

Atomic and Molecular Fluorescence Excited by Photodissociation

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Molecular photodissociation often produces fluorescence from electronically excited fragment atoms or molecules, and maser action appears possible for some systems. The factors which govern the fluorescence line strength and the Doppler width are discussed briefly. Some qualitative features of dissociative electron impact processes are compared with photodissociation. A bibliography of photodissociation processes which lead to electronically excited species is included.

For optical masers using a gas as an active medium, most pumping mechanisms tried thus far have utilized transitions between atomic energy levels to achieve inverted populations of excited species.¹⁻³ Many molecular dissociative processes which produce excited fragments are known, however. These processes offer attractive possibilities for maser systems,⁴ since the pumping is irreversible, may be relatively broad-band, and can produce a strongly inverted population of excited atoms or molecules in either continuous or pulsed operation. Recently, maser action has been obtained from dissociative excitation of a variety of molecules by electron impact or by collisions with metastable rare gas atoms in gaseous discharge.⁵ Several proposals and preliminary experiments for masers based on photodissociation also have been reported.^{4,6,7,*}

In this paper we discuss the factors which govern the strength and shape of fluorescence lines that arise from excited fragments produced in molecular photodissociation. The mechanics of photodissociation can be treated in some detail, as shown elsewhere,⁸ and the principal features of interest for possible maser applications are likely to be qualitatively similar for other more complex dissociative processes. The break-up of the parent molecule only affects the optical gain via

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* *Note added in proof:* The first successful photodissociation laser has just been announced by J. V. V. Kasper and G. C. Pimentel, *Appl. Phys. Letters* **5**, 231 (1964). This laser employs the atomic iodine line at 1.3μ ($^2P_{1/2} \rightarrow ^2P_{3/2}$ transition) which is excited by flash photolysis of either CF_3I or CH_3I .

its influence on the Doppler line shape of the fluorescence, which is determined by the recoil trajectories of the product fragments.⁹ In practice other parameters may be much more critical. The Doppler width of the emission is important, however, since a larger width raises the threshold population required for maser action and adds greatly to the difficulty of selecting a single mode.^{1,4}

General Requisites for Maser Action^{1,10}

The optical gain coefficient of a maser medium is simply the negative of the familiar spectroscopic absorption coefficient. Thus, for a line of Gaussian shape which is primarily Doppler broadened the gain coefficient at the center of the line is given by¹¹

$$\alpha = \left(\frac{\ln 2}{16\pi^3} \right)^{1/2} \frac{g_2 A_{2 \rightarrow 1} n}{c\nu^3 (\Delta\nu_D/\nu)}, \quad (1)$$

where

$$n = \frac{N_2}{g_2} - \frac{N_1}{g_1}$$

and

- N_1, N_2 = populations (molecules/ml) in lower (1) and upper (2) maser levels,
- g_1, g_2 = statistical weights of levels,
- $A_{2 \rightarrow 1}$ = Einstein coefficient for spontaneous emission (sec^{-1}),
- ν = transition frequency (cm^{-1}),
- $\Delta\nu_D$ = Doppler width, half-width at half maximum (cm^{-1}),
- c = velocity of light (cm/sec).

Positive gain, or net stimulated emission, requires a population inversion ($N_2/g_2 > N_1/g_1$). It implies that the light intensity in the absence of losses would grow by a factor of $e^{\alpha l}$ with each traversal of the maser resonator. This must be sufficient to overbalance the

loss mechanisms if maser action is to occur. With present technology, the losses in gas masers amount to only a few percent per meter, and thus $\alpha \lesssim 5 \times 10^{-4} \text{ cm}^{-1}$ is the rule-of-thumb criterion for feasibility of maser action.

The population inversion required to achieve this gain is determined solely by the strength and Doppler width of the maser fluorescence line. In Eq. (1) the ratio

$$g_2 A_{2 \rightarrow 1} / \nu^3 = (64\pi^4 / 3h) S(2 \rightarrow 1) \quad (2)$$

is proportional to the dipole line strength, given by

$$S(2 \rightarrow 1) = \sum_{ij} |\mu_{2j \rightarrow 1i}|^2, \quad (3)$$

where $\mu_{2 \rightarrow 1}$ is the transition dipole moment matrix element and the summation is over all combinations of degenerate sublevels in the upper and lower states. For an electronic transition in an atom,¹²

