(\theta) \sim \cos^2 \theta \), to \( \beta = -1 \), where \( f(\theta) \sim \sin^2 \theta \). For unpolarized light Eq. (6) still holds, provided \( \theta \) is now measured from the light-beam direction. The asymmetry parameter \( \beta \) is then reduced in range to \(-1 \leq \beta \leq 1\). In electron-impact dissociation, the leading term in the differential cross section also shows the same dipolar pattern, when \( \theta \) is measured from the electron-beam direction.\(^{19}\) For more complex dissociative processes, resort must be made in general to Eq. (5), although under certain simplifying assumptions (e.g.,

\[\begin{array}{llll}
\hline
M\text{-states} & \rightarrow ^1S & \rightarrow ^3P & \rightarrow ^1P & \rightarrow ^3D & \rightarrow ^1D \\
\hline
\hline
\text{selected} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\
\hline
^1S \rightarrow ^3P & \frac{3}{2} & \frac{3}{2} & \frac{3}{2} & \frac{3}{2} \\
\pm 1 & -\frac{3}{2} & \frac{3}{2} & -\frac{3}{2} & \frac{3}{2} \\
\pm 2 & -\frac{3}{2} & -\frac{3}{2} & -\frac{3}{2} & -\frac{3}{2} \\
\hline
\end{array}\]


\[^{19}\text{R. N. Zare, J. Chem. Phys. 47, 204 (1967).}\]
the validity of the Born approximation) the dipole form may still predominate.

To illustrate the calculation of atomic-fluorescence polarization we have considered several simple examples. We have supposed that the atomic fragment is created in an excited \(^1S, \, ^1P, \) or \(^3D\) state, from which it radiates to one of the lower states. By evaluating Eqs. (3) and (4) assuming the spatial distribution of atomic fragments given by Eq. (6), the polarization \(P\) can be expressed as a function of the asymmetry parameter \(\beta\). The results of these calculations are listed in Table I, and Fig. 2 pictures the dependence of \(P(\beta)\) for the particularly simple \(^1P\rightarrow^3S\) transitions. Inspection of Table I and Fig. 2 clearly indicates that sizable polarizations are often to be expected for anisotropic angular distributions, but no polarization of the atomic fluorescence can occur when the distribution is isotropic (\(\beta = 0\)).

It is a straightforward matter to include the presence of fine structure and/or hyperfine structure in calculating atomic-fluorescence polarizations from Eqs. (3) and (4). The effect upon the degree of polarization is generally to reduce its value. As an example, we calculate \(P(\beta)\) for the case of the \(^1P\rightarrow^3S\) transitions, assuming nuclear spin is not present, and assuming the correlation rules are such that \(M_L = 0\) rather than \(M_J\) states are preferentially populated by the dissociation process. We find for the \(^2P_{\frac{L}{2}}\rightarrow^3S_{\frac{1}{2}}\) fine-structure component that no polarization is possible for either \(M_L = 0\), or \(M_L = \pm 1\), whereas for the \(^2P_{\frac{3}{2}}\rightarrow^3S_{\frac{1}{2}}\) component, \(P(\beta) = \frac{3\beta}{(2\beta + 3)}\) for the former, and \(P(\beta) = -\frac{3\beta}{(40 - \beta)}\) for the latter.

It should also be realized that when fine and/or hyperfine structure is present, it is possible for molecular dissociation processes to unequally populate electronic-and/or nuclear-spin states of the separating atoms when the spin is strongly coupled to the internuclear axis. This again follows as a direct consequence of viewing molecular dissociation as a "Stern-Gerlach experiment."

We have assumed in all these calculations that depolarization due to collisions or to external fields is negligible. By the use of Euler angle transformations, Eqs. (4a)–(4d) can be readily generalized to an arbitrary observation direction. Polarization measurements made at different angles \(\theta, \phi\) with respect to the beam direction may permit the determination of more complex forms of the angular distribution than that given by Eq. (6).

**CONCLUSION**

In a previous paper\(^2\) it has been shown how the measurement of the Doppler line shape of atomic fluorescence could be used to determine the angular distribution of dissociation products. Here we have shown that the polarization of the atomic fluorescence can also be used in a similar manner. Polarization measurements are often simpler than line-shape profile studies, and thus this technique commends itself as a possible tool for investigating the mechanics of molecular dissociative processes.\(^30\)

The polarization calculations in the last section have been based on the assumption that dissociation proceeds from a unique known repulsive molecular state. However, there are several experimental observations which are consistent with the hypothesis that more than one repulsive-potential state of differing electronic symmetry participates in the dissociative process. When this is true, the preferential selection of \(M\) states is diminished; the anisotropies in the angular distribution tend to become smoothed out; and the extent of polarization is consequently reduced. For example, whereas Dunn and Kieffer\(^4\) found a strong anisotropy consistent with a dipolar form in the angular distribution of \(H^+\) arising from the dissociative ionization of \(H_2\), Kieffer and Van Brunt\(^5\) in studying the dissociative ionization of \(N_2\), report a nearly isotropic angular distribution, presumably due to the many different repulsive states of \(N_2\) that can contribute to dissociation.

To our knowledge there have been no observations of polarized atomic fluorescence accompanying molecular dissociation, although several attempts have been made to observe this effect. For example, in 1928 Mitchell\(^6\) investigated the atomic sodium emission resulting from the irradiation of \(NaF\) with ultraviolet light from different metallic arc and spark sources. He observed the atomic fluorescence parallel and perpendicular to the incident beam of unpolarized light, but failed to detect any difference in the Doppler line shapes. From

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20 Combined polarization and Doppler width measurements can provide, of course, additional information in favorable cases, but with a corresponding increase in experimental difficulties.


Observation of Metastable Ions in a Cycloidal Mass Spectrometer

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The line shapes that result from metastable-ion transitions in a cycloidal mass spectrometer are discussed and some half-lives of metastable ions are determined by a new method.

INTRODUCTION

The term "metastable ion" is often used rather loosely; however, we intend it to refer to an ion which leaves the source of a mass spectrometer as one entity and then breaks up in flight into a smaller charged fragment (daughter ion) and a neutral fragment. Rather little work has been done in the study of metastable ions using a cycloidal instrument. Robinson\(^1\) gives brief mention and Beynon\(^2\) discusses the general line shape to be expected. In the present paper it is shown how the lifetime of a metastable ion can be calculated from the line shape and the results of some experiments are compared with those obtained using sector instruments. Also, an example is presented that illustrates how the fragmentation pathway can be determined.


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