# Chapter 15

The tools of time-dependent perturbation theory can be applied to transitions among electronic, vibrational, and rotational states of molecules.

# I. Rotational Transitions

Within the approximation that the electronic, vibrational, and rotational states of a molecule can be treated as independent, the total molecular wavefunction of the "initial" state is a product

of an electronic function  $_{ei}$ , a vibrational function  $_{vi}$ , and a rotational function  $_{ri}$ . A similar product expression holds for the "final" wavefunction  $_{f}$ .

In microwave spectroscopy, the energy of the radiation lies in the range of fractions of a cm<sup>-1</sup> through several cm<sup>-1</sup>; such energies are adequate to excite rotational motions of molecules but are not high enough to excite any but the weakest vibrations (e.g., those of weakly bound Van der Waals complexes). In rotational transitions, the electronic and vibrational states are thus left unchanged by the excitation process; hence  $e_i = e_f$  and  $v_i = v_f$ .

Applying the first-order electric dipole transition rate expressions

$$\mathbf{R}_{i,f} = 2 \quad \mathbf{g}(\mathbf{f}_{i,i}) \mid \mathbf{f}_{i,i} \mid^2$$

obtained in Chapter 14 to this case requires that the E1 approximation

$$R_{i,f} = (2 /h^2) g(f_{i,i}) | E_0 \cdot (f_{i,j}) | E_0 | \mu|$$

be examined in further detail. Specifically, the electric dipole matrix elements  $\langle f | \mu | i \rangle$ with  $\mu = j e \mathbf{r}_j + a Z_a e \mathbf{R}_a$  must be analyzed for i and f being of the product form shown above.

The integrations over the electronic coordinates contained in  $< f | \mu | i >$ , as well as the integrations over vibrational degrees of freedom yield "expectation values" of the electric dipole moment operator because the electronic and vibrational components of i and f are identical:

$$\langle e_i | \mu | e_i \rangle = \mu (\mathbf{R})$$

is the dipole moment of the initial electronic state (which is a function of the internal geometrical degrees of freedom of the molecule, denoted  $\mathbf{R}$ ); and

$$\langle v_i | \mu(\mathbf{R}) | v_i \rangle = \mu_{ave}$$

is the vibrationally averaged dipole moment for the particular vibrational state labeled  $_{vi}$ . The vector  $\mu_{ave}$  has components along various directions and can be viewed as a vector "locked" to the molecule's internal coordinate axis (labeled a, b, c as below).



The rotational part of the  $\langle f | \mu | i \rangle$  integral is not of the expectation value form because the initial rotational function ir is not the same as the final fr. This integral has the form:

$$\langle ir | \mu_{ave} | fr \rangle = (Y_{L,M}^{*}(,)) \mu_{ave} Y_{L',M'}(,) \sin d d$$

for linear molecules whose initial and final rotational wavefunctions are  $Y_{L,M}$  and  $Y_{L^\prime,M^\prime}$  , respectively, and

$$< ir | \mu_{ave} | fr > = \sqrt{\frac{2L+1}{8}} \sqrt{\frac{2L'+1}{8}}$$

$$(D_{L,M,K}(, , , ) \mid \mu_{ave} D^*_{L',M',K'}(, , , ) \sin d d d )$$

for spherical or symmetric top molecules (here,  $\sqrt{\frac{2L+1}{8}} D_{L,M,K}^*($ , , ) are the

normalized rotational wavefunctions described in Chapter 13 and in Appendix G). The angles , , and refer to how the molecule-fixed coordinate system is oriented with respect to the space-fixed X, Y, Z axis system.

## A. Linear Molecules

For linear molecules, the vibrationally averaged dipole moment  $\mu_{ave}$  lies along the molecular axis; hence its orientation in the lab-fixed coordinate system can be specified in terms of the same angles ( and ) that are used to describe the rotational functions  $Y_{L,M}$  ( , ). Therefore, the three components of the  $<_{ir} \mid \mu_{ave} \mid_{fr} >$  integral can be written as:

 $\langle ir | \mu_{ave} | fr \rangle_x = \mu (Y^*_{L,M} (, ) sin cos Y_{L',M'} (, ) sin d d)$ 

$$\langle ir | \mu_{ave} | fr \rangle_y = \mu (Y^*_{L,M} (,) sin sin Y_{L',M'} (,) sin d d)$$

$$<_{ir} \mid \mu_{ave} \mid _{fr} \geq_z = \mu \quad (Y^*_{L,M} (,) \cos Y_{L',M'} (,) \sin d d),$$

where  $\mu$  is the magnitude of the averaged dipole moment. If the molecule has no dipole moment, all of the above electric dipole integrals vanish and the intensity of E1 rotational transitions is zero.

The three E1 integrals can be further analyzed by noting that  $\cos Y_{1,0}$ ; sin  $\cos Y_{1,1} + Y_{1,-1}$ ; and  $\sin \sin Y_{1,1} - Y_{1,-1}$  and using the angular momentum coupling methods illustrated in Appendix G. In particular, the result given in that appendix:

when multiplied by  $D^*_{J,M,M'}$  and integrated over sin d d d , yields:

$$(D^*_{J,M,M'} D_{j, m, m'} D_{l, n, n'} \sin d d d$$
  
=  $\frac{8}{2J+1} < J,M|j,m;l,n> < j,m'; l,n'|J,M'>$   
=  $8 \ ^2 \ \frac{j}{m} \frac{1}{n} \frac{J}{-M} \ \frac{j}{m'} \frac{1}{n'} \frac{J}{-M'}$  (-1) <sup>M+M'</sup>.

To use this result in the present linear-molecule case, we note that the  $D_{J,M,K}$  functions and the  $Y_{J,M}$  functions are related by:

)

$$Y_{J,M}(\ ,\ )=\sqrt{(2J{+}1)/4} \ D*_{J,M,0}(\ ,\ ,\ ).$$

The normalization factor is now  $\sqrt{(2J+1)/4}$  rather than  $\sqrt{(2J+1)/8}$  2 because the Y<sub>J,M</sub> are no longer functions of , and thus the need to integrate over 0 2 disappears. Likewise, the -dependence of D\*<sub>J,M,K</sub> disappears for K = 0.

We now use these identities in the three E1 integrals of the form

$$\mu$$
 (Y\*<sub>L,M</sub>(,) Y<sub>1,m</sub>(,) Y<sub>L',M'</sub>(,) sin d d),

with m = 0 being the Z- axis integral, and the Y- and X- axis integrals being combinations of the m = 1 and m = -1 results. Doing so yields:

The last factor of 1/2 is inserted to cancel out the integration over d that, because all K-factors in the rotation matrices equal zero, trivially yields 2 . Now, using the result shown above expressing the integral over three rotation matrices, these E1 integrals for the linear-molecule case reduce to:

$$\begin{split} & \mu \quad (Y^*_{L,M}(\ ,\ )\ Y_{1,m}(\ ,\ )\ Y_{L',M'}(\ ,\ )\ \sin \ d\ d\ ) \\ & = \ \mu \sqrt{\frac{2L+1}{4}\ \frac{2L'+1}{4}\ \frac{3}{4}}\ \frac{8}{2}\ \frac{2}{2}\ \frac{L'\ 1}{M'\ m\ -M}\ \frac{L'\ 1}{0\ 0\ -0}\ (-1)\ M} \\ & = \ \mu \sqrt{(2L+1)(2L'+1)\frac{3}{4}}\ \frac{L'\ 1}{M'\ m\ -M}\ \frac{L'\ 1}{0\ 0\ -0}\ (-1)\ M} \ . \end{split}$$

Applied to the z-axis integral (identifying m = 0), this result therefore vanishes unless:

$$M = M'$$

and

$$L = L' + 1$$
 or  $L' - 1$ .

Even though angular momentum coupling considerations would allow L = L' (because coupling two angular momenta with j = 1 and j = L' should give L'+1, L', and L'-1), the 3-j symbol  $\frac{L' \ 1 \ L}{0 \ 0 \ -0}$  vanishes for the L = L' case since 3-j symbols have the following symmetry

$$\frac{L' \ 1 \ L}{M' \ m \ -M} = (-1)^{L+L'+1} \ \frac{L' \ 1 \ L}{-M' \ -m \ M}$$

with respect to the M, M', and m indices. Applied to the  $\frac{L'}{0}\frac{1}{0}\frac{L}{0}$  3-j symbol, this means that this particular 3-j element vanishes for L = L' since L + L' + 1 is odd and hence  $(-1)^{L + L' + 1}$  is -1.

Applied to the x- and y- axis integrals, which contain  $m = \pm 1$  components, this same analysis yields:

$$\mu \sqrt{(2L+1)(2L'+1)\frac{3}{4}} \quad \frac{L' \ 1 \ L}{M' \ \pm 1 \ -M} \quad \frac{L' \ 1 \ L}{0 \ 0 \ -0} \quad (-1)^{M}$$

which then requires that

$$M = M' \pm 1$$

and

$$L = L' + 1, L' - 1,$$

with L = L' again being forbidden because of the second 3-j symbol.

These results provide so-called "**selection rules**" because they limit the L and M values of the final rotational state, given the L', M' values of the initial rotational state. In the figure shown below, the L = L' + 1 absorption spectrum of NO at 120 °K is given. The intensities of the various peaks are related to the populations of the lower-energy rotational states which are, in turn, proportional to  $(2 L' + 1) \exp(-L'(L'+1) \frac{h^2}{8} 2 IkT)$ . Also included in the intensities are so-called **line strength factors** that are proportional to the squares of the quantities:

$$\mu \sqrt{(2L+1)(2L'+1)\frac{3}{4}} \quad \frac{L' \ 1 \ L}{M' \ m \ -M} \quad \frac{L' \ 1 \ L}{0 \ 0 \ -0} \quad (-1) \ M$$

which appear in the E1 integrals analyzed above (recall that the rate of photon absorption  $R_{i,f} = (2 /h^2) g(_{f,i}) | E_0 \cdot <_{f} | \mu |_{i} > |^2$  involves the squares of these matrix elements). The book by Zare gives an excellent treatment of line strength factors' contributions to rotation, vibration, and electronic line intensities.





For molecules that are non-linear and whose rotational wavefunctions are given in terms of the spherical or symmetric top functions  $D^*_{L,M,K}$ , the dipole moment  $\mu_{ave}$  can have components along any or all three of the molecule's internal coordinates (e.g., the three molecule-fixed coordinates that describe the orientation of the principal axes of the moment of inertia tensor). For a spherical top molecule,  $|\mu_{ave}|$  vanishes, so E1 transitions do not occur.