$$S(2 \rightarrow 1) = 2.13 \times 10^6 (f/\nu), \quad (4)$$

where f is the oscillator strength, S is expressed in D^2 units ($D = \text{Debye unit} = 10^{-18} \text{ esv}$), and ν in cm^{-1} . The fractional Doppler width, $\Delta\nu_D/\nu$, is simply proportional to the average thermal velocity of the atoms, if the maser medium is an atomic vapor, and

$$\Delta\nu_D/\nu = [(2kT/m)\ln 2]^{1/2}/c, \quad (5)$$

where k is the Boltzmann constant, T is the absolute temperature, and m is the atomic weight. The width can be much larger for a photodissociation maser, since in the break-up of the parent molecule the fragment which emits the maser line may acquire a large recoil velocity; however, as discussed below, in favorable cases other features can be exploited to offset this.

The optical gain coefficient in cm^{-1} units thus may be written as

$$\alpha = 3.91 \times 10^{-19} n S(2 \rightarrow 1) / (\Delta\nu_D/\nu). \quad (6)$$

For a strongly allowed electronic transition in an atom ($S \sim 25D^2$, corresponding to $f \sim 0.5$ and a spontaneous radiative lifetime $1/A_{2 \rightarrow 1} \sim 10^{-7}$ sec to 10^{-8} sec in the visible region) with a typical Doppler width ($\Delta\nu_D/\nu \sim 7 \times 10^{-7}$, corresponding to $T = 400^\circ\text{K}$ and $m = 100 \text{ gm/mole}$) the gain is $\alpha \sim 10^{-12} n \text{ cm}^{-1}$ and hence the minimum population inversion required for maser action is about $n \gtrsim 10^8$ molecules/ml. It will be seen that, if the optimal specifications could be met, a population inversion of the same order of magnitude would be sufficient for a photodissociation maser.

Fluorescence Line Strength

Molecular dissociation processes which produce an excited atom rather than an excited molecular fragment will in general enjoy a substantial but not necessarily overwhelming advantage in terms of the threshold condition for maser action. In fluorescence from an excited atom (see Table II), all the intensity is usually confined to one line or to a few fine structure components. In fluorescence from a molecule (see Table III), the intensity may be thinly spread over many fre-

quencies, since (a) the total population of molecules in the excited electronic state may be distributed over many vibrational (v' quantum number) and rotational (J' quantum number) levels and (b) from each of these transitions to many (v, J) levels of the ground electronic state may be possible.

In fortunate cases (a) may be partially offset because the dissociation process may strongly favor a narrow range of (v', J') levels. This occurs for the excited OH^* radicals produced by photolysis of H_2O , for example,¹³ but there are no rules to suggest when such concentration might be expected.

The distribution of line strength due to (b) can be estimated from standard spectroscopic theory.^{14,15} For each of the individual vibration-rotation components of an electronic transition, the line strength can be approximated as

$$S(2, v', J' \rightarrow 1, v, J) \simeq S(2 \rightarrow 1) S(v' \rightarrow v) S(J' \rightarrow J), \quad (7)$$

where

$$\sum_v S(v' \rightarrow v) = 1, \quad (8a)$$

$$\sum_J S(J' \rightarrow J) = 2J' + 1, \quad (8b)$$

and

$$\sum_{v,J} S(2, v', J' \rightarrow 1, v, J) = (2J' + 1) S(2 \rightarrow 1). \quad (8c)$$

Here the electronic factor, $S(2 \rightarrow 1)$, is comparable to the strength of an atomic line and is related to the molecular oscillator strength via Eq. (4).^{15,16} The vibrational factor, $S(v' \rightarrow v)$, is called the Franck-Condon factor; it is the square of the overlap integral for the initial and final vibrational wavefunctions. The rotational factor, $S(J' \rightarrow J)$, is usually denoted by S_J and called the Hönl-London factor; it is the square of the rotational transition moment summed over the magnetic quantum numbers M' and M .

Except for small J , the S_J factors are approximately proportional to $g_{J'} = 2J' + 1$ or $g_J = 2J + 1$ (and $g_{J'} \simeq g_J$), the orientational degeneracy of the rotational angular momentum. Thus, for a linear molecule without electronic orbital angular momentum ($\Lambda_1 = \Lambda_2 = 0$), $S_J \simeq \frac{1}{2}g_J$ for both P and R branch transitions and $S_J = 0$ for Q branches, whereas with electronic angular momentum (Λ_1 and/or $\Lambda_2 \neq 0$) $S_J \simeq \frac{1}{4}g_J$ for P and R branches and $S_J \simeq \frac{1}{2}g_J$ for Q branches.¹⁷ The factors of $g_{J'}$ or g_J cancel versus those which appear in the degeneracy factors g_2 and g_1 in Eqs. (1) and (6), and hence for fairly large J we may simply replace these factors by unity everywhere.

