

Fluctuating Electric Dipoles and the Absorption of Light

Although the concept of a fluctuating atomic or molecular dipole is basic to both the classical and the quantum-mechanical theory of absorption of light, introductory spectroscopy or quantum chemistry texts seldom devote much attention to the idea.

The interactions between electromagnetic radiation and matter give rise to a variety of interesting effects including light-scattering, absorption, and photoluminescence to name a few. These effects form the basis of important physical methods such as absorption spectroscopy and X-ray crystallography which have provided considerable insight into the detailed molecular and electronic structure of molecules. Because phenomena involving electromagnetic radiation have played so prominent a role in the development of modern chemistry, the relevant theory is considered in many undergraduate chemistry courses. In particular the theoretical aspects of absorption spectroscopy are often presented. Although, as we shall see, the concept of a fluctuating atomic or molecular electric dipole is basic to both the classical- and the quantum-mechanical theory of absorption, introductory texts about spectroscopy or quantum chemistry seldom devote much attention to the idea. In the following we will attempt to describe this concept and relate it to our understanding of the energy levels and the associated wavefunctions of atoms and molecules. To keep things simple we will restrict the discussion to electronic transitions in one-electron atoms and molecules, although the ideas are readily extended to vibrational transitions, etc. First we present a qualitative description of the absorption of light.

The wave-like properties of light may be described by oscillating electric and magnetic fields, each perpendicular to the other and to the direction of propagation. When the light wave impinges on an atom, interactions with both the oscillating magnetic and electric fields influence the motion of the particles of the system. Although the interaction involving the magnetic field may be quite important, e.g. in nuclear magnetic resonance spectroscopy, in electronic absorption spectroscopy the dominant interaction involves the oscillating electric field and we will focus our attention on the latter.

According to classical mechanics, the alternating electric field would exert a time dependent force on the electron in the atom and would cause the electron to oscillate in space. Moreover, the electronic energy of the atom in the radiation field would differ from that of the unperturbed atom because of the coupling that would occur between the fluctuating electric dipole, associated with the oscillating electron, and the oscillating electric field associated with the radiation. In other words the latter coupling interaction would provide a mechanism for energy transfer from the radiation field to the atom—the absorption of radiant energy would occur by the electric dipole mechanism. According to the classical theory, light of any frequency could be absorbed; however, experiment shows that only certain frequencies are efficiently absorbed, depending on the atom.

The detailed frequency dependence of the absorption process is only explained by the quantum theory. According to the quantum theory, quantized energy states are associated with atoms and molecules and each state has an associated wavefunction. An atom which is initially in one of the quantized energy states, say the ground state with wavefunction ψ_0 and energy E_0 , can be excited to a higher energy state, with

wave function ψ_j and energy E_j , only if the energy of the incident photons matches the energy gap between these states, i.e. if

$$\Delta E = E_j - E_0 = h\nu$$

where h is Planck's constant and ν is the frequency associated with the electromagnetic radiation. The theory also shows that transitions between certain states are very improbable even if the energy requirement is satisfied, *vide infra*. The latter are termed forbidden transitions.

A quantitative theory for absorption can be derived from a model which assumes a wave-like description of the radiation field, but which invokes a quantum-mechanical description of the atom. In this theory the fluctuating electric vector of the light wave perturbs the energy of the system by interacting with the electric dipole moment associated with the atom and inducing transitions between the discrete energy states.¹ What, we may ask, kind of electric dipole may be associated with an atom having discrete energy states and a charge density that must be described in terms of a probability distribution? The nature of the oscillating electric dipole and a microphysical interpretation of certain symmetry-based, spectroscopic selection rules will be described below after some mathematical results from the quantum theory are summarized. The references in the bibliography should be consulted for details of the latter.