For symmetric top species,  $\mu_{ave}$  lies along the symmetry axis of the molecule, so the orientation of  $\mu_{ave}$  can again be described in terms of and , the angles used to locate the orientation of the molecule's symmetry axis relative to the lab-fixed coordinate system. As a result, the E1 integral again can be decomposed into three pieces:

$$<_{ir} |\mu_{ave}|_{fr} >_x = \mu (D_{L,M,K}(,,) \cos \cos D^*_{L',M',K'}(,,) \sin d d d)$$

$$\langle ir | \mu_{ave} | fr \rangle_y = \mu (D_{L,M,K}(,,) \cos sin D^*_{L',M',K'}(,,) sin d d d)$$

 $<_{ir} \mid \mu_{ave} \mid_{fr} >_z = \mu (D_{L,M,K}(,,) \cos D^*_{L',M',K'}(,,) \sin d d ).$ 

Using the fact that  $\cos D_{1,0,0}^*$ ;  $\sin \cos D_{1,1,0}^* + D_{1,-1,0}^*$ ; and  $\sin \sin D_{1,1,0}^* - D_{1,-1,0}^*$ , and the tools of angular momentum coupling allows these integrals to be expressed, as above, in terms of products of the following 3-j symbols:

$$\frac{L' \ 1 \ L}{M' \ m \ -M} \quad \frac{L' \ 1 \ L}{K' \ 0 \ -K}$$

from which the following selection rules are derived:

$$L = L' + 1, L', L' - 1$$
 (but not  $L = L' = 0$ ),  
 $K = K',$   
 $M = M' + m,$ 

,

with m = 0 for the Z-axis integral and  $m = \pm 1$  for the X- and Y- axis integrals. In addition, if K = K' = 0, the L = L' transitions are also forbidden by the second 3-j symbol vanishing.

### **II. Vibration-Rotation Transitions**

When the initial and final electronic states are identical but the respective vibrational and rotational states are not, one is dealing with transitions between vibration-rotation states of the molecule. These transitions are studied in infrared (IR) spectroscopy using light of energy in the 30 cm<sup>-1</sup> (far IR) to 5000 cm<sup>-1</sup> range. The electric dipole matrix element analysis still begins with the electronic dipole moment integral  $\langle e_i | \mu | e_i \rangle = \mu$  (**R**), but the integration over internal vibrational coordinates no longer produces the vibrationally averaged dipole moment. Instead one forms the vibrational **transition dipole** integral:

 $< v_{f} | \mu(\mathbf{R}) | v_{i} > = \mu_{f,i}$ 

between the initial i and final f vibrational states.

A. The Dipole Moment Derivatives

Expressing  $\mu(\mathbf{R})$  in a power series expansion about the equilibrium bond length position (denoted  $\mathbf{R}_e$  collectively and  $R_{a,e}$  individually):

$$\mu(\mathbf{R}) = \mu(\mathbf{R}_{e}) + a \mu R_{a} (R_{a} - R_{a,e}) + ...,$$

substituting into the  $\langle v_f | \mu(\mathbf{R}) | v_i \rangle$  integral, and using the fact that i and f are orthogonal (because they are eigenfunctions of vibrational motion on the same electronic surface and hence of the same vibrational Hamiltonian), one obtains:

$$< v_{f} | \mu(\mathbf{R}) | v_{i} > = \mu(\mathbf{R}_{e}) < v_{f} | v_{i} > + a \mu / R_{a} < v_{f} | (R_{a} - R_{a,e}) | v_{i} > + ...$$
$$= a (\mu / R_{a}) < v_{f} | (R_{a} - R_{a,e}) | v_{i} > + ...$$

This result can be interpreted as follows:

i. Each independent vibrational mode of the molecule contributes to the  $\mu_{f,i}$  vector an amount equal to  $(\mu/R_a) < v_f | (R_a - R_{a,e}) | v_i > + \dots$ .

ii. Each such contribution contains one part (  $\mu/R_a$ ) that depends on how the molecule's dipole moment function varies with vibration along that particular mode (labeled a),

iii. and a second part  $\langle v_f | (R_a - R_{a,e}) | v_i \rangle$  that depends on the character of the initial and final vibrational wavefunctions.

If the vibration does not produce a **modulation of the dipole moment** (e.g., as with the symmetric stretch vibration of the CO<sub>2</sub> molecule), its infrared intensity vanishes because ( $\mu/R_a$ ) = 0. One says that such transitions are infrared "inactive".

B. Selection Rules on the Vibrational Quantum Number in the Harmonic Approximation

If the vibrational functions are described within the harmonic oscillator approximation, it can be shown that the  $\langle vf | (R_a - R_{a,e}) | v_i \rangle$  integrals vanish unless vf = vi +1, vi -1 (and that these integrals are proportional to  $(vi + 1)^{1/2}$  and  $(vi)^{1/2}$  in the respective cases). Even when vf and  $v_i$  are rather non-harmonic, it turns out that such  $v = \pm 1$  transitions have the largest  $\langle vf | (R_a - R_{a,e}) | v_i \rangle$  integrals and therefore the highest infrared intensities. For these reasons, transitions that correspond to  $v = \pm 1$  are called "**fundamental**"; those with  $v = \pm 2$  are called "first **overtone**" transitions. In summary then, vibrations for which the molecule's dipole moment is modulated as the vibration occurs (i.e., for which ( $\mu/R_a$ ) is non-zero) and for which  $v = \pm 1$  tend to have large infrared intensities; overtones of such vibrations tend to have smaller intensities, and those for which ( $\mu/R_a$ ) = 0 have no intensity.

# C. Rotational Selection Rules for Vibrational Transitions

The result of all of the vibrational modes' contributions to  $_{a}(\mu/R_{a}) < _{vf}|(R_{a} - R_{a,e})|_{vi} > is a vector \mu_{trans}$  that is termed the vibrational "transition dipole" moment. This is a vector with components along, in principle, all three of the internal axes of the molecule. For each particular vibrational transition (i.e., each particular  $_{i}$  and  $_{f}$ ) its orientation in space depends only on the orientation of the molecule; it is thus said to be locked to the molecule's coordinate frame. As such, its orientation relative to the lab-fixed coordinates (which is needed to effect a derivation of rotational selection rules as was done earlier in this Chapter) can be described much as was done above for the vibrationally averaged dipole moment that arises in purely rotational transitions. There are, however, important differences in detail. In particular,

i. For a linear molecule  $\mu_{\text{trans}}$  can have components either along (e.g., when stretching vibrations are excited; these cases are denoted -cases) or perpendicular to (e.g., when bending vibrations are excited; they are denoted cases) the molecule's axis.

ii. For symmetric top species,  $\mu_{trans}$  need not lie along the molecule's symmetry axis; it can have components either along or perpendicular to this axis.

iii. For spherical tops,  $\mu_{trans}$  will vanish whenever the vibration does not induce a dipole moment in the molecule. Vibrations such as the totally symmetric  $a_1$ C-H stretching motion in CH<sub>4</sub> do not induce a dipole moment, and are thus infrared inactive; non-totally-symmetric vibrations can also be inactive if they induce no dipole moment.

As a result of the above considerations, the angular integrals

 $\langle ir | \mu_{trans} | f_{t} \rangle = (Y^{*}_{L,M} (, ) \mu_{trans} Y_{L',M'} (, ) sin d d)$ 

$$<_{ir} |\mu_{trans}|_{fr} = (D_{L,M,K}(,,)) |\mu_{trans} D^*_{L',M',K'}(,,) sin d d d)$$

that determine the rotational selection rules appropriate to vibrational transitions produce similar, but not identical, results as in the purely rotational transition case.

The derivation of these selection rules proceeds as before, with the following additional considerations. The transition dipole moment's  $\mu_{trans}$  components along the lab-fixed axes must be related to its molecule-fixed coordinates (that are determined by the nature of the vibrational transition as discussed above). This transformation, as given in Zare's text, reads as follows:

$$(\mu_{\text{trans}})_{m} = k D^{*}_{1,m,k} (,,) (\mu_{\text{trans}})_{k}$$

where  $(\mu_{trans})_m$  with m = 1, 0, -1 refer to the components along the lab-fixed (X, Y, Z) axes and  $(\mu_{trans})_k$  with k = 1, 0, -1 refer to the components along the molecule- fixed (a, b, c) axes.

This relationship, when used, for example, in the symmetric or spherical top E1 integral:

$$<_{ir} |\mu_{trans}|_{fr} = (D_{L,M,K}(,,)) |\mu_{trans} D^*_{L',M',K'}(,,) sin d d d)$$

gives rise to products of 3-j symbols of the form:

$$\frac{L' \ 1 \ L}{M' \ m \ -M} \quad \frac{L' \ 1 \ L}{K' \ k \ -K} \quad . \label{eq:linear_$$

The product of these 3-j symbols is nonvanishing only under certain conditions that provide the rotational selection rules applicable to vibrational lines of symmetric and spherical top molecules.

Both 3-j symbols will vanish unless

$$L = L' + 1, L', \text{ or } L' - 1.$$

and

In the special case in which L = L' = 0 (and hence with M = M' = 0 = K = K', which means that m = 0 = k), these3-j symbols again vanish. Therefore, transitions with L = L' = 0

are again **forbidden.** As usual, the fact that the lab-fixed quantum number m can range over m = 1, 0, -1, requires that

M = M' + 1, M', M'-1.

The selection rules for K depend on the nature of the vibrational transition, in particular, on the component of  $\mu_{trans}$  along the molecule-fixed axes. For the second 3-j symbol to not vanish, one must have

$$\mathbf{K} = \mathbf{K'} + \mathbf{k},$$

where k = 0, 1, and -1 refer to these molecule-fixed components of the transition dipole. Depending on the nature of the transition, various k values contribute.

#### 1. Symmetric Tops

In a symmetric top molecule such as  $NH_3$ , if the transition dipole lies along the molecule's symmetry axis, only k = 0 contributes. Such vibrations preserve the molecule's symmetry relative to this symmetry axis (e.g. the totally symmetric N-H stretching mode in  $NH_3$ ). The additional selection rule K = 0 is thus obtained. Moreover, for K = K' = 0, all transitions with L = 0 vanish because the second 3-j symbol vanishes. In summary, one has:

K = 0;  $M = \pm 1$ ,0;  $L = \pm 1$ ,0 (but L = L' = 0 is forbidden and all L = 0 are forbidden for K = K' = 0)

for symmetric tops with vibrations whose transition dipole lies along the symmetry axis.

If the transition dipole lies perpendicular to the symmetry axis, only  $k = \pm 1$  contribute. In this case, one finds

 $K = \pm 1$ ;  $M = \pm 1$ ,0;  $L = \pm 1$ ,0 (neither L = L' = 0 nor K = K' = 0 can occur for such transitions, so there are no additional constraints).