With these approximations, the relative optical gain for the various $v', J' \rightarrow v, J$ lines within the electronic transition is essentially just proportional to the Franck-Condon factor and the population difference,

$$\alpha_{rel} \simeq S(v' \rightarrow v) [(N_{2v'J'} / g_2) - (N_{1vJ} / g_1)]. \quad (9)$$

Here a factor of 2 is to be inserted in the case of an allowed Q branch.

As seen in Eqs. (7) and (8), aside from the rotational factors, the total strength associated with each progression of $v' \rightarrow v$ lines originating from a specified upper

v' level is comparable to that in an atomic line. Often the Franck-Condon factor puts most of the intensity in one or two members of each progression. This always will occur if a system is chosen in which the potential curve for the upper electronic state lies almost directly above that for the lower state. This configuration is quite common. The molecular systems for which pulsed maser action recently has been observed in gas discharges, including the First Positive¹⁸ and Second Positive¹⁹ bands of N_2 and the angstrom bands of CO,^{20,21} are all prime examples; for these the difference in the equilibrium internuclear distance for states 1 and 2 is only about 0.1 Å or less. Furthermore, a comparison with theoretical Franck-Condon factors²² available for the First and Second Positive systems of N_2 shows that for each v' only the one or two $v' \rightarrow v$ bands with the largest Franck-Condon factors exhibited stimulated emission.

The rotational transitions likely to show optical gain are likewise apparent from Eq. (9). Because of the approximately twofold advantage in the Hönl-London factor, maser action would be expected to appear first for Q -branch lines, if they are allowed. This is observed in the angstrom bands of CO. If only P - and R -branch transitions are allowed, essentially only the population factor matters. In the case that collision processes maintain the distributions over both the J' and J levels in approximate thermal equilibrium, it is shown readily that the population difference favors P -branch transitions.²³ This is observed in the vibration-rotation bands of the ground electronic state of CO_2 , for which only P -branch transitions are found to show maser action.²⁴

As seen in Eqs. (6) and (7), if the electronic oscillator strength and the Doppler line-width parameters are comparable, the minimum population inversion required for maser action in molecular fluorescence is in typical favorable cases no more than about an order of magnitude higher than in atomic fluorescence, since $S(v' \rightarrow v) \simeq \frac{1}{3}$ to $\frac{1}{2}$ and $S(J' \rightarrow J)/g_J = \frac{1}{4}$ to $\frac{1}{2}$. However, again this refers to a particular $(v', J') \rightarrow (v, J)$ transition, and since many other levels may be populated the total concentration of electronically excited species may have to be much higher than for a maser employing atomic fluorescence.

Fluorescence Line-Width

The Doppler width of fluorescence lines excited by molecular dissociation processes is determined by three factors which may be considered separately: (a) the thermal motion of the parent molecule; (b) the magnitude of the recoil velocity (relative to the center of mass of the parent molecule) of the atomic or molecular fragment which emits the fluorescence line; and (c) the angular distribution of the recoil velocity vectors.

Contribution (a) is usually the least important. It is given by Eq. (5), with m the mass of the parent molecule, and thus is less than the Doppler broadening for an atomic gas at the same temperature by a factor equal to the square root of the ratio of the mass of the atom to that of the parent molecule.

Contribution (b) depends on the final relative kinetic energy E of the fragments A^* and B formed in dissociation of the parent molecule AB . According to an approximate form of the Franck-Condon principle, this is given by^{8,9}

$$E = h\nu_p + E_{AB} - T_{AB} + \frac{1}{2} (L^2/\mu r_0^2). \quad (10)$$

Here $h\nu_p$ is the energy of the pumping light (or electrons); E_{AB} is the energy of the initial vibrational level of AB ; and T_{AB} , the threshold energy, is the sum of the dissociation energy of the AB bond (measured from the zero-point vibrational level) and the electronic excitation of the excited fragment A^* . The remaining contribution is centrifugal energy arising from the rotational angular momentum L of the AB molecule; μ is the reduced mass, $m_A m_B / m_{AB}$, and r_0 is the internuclear distance at which the electron jump occurs. The probability distribution for r_0 for any initial vibrational level of AB is obtained from the vibrational wavefunction. The pumping transition is continuous, and its shape is determined by the r_0 -distribution and by $V(r)$, the repulsive potential energy curve for the unstable excited AB^* molecule, since $h\nu_p + E_{AB} = V(r_0)$.