Stationary States and Their Superposition

If we ignore spin, the wave function ψ of a bound electron is a function of τ , the spatial coordinates of the electron, and t , the time, and is obtained by solving the Schroedinger wave equation

$$H\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (1)$$

where H is the Hamiltonian operator, \hbar is Planck's constant divided by 2π , and $i = \sqrt{-1}$. If the system is not experiencing any time dependent perturbations, the spatial and temporal variables are separable, and the solutions are found to be product functions having the form of eqn. (2)

$$\psi_j(\tau, t) = \psi_j'(\tau)\phi_j(t) \quad (2)$$

where

$$\phi_j(t) = e^{-iE_j t/\hbar}$$

and where ψ_j' denotes the spatial function characteristic of the j^{th} stationary state and E_j denotes the energy of this state. For example, the spatial functions $\psi_j'(\tau)$ for the hydrogen atom are the familiar $1s$, $2s$, $2p$, etc., orbitals and the E_j are the energies associated with these orbitals. For many discussions, when time-dependent effects are unimportant, we can ignore the $\phi_j(t)$ functions and deal only with the spatial functions. If, however, the system is disturbed by a time-dependent interaction, the spatial and temporal variables cannot be separated and we must take account of both when describing the system.

To determine whether the oscillating charge density exhibits electric dipole character in, say the x -direction, we need to consider the details of the net electron density distribution along the x -axis as a function of time.

Note that despite the explicit time dependence in eqn. (2), the probability distribution of the electron in a stationary state is *not* a function of time, because $\phi_j^* \phi_j = 1$. Thus the electron density distribution of a stationary state is fixed in space and does not oscillate, so *fluctuating electric dipole character* is not a property of an atom in a stationary state.

If, on the other hand, the electron is in a state which is a *superposition of stationary states*, an example of which is eqn. (3)

$$\psi = r_1 \psi_1' e^{-iE_1 t/\hbar} + r_2 \psi_2' e^{-iE_2 t/\hbar} \quad (3)$$

the electron density is not fixed in space and does fluctuate in time as is evident from eqn. (4)

$$\psi^* \psi = r_1^2 (\psi_1')^2 + r_2^2 (\psi_2')^2 + r_1 r_2 \psi_1' \psi_2' [2 \cos(E_1 - E_2)t/\hbar] \quad (4)$$

where it is assumed that r_1, r_2, ψ_1' , and ψ_2' are all real-valued. The wavefunction in eqn. (3) describes a non-stationary state of the system. In order that the wavefunction of the non-stationary state given in eqn. (3) be normalized

$$r_1^2 + r_2^2 = 1$$

The first two terms of eqn. (4) represent the contributions of ψ_1 and ψ_2 to $\psi^* \psi$. The third term, called the interference term, represents a special effect that arises from the superposition of ψ_1 and ψ_2 , and it describes the "beating" of the time-varying components of the wavefunction. The "beat" frequency, which is the frequency of oscillation of the charge density, is given by the difference in energies of the two states superposed, divided by Planck's constant.

To determine whether the oscillating charge density exhibits electric dipole character in, say the x -direction, we need to consider the details of the *net* electron density distribution along the x -axis as a function of time. To do this, we sum the electron density over all points with a given x -coordinate by integrating $\psi^* \psi$ from $-\infty$ to $+\infty$ over the y and z coordinates, designating the resulting function as $P(x,t)$. Then $P(x,t)dx$ represents the net probability that the electron may be found in the interval between x and $x + dx$ at time t , and the integral of $P(x,t)$ over x is unity for any time t if the state is normalized. For a stationary state $P(x,t) = P(x)$ since the probability distribution of a stationary state is time-independent. To determine $P(x,t)$ for a superposition such as eqn. (3), we must carry out the integration for each term of eqn. (4), computing $P_1(x), P_2(x)$, and $P_{12}(x,t)$, respectively, where $P_1(x)$ denotes the contribution of ψ_1 , $P_2(x)$ denotes the contribution of ψ_2 , and $P_{12}(x,t)$ denotes the contribution of the interference term. For a given value of t we can plot the $P(x,t)$ distribution for the atom, placing the origin of our coordinate system at the nucleus. If at a given time the average value of the displacement of the electron along the x -axis is not zero, there is net charge separation associated with the state; if this charge separation oscillates about the nucleus in time, the (non-stationary) state has fluctuating electric dipole character.