# 2. Linear Molecules

When the above analysis is applied to a diatomic species such as HCl, only k = 0 is present since the only vibration present in such a molecule is the bond stretching vibration, which has symmetry. Moreover, the rotational functions are spherical harmonics (which can be viewed as  $D^*_{L',M',K'}(, , )$  functions with K' = 0), so the K and K' quantum numbers are identically zero. As a result, the product of 3-j symbols

$$\frac{L' \ 1 \ L}{M' \ m \ -M} \quad \frac{L' \ 1 \ L}{K' \ k \ -K}$$

reduces to

$$\frac{L' \ 1 \ L}{M' \ m \ -M} \quad \frac{L' \ 1 \ L}{0 \ 0 \ 0} \ ,$$

which will vanish unless

$$L = L' + 1, L' - 1,$$

but <u>not</u> L = L' (since parity then causes the second 3-j symbol to vanish), and M = M' + 1, M', M'-1.

The L = L' + 1 transitions are termed **R-branch** absorptions and those obeying L = L' - 1 are called **P-branch** transitions. Hence, the selection rules

$$M = \pm 1,0; L = \pm 1$$

are identical to those for purely rotational transitions.

When applied to linear polyatomic molecules, these same selection rules result if the vibration is of symmetry (i.e., has k = 0). If, on the other hand, the transition is of symmetry (i.e., has  $k = \pm 1$ ), so the transition dipole lies perpendicular to the molecule's axis, one obtains:

$$M = \pm 1,0; L = \pm 1, 0.$$

These selection rules are derived by realizing that in addition to  $k = \pm 1$ , one has: (i) a linear-molecule rotational wavefunction that in the v = 0 vibrational level is described in terms of a rotation matrix  $D_{L',M',0}(,,)$  with no angular momentum along the molecular axis, K' = 0; (ii) a v = 1 molecule whose rotational wavefunction must be given by a rotation matrix  $D_{L,M,1}(,,)$  with one unit of angular momentum about the molecule's axis, K = 1. In the latter case, the angular momentum is produced by the degenerate vibration itself. As a result, the selection rules above derive from the following product of 3-j symbols:

$$\frac{L' \ 1 \ L}{M' \ m \ -M} \quad \frac{L' \ 1 \ L}{0 \ 1 \ -1} \quad .$$

Because L = 0 transitions are allowed for vibrations, one says that vibrations possess **Q- branches** in addition to their R- and P- branches (with L = 1 and -1, respectively).

In the figure shown below, the v = 0 ==> v = 1 (fundamental) vibrational absorption spectrum of HCl is shown. Here the peaks at lower energy (to the right of the figure) belong to P-branch transitions and occur at energies given approximately by:

$$E = h \quad \text{stretch} + (h^2/8 \ ^2I) ((L-1)L - L(L+1))$$
$$= h \quad \text{stretch} -2 (h^2/8 \ ^2I) L.$$

The R-branch transitions occur at higher energies given approximately by:

$$E = h_{stretch} + (h^2/8 \ ^2I) ((L+1)(L+2) - L(L+1))$$
$$= h_{stretch} + 2 (h^2/8 \ ^2I) (L+1).$$

The absorption that is "missing" from the figure below lying slightly below 2900 cm<sup>-1</sup> is the **Q-branch** transition for which L = L'; it is absent because the selection rules forbid it.



It should be noted that the spacings between the experimentally observed peaks in HCl are not constant as would be expected based on the above P- and R- branch formulas. This is because the moment of inertia appropriate for the v = 1 vibrational level is different than that of the v = 0 level. These effects of vibration-rotation coupling can be modeled by allowing the v = 0 and v = 1 levels to have rotational energies written as

$$E = h$$
 stretch (v + 1/2) + (h<sup>2</sup>/8 <sup>2</sup>I<sub>v</sub>) (L (L+1))

where v and L are the vibrational and rotational quantum numbers. The P- and R- branch transition energies that pertain to these energy levels can then be written as:

 $E_{P} = h_{\text{stretch}} - [(h^{2}/8 \ ^{2}I_{1}) + (h^{2}/8 \ ^{2}I_{0})]L + [(h^{2}/8 \ ^{2}I_{1}) - (h^{2}/8 \ ^{2}I_{0})]L^{2}$ 

 $\mathbf{E}_{\mathbf{R}} = \mathbf{h} \quad \text{stretch} + 2 (\mathbf{h}^2/\mathbf{8} \ ^2\mathbf{I}_1)$ 

+ 
$$[3(h^{2}/8 \ ^{2}I_{1}) - (h^{2}/8 \ ^{2}I_{0})]L + [(h^{2}/8 \ ^{2}I_{1}) - (h^{2}/8 \ ^{2}I_{0})]L^{2}$$
.

Clearly, these formulas reduce to those shown earlier in the  $I_1 = I_0$  limit.

If the vibrationally averaged bond length is longer in the v = 1 state than in the v = 0 state, which is to be expected,  $I_1$  will be larger than  $I_0$ , and therefore [  $(h^2/8 \ ^2I_1) - (h^2/8 \ ^2I_0)$ ] will be negative. In this case, the <u>spacing</u> between neighboring P-branch lines will increase as shown above for HCl. In contrast, the fact that [  $(h^2/8 \ ^2I_1) - (h^2/8 \ ^2I_0)$ ] is negative causes the <u>spacing</u> between neighboring R- branch lines to decrease, again as shown for HCl.

III. Electronic-Vibration-Rotation Transitions

When electronic transitions are involved, the initial and final states generally differ in their electronic, vibrational, and rotational energies. Electronic transitions usually require light in the 5000 cm<sup>-1</sup> to 100,000 cm<sup>-1</sup> regime, so their study lies within the domain of visible and ultraviolet spectroscopy. Excitations of inner-shell and core orbital electrons may require even higher energy photons, and under these conditions, E2 and M1 transitions may become more important because of the short wavelength of the light involved.

A. The Electronic Transition Dipole and Use of Point Group Symmetry

Returning to the expression

$$R_{i,f} = (2 /h^2) g(f_{i,i}) | E_0 \cdot \langle f_i | \mu | i \rangle |^2$$

for the rate of photon absorption, we realize that the electronic integral now involves

$$<_{\rm ef} |\mu| = _{\rm ei} > = \mu_{\rm f,i} ({\bf R}),$$

a transition dipole matrix element between the initial  $_{ei}$  and final  $_{ef}$  electronic wavefunctions. This element is a function of the internal vibrational coordinates of the molecule, and again is a vector locked to the molecule's internal axis frame.

Molecular point-group symmetry can often be used to determine whether a particular transition's dipole matrix element will vanish and, as a result, the electronic transition will be "forbidden" and thus predicted to have zero intensity. If the direct product of the symmetries of the initial and final electronic states  $_{ei}$  and  $_{ef}$  do not match the symmetry of the electric dipole operator (which has the symmetry of its x, y, and z components; these symmetries can be read off the right most column of the character tables given in Appendix E), the matrix element will vanish.

For example, the formaldehyde molecule  $H_2CO$  has a ground electronic state (see Chapter 11) that has  ${}^{1}A_{1}$  symmetry in the  $C_{2v}$  point group. Its ==> \* singlet excited state also has  ${}^{1}A_{1}$  symmetry because both the and \* orbitals are of  $b_{1}$  symmetry. In contrast, the lowest n ==> \* singlet excited state is of  ${}^{1}A_{2}$  symmetry because the highest energy oxygen centered n orbital is of  $b_{2}$  symmetry and the \* orbital is of  $b_{1}$  symmetry, so the Slater determinant in which both the n and \* orbitals are singly occupied has its symmetry dictated by the  $b_{2}$  x  $b_{1}$  direct product, which is  $A_{2}$ .

The ==> \* transition thus involves ground  $({}^{1}A_{1})$  and excited  $({}^{1}A_{1})$  states whose direct product  $(A_{1} \times A_{1})$  is of  $A_{1}$  symmetry. This transition thus requires that the electric dipole operator possess a component of  $A_{1}$  symmetry. A glance at the  $C_{2v}$  point group's character table shows that the molecular z-axis is of  $A_{1}$  symmetry. Thus, if the light's electric field has a non-zero component along the  $C_{2}$  symmetry axis (the molecule's z-axis), the ==> \* transition is predicted to be allowed. Light polarized along either of the molecule's other two axes cannot induce this transition.

In contrast, the n ==> \* transition has a ground-excited state direct product of  $B_2$  x  $B_1 = A_2$  symmetry. The  $C_{2v}$  's point group character table clearly shows that the electric dipole operator (i.e., its x, y, and z components in the molecule-fixed frame) has no component of  $A_2$  symmetry; thus, light of no electric field orientation can induce this n ==>

\* transition. We thus say that the n = > \* transition is E1 forbidden (although it is M1 allowed).

Beyond such electronic symmetry analysis, it is also possible to derive vibrational and rotational selection rules for electronic transitions that are E1 allowed. As was done in the vibrational spectroscopy case, it is conventional to expand  $\mu_{f,i}$  (**R**) in a power series about the equilibrium geometry of the initial electronic state (since this geometry is more characteristic of the molecular structure prior to photon absorption):

$$\mu_{f,i}(\boldsymbol{R}) = \mu_{f,i}(\boldsymbol{R}_e) + \ _a \ \mu_{f,i}/ \ R_a \left(R_a - R_{a,e}\right) + \ \ldots$$

### B. The Franck-Condon Factors

The first term in this expansion, when substituted into the integral over the vibrational coordinates, gives  $\mu_{f,i}(\mathbf{R}_e) < |v_i| |v_i| > 0$ , which has the form of the electronic transition dipole multiplied by the "overlap integral" between the initial and final vibrational wavefunctions. The  $\mu_{f,i}(\mathbf{R}_e)$  factor was discussed above; it is the electronic E1 transition integral evaluated at the equilibrium geometry of the absorbing state. Symmetry can often be used to determine whether this integral vanishes, as a result of which the E1 transition will be "forbidden".

Unlike the vibration-rotation case, the vibrational overlap integrals  $\langle vf | v_i \rangle$  do not necessarily vanish because vf and  $v_i$  are no longer eigenfunctions of the same vibrational Hamiltonian. vf is an eigenfunction whose potential energy is the <u>final</u> electronic state's energy surface;  $v_i$  has the <u>initial</u> electronic state's energy surface as its potential. The squares of these  $\langle vf | v_i \rangle$  integrals, which are what eventually enter into the transition rate expression  $R_{i,f} = (2 /\hbar^2) g(f_i) | E_0 \cdot \langle f_i | \mu | i \rangle |^2$ , are called

"**Franck-Condon factors**". Their relative magnitudes play strong roles in determining the relative intensities of various vibrational "bands" (i.e., peaks) within a particular electronic transition's spectrum.