The recoil energy E can be minimized by pumping at an energy only slightly above the threshold for dissociation. However, since the most populated vibrational levels of the ground electronic state usually lie under a strongly sloping portion of the upper, repulsive potential curve, electronic jumps from these levels only occur for pumping at energies well above the threshold. Therefore pumping near the threshold involves a drastic sacrifice of intensity and is impractical. Also, even at the threshold, the thermal distribution of rotational energy still contributes to E via the centrifugal term in Eq. (10).

Another means of limiting the recoil velocity of the fragment A^* which emits the fluorescence is to use a molecule in which B is much lighter than A^* so that most of the recoil velocity will be carried away by B . The recoil velocity of A^* is given by

$$\left(\frac{2m_B}{m_A m_{AB}} \right)^{1/2} E^{1/2}. \quad (11)$$

Unfortunately, other requirements often conflict with this.

For some polyatomic molecules it is possible that an appreciable part of the energy released in the dissociation may appear as internal vibrational or rotational excitation of the fragments rather than in the translational recoil energy. Equation (10) as written applies to a diatomic molecule. For dissociation of a polyatomic molecule it is probably still a useful approximation but since either or both fragments may be polyatomic, E must be replaced by $E + E_{\text{int}}$, where E_{int} is the total vibrational and rotational excitation of the fragments.

The photodissociation of CH_3I in the 2500 Å region produces excited I^* atoms²⁵ and hence offers an example which enjoys a substantial advantage from the kine-

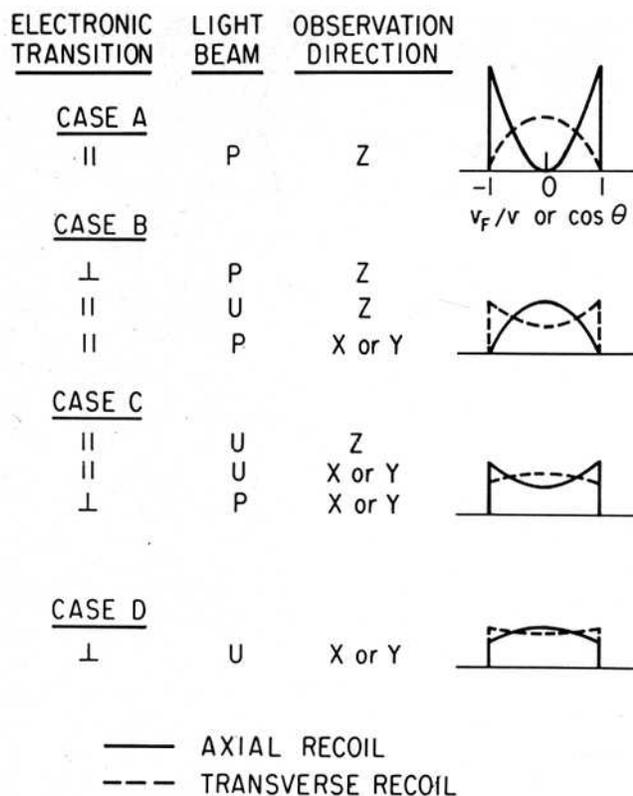


Fig. 1. Form factors for angular distribution of product fragments and Doppler shape of fluorescence lines. *P* denotes polarized light with the electric vector along the *Z* axis and *U* unpolarized light incident along the *Z* axis; v_F/v is the ratio of the component of the recoil velocity v_F along one of the axes ($F = X, Y, Z$) to the total recoil velocity and θ is the polar angle measured from the *Z* axis. The angular distributions peak at right angles to the incident beam in those cases in which the direction of recoil coincides with the transition dipole moment (axial, parallel; or transverse, perpendicular); otherwise the distributions peak forward and backward along the beam.