In Figure 1, $P(x)$ is plotted for the 1s, 2s, and $2p_x$ states of the hydrogen atom.² The graph of $P(x)$ for the $2p_x$ state goes to zero at the nucleus because the equation $x = 0$ defines a

nodal plane for the $2p_x$ state. Note that the *average displacement of the electron along the x -axis* for the states depicted in Figure 1 is zero for all values of t as expected because the states involved in Figure 1 are stationary states. Although the nodal properties of the wavefunctions are better illustrated by plots of the radial distribution functions, the $P(x)$ functions provide a natural representation of the electron density distribution in space. If we could view the atom from a large distance somewhere off in the yz plane and we plotted the apparent net density of the electron cloud as a function of x , we would be plotting $P(x)$.

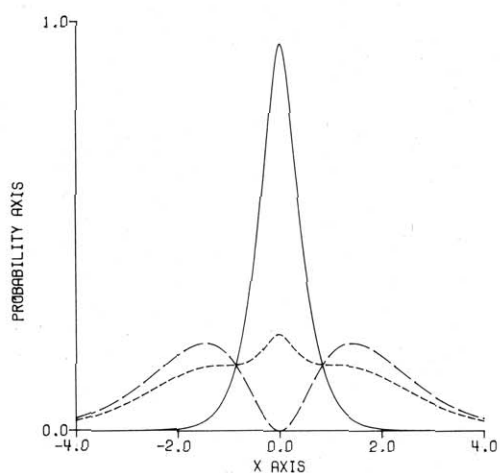


Figure 1. The $P(x)$ functions are shown for the 1s state (—), the 2s state (----), and the $2p_x$ state (- · -) where the distance of the electron from the nucleus in Angstroms is presented along the abscissa. The functions may be calculated analytically by double integration using a cylindrical coordinate system.

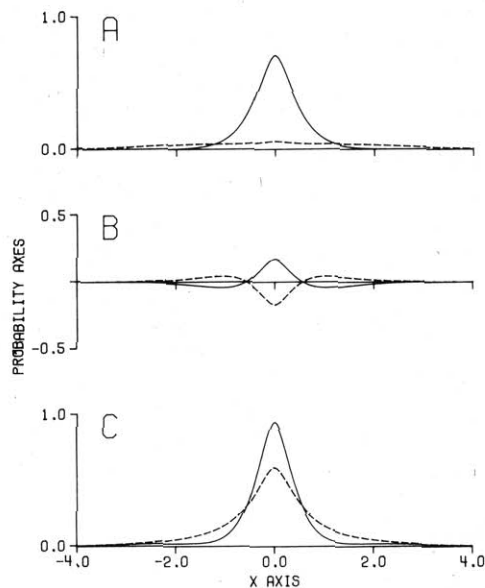


Figure 2. The $P(x,t)$ functions for a superposition Ψ of the 1s and 2s states; A: $0.75 P(x)$ for the 1s state (—), $0.25 P(x)$ for 2s (----); B: $2\sqrt{0.75 \cdot 0.25} P(x,t)$ for the interference term between 1s and 2s with the cosine term = +1 (—) and = -1 (----); C: $P(x,t)$ for $\Psi\Psi^*$ when the cosine term is = +1 (—) and = -1 (----).

¹ Transitions can also occur by the magnetic dipole or the electric quadrupole mechanism, though these mechanisms are much less effective. See problem 6 in the Appendix and also the fourth and eighth of the General References (Kauzmann and Macomber).

² The integration over y and z can be performed using cylindrical coordinates. Details are available from the author.

To obtain a feel for the dynamics of the absorption process, we can appeal to the correspondence between the quantum-mechanical process and the more familiar classical-mechanical process.