Whenever an electronic transition causes a large change in the geometry (bond lengths or angles) of the molecule, the Franck-Condon factors tend to display the characteristic "broad progression" shown below when considered for one initial-state vibrational level vi and various final-state vibrational levels vf:



Notice that as one moves to higher vf values, the energy spacing between the states ( $E_{vf}$ - $E_{vf-1}$ ) decreases; this, of course, reflects the anharmonicity in the excited state vibrational potential. For the above example, the transition to the vf = 2 state has the largest Franck-Condon factor. This means that the overlap of the initial state's vibrational wavefunction vi is largest for the final state's vf function with vf = 2.

As a qualitative rule of thumb, the larger the geometry difference between the initial and final state potentials, the broader will be the Franck-Condon profile (as shown above) and the larger the vf value for which this profile peaks. Differences in harmonic frequencies between the two states can also broaden the Franck-Condon profile, although not as significantly as do geometry differences. For example, if the initial and final states have very similar geometries and frequencies along the mode that is excited when the particular electronic excitation is realized, the following type of Franck-Condon profile may result:



In contrast, if the initial and final electronic states have very different geometries and/or vibrational frequencies along some mode, a very broad Franck-Condon envelope peaked at high-vf will result as shown below:



# C. Vibronic Effects

The second term in the above expansion of the transition dipole matrix element  $_{a}$   $\mu_{f,i}/R_{a}(R_{a} - R_{a,e})$  can become important to analyze when the first term  $\mu_{fi}(\mathbf{R}_{e})$  vanishes (e.g., for reasons of symmetry). This dipole derivative term, when substituted into the integral over vibrational coordinates gives

 $\begin{array}{l} _{a} \ \ \mu_{f,i} / \ R_{a} < \ _{vf} \mid (R_{a} - R_{a,e}) \mid \ _{vi} >. \ Transitions \ for \ which \ \mu_{f,i} (\textbf{R}_{e}) \ vanishes \ but \ for \ which \ \mu_{f,i} / \ R_{a} \ does \ not \ for \ the \ a^{th} \ vibrational \ mode \ are \ said \ to \ derive \ intensity \ through \ "vibronic \ coupling" \ with \ that \ mode. \ The \ intensities \ of \ such \ modes \ are \ dependent \ on \ how \ strongly \ the \ electronic \ dipole \ integral \ varies \ along \ the \ mode \ (i.e, \ on \ \ \mu_{f,i} / \ R_{a} \ ) \ as \ well \ as \ on \ the \ magnitude \ of \ the \ vibrational \ integral \ and \ a$ 

$$\langle v_{\rm f} | (R_{\rm a} - R_{\rm a,e}) | v_{\rm i} \rangle.$$

An example of an E1 forbidden but "vibronically allowed" transition is provided by the singlet n ==> \* transition of H<sub>2</sub>CO that was discussed earlier in this section. As detailed there, the ground electronic state has  ${}^{1}A_{1}$  symmetry, and the n ==> \* state is of  ${}^{1}A_{2}$  symmetry, so the E1 transition integral

 $< e_{f} |\mu| e_{i} > vanishes for all three (x, y, z) components of the electric dipole operator <math>\mu$ . However, vibrations that are of b<sub>2</sub> symmetry (e.g., the H-C-H asymmetric stretch vibration) can induce intensity in the n ==> \* transition as follows:

(i) For such vibrations, the  $b_2$  mode's vi = 0 to vf = 1 vibronic integral

 $< v_{f} | (R_{a} - R_{a,e}) | v_{i} >$  will be non-zero and probably quite substantial (because, for harmonic oscillator functions these "fundamental" transition integrals are dominant- see earlier);

(ii) Along these same  $b_2$  modes, the electronic transition dipole integral <u>derivative</u>  $\mu_{f,i}$ /  $R_a$  will be non-zero, even though the integral itself  $\mu_{f,i}$  ( $\mathbf{R}_e$ ) vanishes when evaluated at the initial state's equilibrium geometry.

To understand why the derivative  $\mu_{f,i}/R_a$  can be non-zero for distortions (denoted  $R_a$ ) of  $b_2$  symmetry, consider this quantity in greater detail:

The third integral vanishes because the derivative of the dipole operator itself  $\mu = i e \mathbf{r}_j + a Z_a e \mathbf{R}_a$  with respect to the coordinates of atomic centers, yields an operator that contains only a sum of scalar quantities (the elementary charge e and the magnitudes of various atomic charges  $Z_a$ ); as a result and because the integral over the electronic wavefunctions  $\langle e_f | e_i \rangle$  vanishes, this contribution yields zero. The first and second integrals need not vanish by symmetry because the wavefunction derivatives

 $_{ef'}$  R<sub>a</sub> and  $_{ei'}$  R<sub>a</sub> do <u>not</u> possess the same symmetry as their respective wavefunctions  $_{ef}$  and  $_{ei}$ . In fact, it can be shown that the symmetry of such a derivative is given by the direct product of the symmetries of its wavefunction and the symmetry of the vibrational mode that gives rise to the / R<sub>a</sub>. For the H<sub>2</sub>CO case at hand, the b<sub>2</sub> mode vibration can induce in the excited <sup>1</sup>A<sub>2</sub> state a derivative component (i.e.,  $_{ef'}$  R<sub>a</sub>) that is of <sup>1</sup>B<sub>1</sub> symmetry) and this same vibration can induce in the <sup>1</sup>A<sub>1</sub> ground state a derivative component of <sup>1</sup>B<sub>2</sub> symmetry.

As a result, the contribution  $\langle ef' R_a | \mu | e_i \rangle$  to  $\mu_{f,i}/R_a$  arising from vibronic coupling within the <u>excited</u> electronic state can be expected to be non-zero for components of the dipole operator  $\mu$  that are of  $(e_{f'} R_a x_{ei}) = (B_1 x A_1) = B_1$  symmetry. Light polarized along the molecule's x-axis gives such a  $b_1$  component to  $\mu$  (see the  $C_{2v}$  character table in Appendix E). The second contribution  $\langle e_f | \mu | e_i / R_a \rangle$  can be non-zero for components of  $\mu$  that are of  $(e_f x_{ei} / R_a) = (A_2 x B_2) = B_1$  symmetry; again, light of x-axis polarization can induce such a transition.

In summary, electronic transitions that are E1 forbidden by symmetry can derive significant (e.g., in H<sub>2</sub>CO the singlet n ==> \* transition is rather intense) intensity through vibronic coupling. In such coupling, one or more vibrations (either in the initial or the final state) cause the respective electronic wavefunction to acquire (through / R<sub>a</sub>) a symmetry component that is different than that of itself. The symmetry of / R<sub>a</sub>, which is given as the direct product of the symmetry of and that of the vibration, can then cause the electric dipole integral < '|µ| / R<sub>a</sub>> to be non-zero even when < '|µ| > is zero. Such vibronically allowed transitions are said to derive their intensity through vibronic borrowing.

#### D. Rotational Selection Rules for Electronic Transitions

Each vibrational peak within an electronic transition can also display rotational structure (depending on the spacing of the rotational lines, the resolution of the spectrometer, and the presence or absence of substantial line broadening effects such as

those discussed later in this Chapter). The selection rules for such transitions are derived in a fashion that parallels that given above for the vibration-rotation case. The major difference between this electronic case and the earlier situation is that the vibrational transition dipole moment  $\mu_{trans}$  appropriate to the former is replaced by  $\mu_{f,i}(\mathbf{R}_e)$  for conventional (i.e., non-vibronic) transitions or  $\mu_{f,i}/R_a$  (for vibronic transitions).

As before, when  $\mu_{f,i}(\mathbf{R}_e)$  (or  $\mu_{f,i}/\mathbf{R}_a$ ) lies along the molecular axis of a linear molecule, the transition is denoted and k = 0 applies; when this vector lies perpendicular to the axis it is called and  $k = \pm 1$  pertains. The resultant **linear-molecule** rotational selection rules are the same as in the vibration-rotation case:

 $L = \pm 1$ , and  $M = \pm 1,0$  (for transitions).

 $L = \pm 1,0$  and  $M = \pm 1,0$  (for transitions).

In the latter case, the L = L' = 0 situation does not arise because a transition has one unit of angular momentum along the molecular axis which would preclude both L and L' vanishing.

For **non-linear molecules** of the spherical or symmetric top variety,  $\mu_{f,i}(\mathbf{R}_e)$  (or  $\mu_{f,i}/|\mathbf{R}_a$ ) may be aligned along or perdendicular to a symmetry axis of the molecule. The selection rules that result are

 $L = \pm 1,0;$   $M = \pm 1,0;$  and K = 0 (L = L' = 0 is not allowed and all L = 0 are forbidden when K = K' = 0)

which applies when  $\mu_{f,i}(\mathbf{R}_e)$  or  $\mu_{f,i}/R_a$  lies along the symmetry axis, and

$$L = \pm 1,0;$$
  $M = \pm 1,0;$  and  $K = \pm 1$  ( $L = L' = 0$  is not allowed)

which applies when  $\mu_{f,i}(\mathbf{R}_e)$  or  $\mu_{f,i}/R_a$  lies perpendicular to the symmetry axis.

### IV. Time Correlation Function Expressions for Transition Rates

The first-order E1 "golden-rule" expression for the rates of photon-induced transitions can be recast into a form in which certain specific physical models are easily introduced and insights are easily gained. Moreover, by using so-called equilibrium averaged time correlation functions, it is possible to obtain rate expressions appropriate to a

large number of molecules that exist in a distribution of initial states (e.g., for molecules that occupy many possible rotational and perhaps several vibrational levels at room temperature).

A. State-to-State Rate of Energy Absorption or Emission

To begin, the expression obtained earlier

$$\mathbf{R}_{i,f} = (2 \ /h^2) \mathbf{g}(\mathbf{f}_i) | \mathbf{E}_0 \bullet < \mathbf{f} | \boldsymbol{\mu} | |_i > |^2,$$

that is appropriate to transitions between a particular initial state i and a specific final state f, is rewritten as

 $R_{i,f} = (2 /h^2) g() | E_0 \cdot \langle f | \mu | i \rangle |^2 (f_{i,i} - ) d$ .