matic factor and probably also from vibrational excitation of the CH_3 group. Recently, stimulated emission in the ${}^2P_{1/2} \rightarrow {}^2P_{3/2}$ iodine atom transition at 7600 Å has been obtained⁷ by flash photolysis of CH_3I . From Eq. (10), the energy release is $E + E_{\text{int}} \simeq 1.6$ eV (with $h\nu_p = 4.87$ eV, $E_{AB} = 0$, $T_{AB} = 2.35 + 0.96$ eV). The methyl group in CH_3I is tetrahedral, whereas the free methyl radical is planar or nearly planar²⁶; consequently the Franck-Condon principle suggests that the out-of-plane bending mode will be highly excited. A rough estimate²⁷ is $E_{\text{int}} \simeq 0.5$ eV. Thus $E \sim 1.1$ eV, and the small mass factor in Eq. (11) permits only about 10% of this to appear in translational recoil of the I^* atom. The corresponding Doppler width is $\Delta\nu_D/\nu = 1.2 \times 10^{-6}$, only about a factor of 2 larger than the thermal Doppler broadening.**

** The total Doppler width is appreciably less than the sum of the width for thermal motion plus that from recoil, since a vector average is involved. Reference 9 gives a detailed calculation. The thermal contribution may be neglected when the recoil motion is more than two or three times the most probable thermal velocity.

For the analogous photolysis of HI the kinematic factor is of course extremely favorable. This also produces excited ${}^2P_{1/2}$ iodine atoms²⁸ (although the concurrent yield of ground state ${}^2P_{3/2}$ atoms is substantial) but stimulated emission has not been reported yet. For pumping at 2537 Å the calculated Doppler width of the iodine atom fluorescence is only $\Delta\nu_D/\nu = 3 \times 10^{-7}$.

Finally, in principle the angular distribution factor (c) could sometimes be exploited. As indicated in Fig. 1, under certain conditions the angular distribution of recoil velocity vectors will be quite anisotropic,^{9,29} and therefore the Doppler width may be minimized by viewing the fluorescence at right angles to the preferred direction of recoil.

The anisotropy is another consequence of the Franck-Condon principle. Since the position and momenta of the atomic nuclei remain nearly constant during the electronic jump and the excited electronic state ordinarily dissociates in a time short compared with a rotational period of the molecule, the distribution of trajectories of the dissociation fragments reflects the initial orientation of the parent molecule. If the excitation occurs in some definitely nonisotropic way, as by absorption from a beam of light or by impact of an electron beam, the dissociation probability will, in general, favor a particular range of orientations and thus the angular distribution of fragments will show a corresponding anisotropy.

For photodissociation the angular distribution can be obtained from a simple semiclassical treatment.⁹ The absorption probability is greatest when the transition dipole moment \mathbf{u} of the molecule is aligned with the electric vector $\boldsymbol{\epsilon}$ of the light beam, and the calculation amounts to averaging the angular dependence of the transition probability, proportional to $|\mathbf{u} \cdot \boldsymbol{\epsilon}|^2$, over all rotational orientations of the molecule. The fluorescence line shape then may be derived by projecting the distribution of recoil vectors along the direction of observation. Several distinct cases appear. As indicated in Fig. 1, these are specified by the *polarization* of the exciting beam of light; by the orientation of \mathbf{u} , which is taken as either *parallel* or *perpendicular* to the molecular axis (the *A-B* bond); by the *direction of observation* of the fluorescence; and by the direction of departure of the fragment A^* , which is regarded as undergoing either *axial recoil* along the initial direction of the molecular axis, or *transverse recoil* perpendicular to it.

In the most anisotropic case (shown as A in Fig. 1), the incident light is plane polarized, the electronic transition dipole and the product recoil direction are parallel to the molecular axis, and the fluorescence is viewed along the direction of the electric vector. The products then peak forward and backward along the direction of the electric vector and hence the Doppler line shape of the fluorescence is bimodal. The anisotropy is much weakened if one or more of these specifications is relaxed (shown as cases B, C, D in Fig. 1).

To obtain the angular distribution and line shape for a given photodissociation process, the form factors for

the special cases shown in Fig. 1 must be compounded with the distribution of center-of-mass velocity vectors of the parent molecule; the distribution in magnitude of the recoil velocity, which depends on the intensity profile of the pumping light and the shape of the potential energy curves; and the mixing of axial and transverse recoil, which is essentially governed by the centrifugal repulsion contribution in Eq. (10). Except in very special situations, the contribution from the axial recoil will be preponderant, and the line shapes of Fig. 1 (solid curves) are merely somewhat blurred and broadened.