Here, the  $(f_{,i} - f_{,i} - f_{,i})$  function is used to specifically enforce the "resonance condition" that resulted in the time-dependent perturbation treatment given in Chapter 14; it states that the photons' frequency must be resonant with the transition frequency  $f_{,i}$ . It should be noted that by allowing to run over positive and negative values, the photon absorption (with  $f_{,i}$  positive and hence positive) and the stimulated emission case (with  $f_{,i}$ negative and hence negative) are both included in this expression (as long as g() is defined as g(| - |) so that the negative- contributions are multiplied by the light source intensity at the corresponding positive value).

The following integral identity can be used to replace the -function:

$$(f_{i}, i - i) = \frac{1}{2} \exp[i(f_{i}, i - i)t] dt$$

by a form that is more amenable to further development. Then, the state-to-state rate of transition becomes:

$$R_{i,f} = (1/h^2) \quad g(\ ) \ | \ E_0 \ \bullet \ < \ _f \ | \ \mu \ | \ _i \! > \! |^2 \ exp[i( \ _{f,i} \ - \ )t] \ dt \ d \ .$$

-

B. Averaging Over Equilibrium Boltzmann Population of Initial States

If this expression is then multiplied by the **equilibrium probability** i that the molecule is found in the state i and summed over all such initial states and summed over all final states f that can be reached from i with photons of energy h, the <u>equilibrium</u> <u>averaged rate of photon absorption</u> by the molecular sample is obtained:

 $R_{eq.ave.} = (1/\hbar^2)$  i, f i

g( ) 
$$| \mathbf{E}_0 \cdot \langle f | \mu | |_i > |^2 \exp[i(f_{,i} - f_{,i})t] dt d$$
.

This expression is appropriate for an ensemble of molecules that can be in various initial states  $_{i}$  with probabilities  $_{i}$ . The corresponding result for transitions that originate in a particular state ( $_{i}$ ) but end up in any of the "allowed" (by energy and selection rules) final states reads:

$$R_{\text{state i.}} = (1/\hbar^2) \quad f \quad g() \mid E_0 \cdot < f \mid \mu \mid i \geq |2|$$

$$\exp[i(f_{i}, i - t_{i})t] dt d$$

For a canonical ensemble, in which the number of molecules, the temperature, and the system volume are specified,  $_{i}$  takes the form:

$$_{i} = \frac{g_{i} \exp(-E_{i}^{0}/kT)}{Q}$$

\_

where Q is the canonical partition function of the molecules and  $g_i$  is the degeneracy of the state <sub>i</sub> whose energy is  $E_i^{0}$ .

In the above expression for  $R_{eq.ave.}$ , a double sum occurs. Writing out the elements that appear in this sum in detail, one finds:

$$i, f \quad i \mathbf{E}_0 \bullet < i |\mu| \quad f \ge \mathbf{E}_0 \bullet < f |\mu| \quad i \ge \exp((f, i))t.$$

In situations in which one is interested in developing an expression for the intensity arising from transitions to <u>all</u> allowed final states, the sum over these final states can be carried out explicitly by first writing

 $< f \mid \mu \mid i > expi(f_i)t = (f_i)t = (f_i)t + ($ 

and then using the fact that the set of states  $\{k\}$  are complete and hence obey

$$|_{k}|_{k} > < |_{k}| = 1.$$

The result of using these identities as well as the **Heisenberg definition** of the timedependence of the dipole operator

$$\mu(t) = \exp(iHt/\hbar) \mu \exp(-iHt/\hbar),$$

is:

$$i i < i | \mathbf{E}_0 \bullet \boldsymbol{\mu} \mathbf{E}_0 \bullet \boldsymbol{\mu}(t) | i > .$$

In this form, one says that the time dependence has been reduce to that of an equilibrium averaged (n.b., the i < i | i > i) **time correlation function** involving the component of the dipole operator along the external electric field at t = 0 ( $\mathbf{E}_0 \cdot \boldsymbol{\mu}$ ) and this component at a different time t ( $\mathbf{E}_0 \cdot \boldsymbol{\mu}$ (t)).

### C. Photon Emission and Absorption

If  $f_{i,i}$  is positive (i.e., in the photon absorption case), the above expression will yield a non-zero contribution when multiplied by exp(-i t) and integrated over positive values. If  $f_{i,i}$  is negative (as for stimulated photon emission), this expression will contribute, again when multiplied by exp(-i t), for negative -values. In the latter situation,  $f_{i}$  is the equilibrium probability of finding the molecule in the (excited) state from which emission will occur; this probability can be related to that of the lower state  $f_{f}$  by

$$excited = lower exp[ - (E^0_{excited} - E^0_{lower})/kT ]$$

$$= lower \exp[-h/kT].$$

In this form, it is important to realize that the excited and lower states are treated as individual <u>states</u>, not as levels that might contain a degenerate set of states.

The absorption and emission cases can be combined into a single <u>net</u> expression for the rate of photon absorption by recognizing that the latter process leads to photon production, and thus must be entered with a negative sign. The resultant expression for the <u>net rate of decrease of photons</u> is:

$$R_{eq.ave.net} = (1/h^2) \quad i \quad i (1 - exp(-h /kT))$$

$$g() < i \mid (\mathbf{E}_0 \cdot \boldsymbol{\mu}) \mathbf{E}_0 \cdot \boldsymbol{\mu}(t) \mid i > \exp(-i t) d dt$$

#### D. The Line Shape and Time Correlation Functions

Now, it is convention to introduce the so-called "line shape" function I ( ):

I ( ) = 
$$i i < i | (\mathbf{E}_0 \cdot \boldsymbol{\mu}) \mathbf{E}_0 \cdot \boldsymbol{\mu}(t) | i > \exp(-i t) dt$$

in terms of which the net photon absorption rate is

 $R_{eq.ave.net} = (1/\hbar^2) (1 - exp(-\hbar /kT)) g() I() d$ .

As stated above, the function

$$\mathbf{C}(\mathbf{t}) = \mathbf{i} \quad \mathbf{i} < \mathbf{i} \mid (\mathbf{E}_0 \bullet \boldsymbol{\mu}) \mathbf{E}_0 \bullet \boldsymbol{\mu}(\mathbf{t}) \mid \mathbf{i} > \mathbf{E}_0 \bullet \boldsymbol{\mu}(\mathbf{t}) \mid \mathbf{i} > \mathbf{E}_0 \bullet \boldsymbol{\mu}(\mathbf{t}) \mid \mathbf{i} > \mathbf{i} < \mathbf{i$$

is called the equilibrium averaged **time correlation function** of the component of the electric dipole operator along the direction of the external electric field  $\mathbf{E}_0$ . Its Fourier transform is I ( ), the **spectral line shape** function. The convolution of I ( ) with the light source's g ( ) function, multiplied by

 $(1 - \exp(-h/kT))$ , the correction for stimulated photon emission, gives the net rate of photon absorption.

E. Rotational, Translational, and Vibrational Contributions to the Correlation Function

To apply the time correlation function machinery to each particular kind of spectroscopic transition, one proceeds as follows:

1. For purely **rotational transitions**, the initial and final electronic and vibrational states are the same. Moreover, the electronic and vibrational states are not summed over in the analog of the above development because one is interested in obtaining an expression for a particular  $_{iv}$   $_{ie} ==> _{fv} _{fe}$  electronic-vibrational transition's lineshape. As a result, the sum over final states contained in the expression (see earlier)  $_{i, f}$   $_{i} E_{0} \cdot < _{i} |\mu| _{f} > E_{0} \cdot < _{f} |\mu(t)| _{i} > \exp((_{f,i})t)$  applies only to summing over final rotational states. In more detail, this can be shown as follows:

i, f i 
$$\mathbf{E}_0 \bullet < i | \mu |$$
 f>  $\mathbf{E}_0 \bullet < f | \mu (t) |$  i>

 $= \quad \text{i, f} \quad \text{i} \ \mathbf{E}_0 \bullet < \text{ir} \quad \text{iv} \quad \text{ie} \mid \mu \mid \quad \text{fr} \quad \text{iv} \quad \text{ie} > \mathbf{E}_0 \bullet < \text{fr} \quad \text{iv} \quad \text{ie} \mid \mu(t) \mid \quad \text{ir} \quad \text{iv} \quad \text{ie} >$ 

$$= i, f \quad ir \quad iv \quad ie \mathbf{E}_0 \bullet < ir | \mu_{ave.iv} | \quad fr > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv} (t) | \quad ir > \mathbf{E}_0 \bullet < fr | \mu_{ave.iv}$$

$$= i \quad ir \quad iv \quad ie \mathbf{E}_0 \bullet < ir \mid \mu_{ave.iv} \mathbf{E}_0 \bullet \mid \mu_{ave.iv}(t) \mid ir > .$$

In moving from the second to the third lines of this derivation, the following identity was used:

where H is the full (electronic plus vibrational plus rotational) Hamiltonian and  $H_{v,r}$  is the vibrational and rotational Hamiltonian for motion on the electronic surface of the state ie whose dipole moment is  $\mu(\mathbf{R})$ . From the third line to the fourth, the (approximate) separation of rotational and vibrational motions in  $H_{v,r}$ 

$$H_{v,r} = H_v + H_r$$

has been used along with the fact that iv is an eigenfunction of  $H_v$ :

$$H_v iv = E_{iv} iv$$

to write

$$\langle i_{v} | \mu(\mathbf{R},t) | i_{v} \rangle = \exp(i H_{r} t/h) \langle i_{v} | \exp(i H_{v} t/h)$$

 $\mu \ (\textbf{R}) \ exp(\text{--} iH_v \ t/h) \mid \quad_{iv} > exp(\text{--} iH_r \ t/h)$ 

$$= \exp(i H_r t/h) < i_{V} | \exp(iE_{iV} t/h)$$

$$\mu (\mathbf{R}) \exp(-iE_{iv} t/h) \mid iv > \exp(-iH_r t/h)$$

$$= \exp(i H_r t/h) < i_V |\mu(\mathbf{R})| i_V > \exp(-iH_r t/h)$$

$$= \mu_{ave.iv} (t).$$

In effect,  $\mu$  is replaced by the vibrationally averaged electronic dipole moment  $\mu_{ave,iv}$  for each initial vibrational state that can be involved, and the time correlation function thus becomes:

$$C(t) = i \quad ir \quad iv \quad ie < ir \mid (\mathbf{E}_0 \bullet \mu_{ave,iv}) \mathbf{E}_0 \bullet \mu_{ave,iv}(t) \mid ir > ,$$

where  $\mu_{ave,iv}$  (t) is the averaged dipole moment for the vibrational state <sub>iv</sub> at time t, given that it was  $\mu_{ave,iv}$  at time t = 0. The time dependence of  $\mu_{ave,iv}$  (t) is induced by the rotational Hamiltonian H<sub>r</sub>, as shown clearly in the steps detailed above:

$$\mu_{\text{ave,iv}}(t) = \exp(i H_r t/h) < i_V |\mu(\mathbf{R})| \quad i_V > \exp(-iH_r t/h).$$

In this particular case, the equilibrium average is taken over the initial rotational states whose probabilities are denoted  $_{\rm ir}$ , any initial vibrational states that may be populated, with probabilities  $_{\rm iv}$ , and any populated electronic states, with probabilities  $_{\rm ie}$ .