Detailed calculations for the photodissociation of NaI to produce excited Na* are described elsewhere.^{8,9} Although the recoil energy carried by the Na* atom is about 0.25 eV, the calculated fluorescence width is only about $\Delta\nu_D/\nu = 10^{-6}$ for case A, as the effective Doppler width is that of just one of the two lobes. For case B, the width is about four times larger and for isotropic recoil about six times larger. For atomic Na vapor at the same temperature, the Doppler width would be $\Delta\nu_D/\nu = 2 \times 10^{-6}$.

As indicated by these calculations, the anisotropy in the angular distributions is not pronounced enough to make it worthwhile to attempt to exploit this to offset part of the recoil broadening. Only in case A is there a substantial advantage in the Doppler width; however, this would be cancelled by a loss of intensity, since case A requires the use of polarized light. Furthermore, for NaI and many other molecules of possible interest for photodissociation masers, the dissociation occurs via a bundle of unresolved repulsive states of various symmetry types. Since both parallel and perpendicular transitions contribute, and probably with comparable intensity,³⁰ the angular distribution is likely to be practically isotropic.

There have been many experimental studies of atomic or molecular fluorescence excited by molecular photodissociation (Tables II and III). In several cases, the presence of large Doppler broadening due to recoil has been established. However, an early study of the NaI photodissociation by Mitchell appears to be the only attempt that has been made to observe anisotropy in the angular distribution of products.³¹ He viewed the fluorescent light through a sodium vapor filter, which transmitted only that part of the light for which the Doppler shift exceeded the absorption width of the filter. As he found no observable difference in the intensity of this filtered light emitted parallel and perpendicular to the incident beam, Mitchell concluded that the angular distribution of products was isotropic. Recently, Hanson has resolved the $^2P_{3/2}$ and $^2P_{1/2}$ components of the sodium atom D line fluorescence and finds these have the same Doppler width³²; this is also indirect evidence for an isotropic angular distribution.⁸

The anisotropy of the photodissociation probability has been confirmed and exploited in an elegant experiment on the H_2^+ molecular ion by Dehmelt and Jefferts.³³ This is not concerned with angular distributions or fluorescence, but with the total photodissociation rates for the various spectroscopic states. The

Table I. Comparison of Dissociative Electron Impact with Photodissociation

Electronic transition	Angular distribution ^a	Fluorescence ^a	
		Z	X or Y
Momentum transfer along beam ($\kappa = 0^\circ$)			
$\Delta\lambda = 0$	A	A	B
$\Delta\lambda \neq 0$	B	B	C
Momentum transfer transverse to beam ($\kappa = 90^\circ$)			
$\Delta\lambda = 0$	B	B	C
$\Delta\lambda \neq 0$	C	C	D

^a Here A to D designate form factors which are expected to resemble qualitatively those given for axial recoil in Fig. 1. The electron beam is incident along the Z axis.

orientation dependence of these rates provides a means to accumulate molecules selectively in particular magnetic substates and to monitor the population changes induced by absorption of radiofrequency radiation.

Comparison of Electron Impact with Photodissociation

Pumping by dissociative electron impact rather than photodissociation is likely to affect primarily the population factor n in the optical gain coefficient, Eq. (6). The line strength S for a given fluorescence transition of the excited product A^* is, of course, independent of the excitation process, and since the recoil velocity is again governed by the Franck-Condon principle, the Doppler width is the same unless the angular distribution of A^* is appreciably changed for electron impact.

If the form factors of Fig. 1 were replaced by functions appropriate to electron impact, a calculation of the product distributions and fluorescence line shape would proceed just as for photodissociation. However, even in the Born approximation limit, the evaluation of the orientation dependent transition probability $P(\phi, \theta, \psi)$ which replaces $|\mathbf{u} \cdot \mathbf{e}|^2$ is a formidable problem. Dunn²⁹ has given a qualitative characterization of the anisotropies of $P(\phi, \theta, \psi)$ based on a symmetry analysis for the two configurations in which the momentum transfer vector \mathbf{K} is aligned either parallel or perpendicular to the molecular axis. For many types of electronic transitions $P(\phi, \theta, \psi)$ vanishes for one or another of these configurations, and then the dissociation products will peak parallel or perpendicular to \mathbf{K} (only axial recoil is considered). In the case of dissociative electron capture or attachment, \mathbf{K} is identical to the propagation vector \mathbf{k} of the electron beam. For dissociative excitation or ionization, \mathbf{K} will have a range of orientations relative to \mathbf{k} (and described by an angle κ), and the factors involved in estimating this also are discussed by Dunn.

The peaking of the $P(\phi, \theta, \psi)$ functions with respect to \mathbf{K} may be expected to resemble qualitatively the peaking with respect to the electric vector which appears in photodissociation. Thus it is useful to note the connections given in Table I, which obtain when \mathbf{K} is parallel ($\kappa = 0^\circ$) or perpendicular ($\kappa = 90^\circ$) to \mathbf{k} . These connections become quantitative relations at

Table II. Studies of Atomic Fluorescence Excited in Molecular Photodissociation

Parent molecule	$\lambda_F(\text{\AA})$	$\lambda_P(\text{\AA})$	D_0^0 (eV)	References
LiBr	6708	2000 ± 90	4.35 ± 0.3	13, 14, 15
LiI	6708	2320 ± 85	3.5 ± 0.2	13, 14, 15
Na ₂	5896/90	4350 ± 50	0.75 ± 0.03	8, 10
NaBr	5896/90	2100 ± 35	3.8 ± 0.1	3, 5, 12, 13, 14, 15, 19, 32
NaCl	5896/90	1955 ± 15	4.24 ± 0.05	5, 12, 32
NaI	5896/90	2400 ± 50	3.07 ± 0.1	1, 2, 3, 4, 5, 6, 7, 9, 12, 19, 20, 21, 24, 32, 36, 37
KBr	7699/65	2235 ± 20	3.94 ± 0.05	3, 5, 12, 32
KCl	7699/65	2060 ± 15	4.40 ± 0.05	3, 5, 12, 32
KI	7699/65	2515 ± 25	3.32 ± 0.05	3, 5, 12, 32
CuI	3274/48	2140 ± 70	2.0 ± 0.2	7
RbBr	7948/7800	2215 ± 90	4.0 ± 0.25	5, 12
RbCl	7948/7800	2035 ± 65	4.5 ± 0.2	12, 32
RbI	7948/7800	2510 ± 50	3.35 ± 0.1	5, 12, 20, 22, 30, 31
AgI	3383	1980 ± 80	2.6 ± 0.25	16, 17, 29
	3281	1945 ± 75		
InBr	4511	2020 ± 60	3.4 ± 0.2	33, 34, 35
	4105	1930 ± 60		
InCl	4511	1740 ± 25	4.5 ± 0.1	34, 35
	4105	1670 ± 20		
InI	4511	2240 ± 75	2.8 ± 0.2	33, 34, 35
	4105	2130 ± 70		
CsBr	8944/8521	2230 ± 95	4.1 ± 0.25	5, 12
	4593/55	1830 ± 80		
CsCl	8944/8521	2045 ± 65	4.6 ± 0.2	5, 20
	4593/55	1705 ± 45		
CsI	8944/8521	2555 ± 50	3.4 ± 0.1	1, 3, 5, 7, 12, 18, 20
	4593/4551	2040 ± 35		
TlBr	5351/3776	1945 ± 30	3.2 ± 0.1	6, 7, 11, 16, 29
TiCl	5351/3776	1780 ± 25	3.78 ± 0.1	7, 11, 16, 29
TlI	5351/3776	2145 ± 35	2.6 ± 0.1	6, 7, 11, 16, 23, 26, 27, 28, 29
BiI	3068	1895 ± 250	2.5 ± 1	25

sufficiently high energies, where the transition probability can be expanded with $|\mathbf{u} \cdot \mathbf{K}|^2$ as the leading term. Again there appear two classes of electronic transitions, now classified as $\Delta\Lambda = 0$ ($\Sigma \rightarrow \Sigma$, $\Pi \rightarrow \Pi$, $\Delta \rightarrow \Delta$) and $\Delta\Lambda \neq 0$ ($\Sigma \rightarrow \Pi$, $\Sigma \rightarrow \Delta$, $\Pi \rightarrow \Delta$).

From Table I we see that the case of dissociative electron capture (for which $\kappa = 0^\circ$ always) is essentially equivalent to photodissociation with polarized light, except that some additional transitions become allowed. For dissociative electron excitation or ionization, we may expect to obtain a practical approximation to the general result by taking

$$I(\theta) = \cos^2\kappa I_c(\theta) + \sin^2\kappa I_s(\theta) \quad (12)$$

and analogous expressions for the fluorescence form factors. (These mixing formulas are readily justified when the $|\mathbf{u} \cdot \mathbf{K}|^2$ term dominates the transition probability.) Here $I_c(\theta)$ denotes the result which applies

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for electron capture or polarized photodissociation, as given in the upper part of Table I. In Eq. (12) this is reached in the limit of large momentum transfer (where $k \simeq K$ and hence $\kappa \simeq 0^\circ$), which obtains near the excitation or ionization threshold. We denote by $I_s(\theta)$ the result for small momentum transfer (where $k \gg K$ and the conservation laws require $\kappa \simeq 90^\circ$), which obtains at high energy. This limit resembles closely photodissociation by unpolarized light, and is given in the lower part of Table I.