2. For **vibration-rotation transitions** within a single electronic state, the initial and final electronic states are the same, but the initial and final vibrational and rotational states differ. As a result, the sum over final states contained in the expression  $i, f \in \mathbf{E}_0 \cdot \mathbf{e}_i \mid \mu \mid \mathbf{f} > \mathbf{E}_0 \cdot \mathbf{e}_i \mid \mathbf{f} \mid \mathbf{f$ 

i, f i 
$$\mathbf{E}_0 \bullet \langle i | \mu | f \geq \mathbf{E}_0 \bullet \langle f | \mu(t) | i \rangle$$

$$= i, f \quad ir \quad iv \quad ie \mathbf{E}_0 \bullet < ir \quad iv \mid \mu(\mathbf{R}) \mid \quad fr \quad fv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \quad iv > \mathbf{E}_0 \bullet < fr \quad fv \mid \mu(\mathbf{R},t) \mid \quad ir \mid \mu(\mathbf{R},t) \mid \quad$$

where the vibrational transition dipole matrix element is defined as before

$$\mu_{trans} = a < iv |(R_a - R_{a,eq})| fv > \mu / R_a$$

and derives its time dependence above from the rotational Hamiltonian:

$$\mu_{\text{trans}}(t) = \exp(iH_r t/h) \mu_{\text{trans}} \exp(-iH_r t/h).$$

The corresponding final expression for the time correlation function C(t) becomes:

 $C(t) = i \quad ir \quad iv \quad ie < ir \mid (\mathbf{E}_0 \bullet \mu_{trans}) \mathbf{E}_0 \bullet \mu_{trans}(t) \mid ir > exp(i \quad fv, ivt).$ 

The net rate of photon absorption remains:

$$R_{eq.ave.net} = (1/h^2) (1 - exp(-h)) g() I() d ,$$

where I() is the Fourier transform of C(t).

 $\label{eq:contains} \begin{array}{l} The expression for C(t) clearly contains two types of time dependences: (i) the \\ exp(i \ _{fv,iv}t), upon Fourier transforming to obtain I( \ ), produces \ -function "spikes" at \\ \end{array}$ 

frequencies =  $f_{v,iv}$  equal to the spacings between the initial and final vibrational states, and (ii) rotational motion time dependence that causes  $\mu_{trans}$  (t) to change with time. The latter appears in the form of a correlation function for the component of  $\mu_{trans}$  along  $E_0$  at time t = 0 and this component at another time t. The convolution of both these time dependences determines the from of I(\_).

3. For **electronic-vibration-rotation transitions**, the initial and final electronic states are different as are the initial and final vibrational and rotational states. As a result, the sum over final states contained in the expression  $i, f \in \mathbf{E}_0 \cdot \mathbf{E}_0 \cdot$ 

$$\begin{split} i, f & i \mathbf{E}_{0} \cdot < i | \mu | \quad f \geq \mathbf{E}_{0} \cdot < f | \mu (t) | \quad i > \\ \\ = & i, f & i \mathbf{E}_{0} \cdot < ir \quad iv \quad ie | \mu | \quad fr \quad fv \quad fe \geq \mathbf{E}_{0} \cdot < fr \quad fv \quad fe | \mu (t) | \quad ir \quad iv \quad ie > \\ \\ = & i, f & ir \quad iv \quad ie \mathbf{E}_{0} \cdot < ir \quad iv | \mu_{i,f}(\mathbf{R}) | \quad fr \quad fv > \mathbf{E}_{0} \cdot < fr \quad fv | \mu_{i,f}(\mathbf{R},t) | \quad ir \quad iv \\ \\ = & i, f & ir \quad iv \quad ie \mathbf{E}_{0} \cdot < ir | \mu_{i,f}(\mathbf{R}_{e}) | \quad fr > | < iv | \quad fv > |^{2} \\ \\ \mathbf{E}_{0} \cdot < fr | exp(iH_{r}t/h) \mu_{i,f}(\mathbf{R}_{e}) exp(-iH_{r}t/h) | \quad ir > exp(i \quad fv,ivt + i \quad E_{i,f}t/h) \\ \\ = & i, f & ir \quad iv \quad ie < ir | \mathbf{E}_{0} \cdot \mu_{i,f}(\mathbf{R}_{e}) \mathbf{E}_{0} \cdot \mu_{i,f}(\mathbf{R}_{e,t}) | \quad ir > | < iv | \quad fv > |^{2} \\ \\ & exp(i \quad fv,ivt + i \quad E_{i,f}t/h), \end{split}$$

where

$$\mu_{i,f}(\mathbf{R}_{e},t) = \exp(iH_{r}t/h) \ \mu_{i,f}(\mathbf{R}_{e}) \ \exp(-iH_{r}t/h)$$

is the electronic transition dipole matrix element, evaluated at the equilibrium geometry of the absorbing state, that derives its time dependence from the rotational Hamiltonian  $H_r$  as in the time correlation functions treated earlier.

This development thus leads to the following definition of C(t) for the electronic, vibration, and rotation case:

$$C(t) = \underset{i, f}{\text{ ir } iv } ie < \underset{ir}{\text{ ir } | \mathbf{E}_0 \bullet \mu_{i,f}(\mathbf{R}_e) \mathbf{E}_0 \bullet \mu_{i,f}(\mathbf{R}_e,t) | iv < | < iv | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v | v > | < v > | < v | v > | < v | v > | < v | v > | < v | v > | < v > | < v | v > | < v | < v > | < v | v > | < v | < v > | < v | v > | < v > | < v > | < v > | < v | v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | < v > | <$$

$$exp(i f_{v,iv}t + i E_{i,f}t/h)$$

but the net rate of photon absorption remains:

$$R_{eq.ave.net} = (1/\hbar^2) (1 - exp(-\hbar /kT)) g() I() d$$
.

Here, I( ) is the Fourier transform of the above C(t) and  $E_{i,f}$  is the adiabatic electronic energy difference (i.e., the energy difference between the v = 0 level in the final electronic state and the v = 0 level in the initial electronic state) for the electronic transition of interest. The above C(t) clearly contains Franck-Condon factors as well as time dependence  $exp(i f_{v,iv}t + i E_{i,f}t/h)$  that produces -function spikes at each electronic-vibrational transition frequency and rotational time dependence contained in the time correlation function quantity  $< i_{Ir} | E_0 \cdot \mu_{i,f}(R_e) E_0 \cdot \mu_{i,f}(R_e,t) | i_{Ir} > .$ 

To summarize, the line shape function I(  $\$ ) produces the net rate of photon absorption

$$R_{eq.ave.net} = (1/\hbar^2) (1 - exp(-\hbar /kT)) g() I() d$$

in all of the above cases, and  $I(\ )$  is the Fourier transform of a corresponding timedependent C(t) function in all cases. However, the pure rotation, vibration-rotation, and electronic-vibration-rotation cases differ in the form of their respective C(t)'s. Specifically,

$$C(t) = i \quad ir \quad iv \quad ie < ir \mid (\mathbf{E}_0 \bullet \mu_{ave,iv}) \mathbf{E}_0 \bullet \mu_{ave,iv}(t) \mid ir > ir > ir$$

in the pure rotational case,

$$C(t) = i \quad ir \quad iv \quad ie < ir \mid (\mathbf{E}_0 \bullet \mu_{trans}) \mathbf{E}_0 \bullet \mu_{trans}(t) \mid ir > exp(i \quad f_{v,iv}t)$$

in the vibration-rotation case, and

$$C(t) = i, f \text{ ir } iv \text{ ie } < ir | \mathbf{E}_0 \bullet \mu_{i,f}(\mathbf{R}_e) \mathbf{E}_0 \bullet \mu_{i,f}(\mathbf{R}_e,t) | ir > | < iv | fv > |^2$$
$$exp(i fv,ivt + E_{i,f}t/h)$$

in the electronic-vibration-rotation case.

All of these time correlation functions contain time dependences that arise from rotational motion of a dipole-related vector (i.e., the vibrationally averaged dipole  $\mu_{ave,iv}$  (t), the vibrational transition dipole  $\mu_{trans}$  (t), or the electronic transition dipole  $\mu_{i,f}(\mathbf{R}_{e,t})$ ) and the latter two also contain oscillatory time dependences (i.e.,  $\exp(i_{fv,iv}t)$  or  $\exp(i_{fv,iv}t + i_{i,ft}/h)$ ) that arise from vibrational or electronic-vibrational energy level differences. In the treatments of the following sections, consideration is given to the rotational contributions under circumstances that characterize, for example, dilute gaseous samples where the collision frequency is low and liquid-phase samples where rotational motion is better described in terms of diffusional motion.

# F. Line Broadening Mechanisms

If the rotational motion of the molecules is assumed to be entirely unhindered (e.g., by any environment or by collisions with other molecules), it is appropriate to express the time dependence of each of the dipole time correlation functions listed above in terms of a "free rotation" model. For example, when dealing with diatomic molecules, the electronic-vibrational-rotational C(t) appropriate to a specific electronic-vibrational transition becomes:

$$C(t) = (q_r q_v q_e q_t)^{-1} \quad J \quad (2J+1) \exp(-h^2 J (J+1)/(8^{-2} I k T)) \exp(-h_{vib} vi / k T)$$

$$g_{ie} < J | \mathbf{E}_0 \bullet \mu_{i,f}(\mathbf{R}_e) \mathbf{E}_0 \bullet \mu_{i,f}(\mathbf{R}_e,t) | J > | < iv | iv | v > |^2$$

$$\exp(i [h_{vib}] t + i E_{i,f} t/h).$$

Here,

$$q_r = (8 \ ^2 IkT/h^2)$$

is the rotational partition function (I being the molecule's moment of inertia  $I = \mu R_e^2$ , and  $h^2 J(J+1)/(8 \ ^2I)$  the molecule's rotational energy for the state with quantum number J and degeneracy 2J+1)

$$q_v = \exp(-h_{vib}/2kT) (1-\exp(-h_{vib}/kT))^{-1}$$

is the vibrational partition function ( $_{vib}$  being the vibrational frequency),  $g_{ie}$  is the degeneracy of the initial electronic state,

$$q_t = (2 \text{ mkT/h}^2)^{3/2} \text{ V}$$

is the translational partition function for the molecules of mass m moving in volume V, and  $E_{i,f}$  is the adiabatic electronic energy spacing.

The functions  $\langle J | E_0 \cdot \mu_{i,f}(\mathbf{R}_e) E_0 \cdot \mu_{i,f}(\mathbf{R}_e,t) | J \rangle$  describe the time evolution of the dipole-related vector (the electronic transition dipole in this case) for the rotational state J. In a "free-rotation" model, this function is taken to be of the form:

$$< J | \mathbf{E}_0 \bullet \mu_{i,f}(\mathbf{R}_e) \mathbf{E}_0 \bullet \mu_{i,f}(\mathbf{R}_e,t) | J >$$
$$= < J | \mathbf{E}_0 \bullet \mu_{i,f}(\mathbf{R}_e) \mathbf{E}_0 \bullet \mu_{i,f}(\mathbf{R}_e,0) | J > \cos \frac{h J(J+1) t}{4 I} ,$$

where

$$\frac{\mathrm{h} \mathrm{J}(\mathrm{J}+1)}{4 \mathrm{I}} = \mathrm{J}$$

is the rotational frequency (in cycles per second) for rotation of the molecule in the state labeled by J. This oscillatory time dependence, combined with the exp(i  $f_{v,iv}t + i E_{i,f}t/h$ ) time dependence arising from the electronic and vibrational factors, produce, when this C(t) function is Fourier transformed to generate I() a series of -function "peaks" whenever

$$= f_{v,iv} + E_{i,f}/h \pm J$$
.

The intensities of these peaks are governed by the

$$(q_r q_v q_e q_t)^{-1}$$
 J (2J+1) exp(- h<sup>2</sup>J(J+1)/(8 <sup>2</sup>IkT)) exp(- h vibvi/kT) gie

Boltzmann population factors as well as by the  $|\langle_{iv}|_{fv} > |^2$  Franck-Condon factors and the  $\langle_J | \mathbf{E}_0 \cdot \mu_{i,f}(\mathbf{R}_e) \mathbf{E}_0 \cdot \mu_{i,f}(\mathbf{R}_e, 0) |_J > \text{terms.}$ 

This same analysis can be applied to the pure rotation and vibration-rotation C(t) time dependences with analogous results. In the former, -function peaks are predicted to occur at

and in the latter at

$$= f_{v,iv} \pm J;$$

with the intensities governed by the time independent factors in the corresponding expressions for C(t).

In experimental measurements, such sharp -function peaks are, of course, not observed. Even when very narrow band width laser light sources are used (i.e., for which g() is an extremely narrowly peaked function), spectral lines are found to possess finite widths. Let us now discuss several sources of line broadening, some of which will relate to deviations from the "unhindered" rotational motion model introduced above.

#### 1. Doppler Broadening

In the above expressions for C(t), the averaging over initial rotational, vibrational, and electronic states is explicitly shown. There is also an average over the translational motion implicit in all of these expressions. Its role has not (yet) been emphasized because the molecular energy levels, whose spacings yield the characteristic frequencies at which light can be absorbed or emitted, do not depend on translational motion. However, the frequency of the electromagnetic field experienced by moving molecules does depend on the velocities of the molecules, so this issue must now be addressed.

Elementary physics classes express the so-called **Doppler shift** of a wave's frequency induced by movement either of the light source or of the molecule (Einstein tells us these two points of view must give identical results) as follows:

observed = nominal  $(1 + v_z/c)^{-1}$  nominal  $(1 - v_z/c + ...)$ .

Here, nominal is the frequency of the unmoving light source seen by unmoving molecules,  $v_z$  is the velocity of relative motion of the light source and molecules, c is the speed of light, and observed is the Doppler shifted frequency (i.e., the frequency seen by the molecules). The second identity is obtained by expanding, in a power series, the  $(1 + v_z/c)^{-1}$  factor, and is valid in truncated form when the molecules are moving with speeds significantly below the speed of light.

For all of the cases considered earlier, a C(t) function is subjected to Fourier transformation to obtain a spectral lineshape function I( ), which then provides the essential ingredient for computing the net rate of photon absorption. In this Fourier transform process, the variable is assumed to be the frequency of the electromagnetic field <u>experienced by the molecules</u>. The above considerations of Doppler shifting then leads one to realize that the correct functional form to use in converting C(t) to I( ) is:

$$I() = C(t) \exp(-it (1-v_z/c)) dt$$
,

where is the nominal frequency of the light source.

As stated earlier, within C(t) there is also an equilibrium average over translational motion of the molecules. For a gas-phase sample undergoing random collisions and at thermal equilibrium, this average is characterized by the well known Maxwell-Boltzmann velocity distribution:

$$(m/2 \ kT)^{3/2} \exp(-m (v_x^2 + v_y^2 + v_z^2)/2kT) dv_x dv_y dv_z.$$

Here m is the mass of the molecules and  $v_x$ ,  $v_y$ , and  $v_z$  label the velocities along the labfixed cartesian coordinates.

Defining the z-axis as the direction of propagation of the light's photons and carrying out the averaging of the Doppler factor over such a velocity distribution, one obtains:

$$exp(-it (1-v_z/c)) (m/2 kT)^{3/2} exp(-m (v_x^2+v_y^2+v_z^2)/2kT) dv_x dv_y dv_z$$

$$= \exp(-i t) (m/2 kT)^{1/2} \exp(i tv_z/c) \exp(-mv_z^2/2kT) dv_z$$
$$-$$
$$= \exp(-i t) \exp(- \frac{2t^2kT}{(2mc^2)}).$$

This result, when substituted into the expressions for C(t), yields expressions identical to those given for the three cases treated above <u>but</u> with one modification. The translational motion average need no longer be considered in each C(t); instead, the earlier expressions for C(t) must each be multiplied by a factor  $exp(- 2t^2kT/(2mc^2))$  that embodies the translationally averaged Doppler shift. The spectral line shape function I() can then be obtained for each C(t) by simply Fourier transforming:

 $I() = \exp(-i t) C(t) dt.$ 

When applied to the rotation, vibration-rotation, or electronic-vibration-rotation cases within the "unhindered" rotation model treated earlier, the Fourier transform involves integrals of the form:

$$I() = \exp(-i t) \exp(-\frac{2t^2kT}{(2mc^2)})\exp(i(f_{v,iv} + E_{i,f}/\hbar \pm J)t) dt.$$

This integral would arise in the electronic-vibration-rotation case; the other two cases would involve integrals of the same form but with the  $E_{i,f}/h$  absent in the vibration-rotation situation and with  $f_{v,iv} + E_{i,f}/h$  missing for pure rotation transitions. All such integrals can be carried out analytically and yield:

I( ) = 
$$\sqrt{\frac{2mc^2}{^2kT}} \exp[-(-f_{v,iv} - E_{i,f}/h \pm J)^2 mc^2/(2 kT)].$$

The result is a series of Gaussian "peaks" in -space, centered at:

$$= f_{v,iv} + E_{i,f}/h \pm J$$

with widths ( ) determined by

$$^{2} = \frac{2kT}{mc^{2}},$$

given the temperature T and the mass of the molecules m. The hotter the sample, the faster the molecules are moving on average, and the broader is the distribution of Doppler shifted frequencies experienced by these molecules. The net result then of the Doppler effect is to produce a line shape function that is similar to the "unhindered" rotation model's series of -functions but with each -function peak broadened into a Gaussian shape.

#### 2. Pressure Broadening

To include the effects of collisions on the rotational motion part of any of the above C(t) functions, one must introduce a model for how such collisions change the dipolerelated vectors that enter into C(t). The most elementary model used to address collisions applies to gaseous samples which are assumed to undergo unhindered rotational motion until struck by another molecule at which time a randomizing "kick" is applied to the dipole vector and after which the molecule returns to its unhindered rotational movement.

The effects of such collisionally induced kicks are treated within the so-called **pressure broadening** (sometimes called collisional broadening) model by modifying the free-rotation correlation function through the introduction of an exponential damping factor exp(-|t|/):

$$< J | \mathbf{E}_{0} \cdot \mu_{i,f}(\mathbf{R}_{e}) \mathbf{E}_{0} \cdot \mu_{i,f}(\mathbf{R}_{e},0) | J > \cos \frac{h J(J+1) t}{4 I}$$

$$< J | \mathbf{E}_{0} \cdot \mu_{i,f}(\mathbf{R}_{e}) \mathbf{E}_{0} \cdot \mu_{i,f}(\mathbf{R}_{e},0) | J > \cos \frac{h J(J+1) t}{4 I} \exp(-|t|/).$$

This damping function's time scale parameter is assumed to characterize the average time between collisions and thus should be inversely proportional to the collision frequency. Its magnitude is also related to the effectiveness with which collisions cause the dipole function to deviate from its unhindered rotational motion (i.e., related to the collision strength). In effect, the exponential damping causes the time correlation function  $< J | E_0 \cdot$ 

 $\mu_{i,f}(\mathbf{R}_e) \mathbf{E}_0 \cdot \mu_{i,f}(\mathbf{R}_e,t) \mid J > to$  "lose its memory" and to decay to zero; this "memory" point of view is based on viewing  $< J \mid \mathbf{E}_0 \cdot \mu_{i,f}(\mathbf{R}_e) \mathbf{E}_0 \cdot \mu_{i,f}(\mathbf{R}_e,t) \mid J > as$  the projection of  $\mathbf{E}_0 \cdot \mu_{i,f}(\mathbf{R}_e,t)$  along its t = 0 value  $\mathbf{E}_0 \cdot \mu_{i,f}(\mathbf{R}_e,0)$  as a function of time t.

Introducing this additional exp( -|t|/ ) time dependence into C(t) produces, when C(t) is Fourier transformed to generate I( ),

$$I() = \exp(-i t)\exp(-|t|/)\exp(-2t^{2}kT/(2mc^{2}))\exp(i(f_{v,iv} + E_{i,f}/h \pm J)t)dt.$$

In the limit of very small Doppler broadening, the  $(^{2}t^{2}kT/(2mc^{2}))$  factor can be ignored (i.e., exp(-  $^{2}t^{2}kT/(2mc^{2}))$  set equal to unity), and

$$I( ) = \exp(-i t)\exp(-|t|/ )\exp(i( f_{v,iv} + E_{i,f}/h \pm J)t)dt$$

results. This integral can be performed analytically and generates:

$$I(\ )= \ \frac{1}{4} \ \ \{ \ \frac{1/}{(1/\ )^2 + \ (\ - \ _{fv,iv} - \ E_{i,f}/h \ \pm \ \ _J)^2} \ + \ \frac{1/}{(1/\ )^2 + \ (\ + \ _{fv,iv} + \ E_{i,f}/h \ \pm \ \ _J)^2} \ \ \},$$

a pair of Lorentzian peaks in -space centered again at

$$= \pm \begin{bmatrix} f_{V,iV} + E_{i,f}/h \pm J \end{bmatrix}.$$

\_

The full width at half height of these Lorentzian peaks is 2/. One says that the individual peaks have been pressure or collisionally broadened.