According to Eq. (12) and Fig. 1, in dissociative excitation the anisotropy in the form factors for a given transition will be a maximum at threshold, but will be first suppressed and then reversed in sense if the bombarding electron energy is increased sufficiently. This behavior has been observed recently by Dunn and Kieffer²⁴ in the angular distribution of protons from dissociative ionization of H₂ by electron impact. Since

Table III. Studies of Molecular Fluorescence Excited in Molecular Photodissociation

Photodissociation processes	References
Triatomic molecules	
H ₂ O → OH* + H	16, 29, 30, 33
H ₂ S → HS* + H	30
BrCN → CN* + Br	21
ICN → CN* + I	10, 21
N ₂ O → NO* + N	11
ZnI ₂ → ZnI* + I	1, 15
CdI ₂ → CdI* + I	1, 15
InCl ₂ → InCl* + Cl	26
InBr ₂ → InBr* + Br	26
InI ₂ → InI* + I	26
SnCl ₂ → SnCl* + Cl	14
HgCl ₂ → HgCl* + Cl	1, 9, 18, 20, 24, 27, 28
HgBr ₂ → HgBr* + Br	1, 4, 9, 20, 25
HgI ₂ → HgI* + I	1, 7, 8, 20
PbBr ₂ → PbBr* + Br	6, 17
PbI ₂ → PbI* + I	1
Polyatomic molecules	
H ₂ O ₂ → OH* + OH	3, 30
CH ₃ OH → OH* + CH ₃	16
C ₂ H ₅ OH → OH* + C ₂ H ₅	16
CH ₃ COOH → OH* + CH ₃ CO	16
NH ₃ → NH* + H ₂	34, 35, 36
NH ₃ → NH ₂ * + H	16
H ₂ NNH ₂ → NH ₂ * + NH ₂	16
C ₂ N ₂ → CN* + CN	23
CH ₃ CN → CN* + CH ₃	16
HCOOH → HCO ₂ * + H	16, 31, 32
HCOOCH ₃ → HCO ₂ * + CH ₃	31, 32
HCOOC ₂ H ₅ → HCO ₂ * + C ₂ H ₅	31, 32
COCl ₂ → Cl ₂ * + CO	31
Cu ₂ Cl ₂ → CuCl* + CuCl	2, 22
Cu ₂ Br ₂ → CuBr* + CuBr	22
Cu ₂ I ₂ → CuI* + CuI	2, 22
CH ₂ I ₂ → I ₂ * + CH ₂	31, 32
SnI ₄ → I ₂ * + SnI ₂	13, 19
BiI ₃ → I ₂ * + BiI	5, 19
CH ₃ HgBr → HgBr* + CH ₃	12
CH ₃ HgI → HgI* + CH ₃	12

the pumping transition has $\Delta\Lambda = 0(^1\Sigma_g^+ \rightarrow ^2\Sigma_u^+)$, the qualitative arguments predict that near threshold a case A distribution would appear and at high energies go over to a case B distribution. The observed distribution displays this nicely: at bombarding energies below about 50 eV it is strongly peaked forwards and backwards along the incident electron beam; at about 300 eV it becomes nearly isotropic; and at higher energies shows a broad peak sideways to the beam.

Bibliography for Atomic and Molecular Fluorescence Excited by Photodissociation

A summary of experimental studies of atomic fluorescence produced by molecular photodissociation of diatomic molecules is given in Table II. In every case the observed emission comes from the metal atom rather than the halogen. The wavelength of the atomic fluorescence lines is denoted by $\lambda_F(\text{\AA})$, and the wavelength of the pumping light required to dissociate the

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molecule (in its ground vibrational state) and excite the fluorescence is denoted by $\lambda_P(\text{\AA})$. Values of the dissociation energy $D_0^0(\text{eV})$ have been taken from Gaydon,³⁵ although in many cases more recent data are available. The indicated uncertainty in λ_P arises mainly from that in the D_0^0 values. Similarly, Table III lists experimental studies of molecular fluorescence produced by molecular photodissociation.

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