When the Doppler broadening can not be neglected relative to the collisional broadening, the above integral

$$I() = \exp(-i t)\exp(-|t|/)\exp(-2t^{2}kT/(2mc^{2}))\exp(i(t_{fv,iv} + E_{i,f}/h_{t} + J)t)dt$$

is more difficult to perform. Nevertheless, it can be carried out and again produces a series of peaks centered at

$$= f_{v,iv} + E_{i,f}/h \pm J$$

but whose widths are determined both by Doppler and pressure broadening effects. The resultant line shapes are thus no longer purely Lorentzian nor Gaussian (which are compared in the figure below for both functions having the same full width at half height and the same integrated area), but have a shape that is called a **Voight** shape.



# 3. Rotational Diffusion Broadening

Molecules in liquids and very dense gases undergo frequent collisions with the other molecules; that is, the mean time between collisions is short compared to the rotational period for their unhindered rotation. As a result, the time dependence of the dipole related correlation function can no longer be modeled in terms of free rotation that is interrupted by (infrequent) collisions and Dopler shifted. Instead, a model that describes the incessant buffeting of the molecule's dipole by surrounding molecules becomes appropriate. For liquid samples in which these frequent collisions cause the molecule's dipole to undergo angular motions that cover all angles (i.e., in contrast to a frozen glass or

solid in which the molecule's dipole would undergo strongly perturbed pendular motion about some favored orientation), the so-called **rotational diffusion** model is often used.

In this picture, the rotation-dependent part of C(t) is expressed as:

$$< J | \mathbf{E}_{0} \cdot \mu_{i,f}(\mathbf{R}_{e}) \mathbf{E}_{0} \cdot \mu_{i,f}(\mathbf{R}_{e,t}) | J >$$
$$= < J | \mathbf{E}_{0} \cdot \mu_{i,f}(\mathbf{R}_{e}) \mathbf{E}_{0} \cdot \mu_{i,f}(\mathbf{R}_{e,0}) | J > exp(-2D_{rot}|t|),$$

where  $D_{rot}$  is the <u>rotational diffusion constant</u> whose magnitude details the time decay in the averaged value of  $\mathbf{E}_0 \cdot \mu_{i,f}(\mathbf{R}_{e,t})$  at time t with respect to its value at time t = 0; the larger  $D_{rot}$ , the faster is this decay.

As with pressure broadening, this exponential time dependence, when subjected to Fourier transformation, yields:

$$I( ) = \exp(-i t)\exp(-2D_{rot}|t|)\exp(-2t^{2}kT/(2mc^{2}))\exp(i(t_{v,iv}+t_{i,f}/t_{i,v}+t_{i,f}/t_{i$$

Again, in the limit of very small Doppler broadening, the  $(^{2}t^{2}kT/(2mc^{2}))$  factor can be ignored (i.e., exp(-  $^{2}t^{2}kT/(2mc^{2}))$ ) set equal to unity), and

$$I() = \exp(-i t)\exp(-2D_{rot}|t|)\exp(i(f_{v,iv} + E_{i,f}/h \pm J)t)dt$$

results. This integral can be evaluated analytically and generates:

$$\begin{split} I(\ ) &= \frac{1}{4} \ \{ \frac{2D_{rot}}{(2D_{rot})^2 + \ (\ -\ fv,iv^- \ E_{i,f}/h \ \pm \ J)^2} \\ &+ \frac{2D_{rot}}{(2D_{rot})^2 + \ (\ +\ fv,iv^+ \ E_{i,f}/h \ \pm \ J)^2} \ \}, \end{split}$$

a pair of Lorentzian peaks in -space centered again at

$$= \pm [ f_{V,iV} + E_{i,f}/h \pm J].$$

The full width at half height of these Lorentzian peaks is  $4D_{rot}$ . In this case, one says that the individual peaks have been broadened via rotational diffusion. When the Doppler broadening can not be neglected relative to the collisional broadening, the above integral

$$I() = \exp(-i t)\exp(-2D_{rot}|t|)\exp(-2t^{2}kT/(2mc^{2}))\exp(i(f_{v,iv} + E_{i,f}/h \pm J)t)dt.$$

is more difficult to perform. Nevertheless, it can be carried out and again produces a series of peaks centered at

$$= \pm [f_{v,iv} + E_{i,f}/h \pm J]$$

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but whose widths are determined both by Doppler and rotational diffusion effects.

# 4. Lifetime or Heisenberg Homogeneous Broadening

Whenever the absorbing species undergoes one or more processes that depletes its numbers, we say that it has a finite lifetime. For example, a species that undergoes unimolecular dissociation has a finite lifetime, as does an excited state of a molecule that decays by spontaneous emission of a photon. Any process that depletes the absorbing species contributes another source of time dependence for the dipole time correlation functions C(t) discussed above. This time dependence is usually modeled by appending, in a multiplicative manner, a factor exp(-|t|/). This, in turn modifies the line shape function I() in a manner much like that discussed when treating the rotational diffusion case:

$$I( ) = exp(-i t)exp(-|t|/ )exp(- {}^{2}t^{2}kT/(2mc^{2}))exp(i( {}_{fv,iv}+ E_{i,f}/h \pm J)t)dt$$

Not surprisingly, when the Doppler contribution is small, one obtains:

$$\begin{split} I(\ ) &= \frac{1}{4} \ \{ \frac{1/}{(1/\ )^2 + \ (\ -\ _{fv,iv} -\ E_{i,f}/h \ \pm \ _J)^2} \\ &+ \frac{1/}{(1/\ )^2 + \ (\ +\ _{fv,iv} +\ E_{i,f}/h \ \pm \ _J)^2} \ \}. \end{split}$$

In these Lorentzian lines, the parameter describes the kinetic decay lifetime of the molecule. One says that the spectral lines have been **lifetime or Heisenberg broadened** by an amount proportional to 1/. The latter terminology arises because the finite lifetime of the molecular states can be viewed as producing, via the Heisenberg uncertainty relation E t > h, states whose energy is "uncertain" to within an amount E.

# 5. Site Inhomogeneous Broadening

Among the above line broadening mechanisms, the pressure, rotational diffusion, and lifetime broadenings are all of the **homogeneous** variety. This means that each molecule in the sample is affected in exactly the same manner by the broadening process. For example, one does not find some molecules with short lifetimes and others with long lifetimes, in the Heisenberg case; the entire ensemble of molecules is characterized by a single lifetime.

In contrast, Doppler broadening is **inhomogeneous** in nature because each molecule experiences a broadening that is characteristic of its particular nature (velocity  $v_z$  in this case). That is, the fast molecules have their lines broadened more than do the slower molecules. Another important example of inhomogeneous broadening is provided by so-called **site broadening**. Molecules imbedded in a liquid, solid, or glass do not, at the instant of photon absorption, all experience exactly the same interactions with their surroundings. The distribution of instantaneous "solvation" environments may be rather "narrow" (e.g., in a highly ordered solid matrix) or quite "broad" (e.g., in a liquid at high temperature). Different environments produce different energy level splittings =

 $_{fv,iv}$ +  $E_{i,f}$ / $h \pm _J$  (because the initial and final states are "solvated" differently by the surroundings) and thus different frequencies at which photon absorption can occur. The distribution of energy level splittings causes the sample to absorb at a range of frequencies as illustrated in the figure below where homogeneous and inhomogeneous line shapes are compared.



Homogeneous (a) and inhomogeneous (b) band shapes having inhomogeneous width  $INH^{+}$  and homogeneous width  $H^{-}$ 

The spectral line shape function  $I(\ )$  is further broadened when site inhomogeneity is present and significant. These effects can be modeled by convolving the kind of  $I(\ )$ function that results from Doppler, lifetime, rotational diffusion, and pressure broadening with a Gaussian distribution P( E) that describes the inhomogeneous distribution of energy level splittings:

$$I() = I^{0}(; E) P(E) d E$$
.

Here  $I^0(; E)$  is a line shape function such as those described earlier each of which contains a set of frequencies (e.g.,  $= f_{V,iv} + E_{i,f}/h \pm J = + E/h$ ) at which absorption or emission occurs.

A common experimental test for inhomogeneous broadening involves **hole burning**. In such experiments, an intense light source (often a laser) is tuned to a frequency <sub>burn</sub> that lies within the spectral line being probed for inhomogeneous broadening. Then, a second tunable light source is used to scan through the profile of the spectral line, and, for example, an absorption spectrum is recorded. Given an absorption profile as shown below in the absence of the intense burning light source:



one expects to see a profile such as that shown below:



if inhomogeneous broadening is operative.

The interpretation of the change in the absorption profile caused by the bright light source proceeds as follows:

(i) In the ensemble of molecules contained in the sample, some molecules will absorb at or near the frequency of the bright light source <sub>burn</sub>; other molecules (those whose environments do not produce energy level splittings that match <sub>burn</sub>) will not absorb at this frequency.

(ii) Those molecules that do absorb at burn will have their transition saturated by the <u>intense</u> light source, thereby rendering this frequency region of the line profile transparent to <u>further</u> absorption.

(iii) When the "probe" light source is scanned over the line profile, it will induce absorptions for those molecules whose local environments did not allow them to be saturated by the burn light. The absorption profile recorded by this probe light source's detector thus will match that of the original line profile, <u>until</u> (iv) the probe light source's frequency matches <sub>burn</sub>, upon which no absorption of the probe source's photons will be recorded because molecules that absorb in this frequency regime have had their transition saturated.

(v) Hence, a "**hole**" will appear in the spectrum recorded by the probe light source's detector in the region of <sub>burn</sub>.

Unfortunately, the technique of hole burning does not provide a fully reliable method for identifying inhomogeneously broadened lines. If a hole is observed in such a burning experiment, this provides ample evidence, but if one is not seen, the result is not definitive. In the latter case, the transition may not be strong enough (i.e., may not have a large enough "rate of photon absorption" ) for the intense light source to saturate the transition to the extent needed to form a hole.

This completes our introduction to the subject of molecular spectroscopy. More advanced treatments of many of the subjects treated here as well as many aspects of modern experimental spectroscopy can be found in the text by Zare on angular momentum as well as in Steinfeld's text <u>Molecules and Radiation</u>, 2<sup>nd</sup> Edition, by J. I. Steinfeld, MIT Press (1985).