In Figure 2 the $P(x,t)$ is presented for the superposition of the 1s and 2s states given by eqn. (5). The coefficients in the superposition were chosen arbitrarily, except for the normalization requirement. The plot of $P(x,t)$ is presented for two values of t , the time, as indicated

$$\psi = \frac{\sqrt{3}}{2} \psi_{1s} e^{-iE_{1s}t/\hbar} + \frac{1}{2} \psi_{2s} e^{-iE_{2s}t/\hbar} \quad (5)$$

in the figure caption. It is apparent that the charge cloud of the atom fluctuates in space for this state; however, the average displacement of the electron is zero at all times. In Figures 2A and 2B the components of $P(x,t)$ for the superposition given by eqn. (5) are presented, and it is clear that the time-dependent character of the charge density derives from the interference term in Figure 2B. (See also eqn. (4).) The interference term alternately results in enhanced electron density near the nucleus and depleted electron density in the regions remote from the nucleus along the x -axis and *vice versa*. The oscillating charge density lacks electric dipole character because of the symmetrical nature of interference pattern between the 1s and the 2s orbital. No choice of coefficients for the superposition of the 1s and 2s orbitals, not even time-dependent coefficients, would result in fluctuating electric dipole character for a superposition of these two states. As seen below other superpositions do exhibit electric dipole character and electric dipole transitions may be excited between the states involved in the latter.

Time-Dependent Perturbation Theory and Electronic Excitation

Suppose an atom is in the ground (stationary) state ψ_0 and is perturbed by radiation with the electric vector oscillating in the x -direction. Because of the interaction with the radiation, another term H' must be included in the Hamiltonian operator of the atom

$$H' = -\mu_x E_x(t)$$

where μ_x is the x -component of the electric dipole moment operator and $E_x(t)$ describes the oscillating electric field associated with the light wave. The exact solution of eqn. (1) for an atom which is under the influence of a radiation field has not been found. The problem can be handled approximately, however, using time-dependent perturbation theory, if the interaction with the radiation field is weak compared to the interatomic interactions, as is usually the case for spectroscopic studies. The perturbation treatment shows that, in the presence of radiation, ψ_0 no longer suffices to describe the system and that the wavefunction evolves in time. The new state may, however, be described by a linear combination of stationary states

$$\psi(t) = \sum a_k(t) \psi_k(\tau, t)$$

where the coefficients $a_k(t)$ of the linear combination develop in time. The details of the perturbation treatment and explicit expressions for the time-dependent coefficients may be found in Kauzmann (fourth reference of the General References). Qualitatively, the theory shows that the light wave induces a dynamic mixing of excited states into the ground state; i.e., the system evolves into a non-stationary state which can be described by a superposition of stationary states. When $a_0(t) = 0$ and $a_k(t) = 1$, the system has absorbed a photon and the transition $\psi_0 \rightarrow \psi_k$ has occurred.

To obtain a feel for the dynamics of the absorption process, we can appeal to the correspondence between the quantum-

mechanical process and the more familiar classical-mechanical process. Recall that in the latter the oscillating electric field of the radiation accelerates the electron in alternate directions and gives rise to oscillating charge density with electric dipole character that mediates the absorption of energy. In the quantum-mechanical picture the electromagnetic radiation still acts to induce an oscillating charge cloud. Consequently the atom must evolve into a new state because, as we have seen, the ground state charge distribution does not oscillate. The coulombic interaction with the positively charged nucleus remains as the dominate force on the electron, however, and therefore the system does not "forget" entirely the energy level structure associated with the unperturbed atom. Instead it develops oscillating electric dipole character by evolving into a state which is a superposition of the ground and excited state(s) of the unperturbed atom. Thus we might say that the atom responds to the periodic disturbance within the framework of the quantized energy states available to it. Only certain excited states are mixed in—those which engender oscillating electric dipole character. Whether or not the system is promoted into an excited state depends on energy considerations. If, for example, the energy of the perturbing radiation is much smaller than the energy gap between the ground and excited states, the radiation is simply scattered by the atom. If, on the other hand, there is an energy match between the photons and the energy separation of the states involved, absorption occurs. It can be noted that the energy criterion is satisfied when the "beat" frequency (see eqn. (4)) associated with the superposed ground and excited states matches the frequency associated with the radiation field.

Constraints on absorption are expressed mathematically by the equations for the $a_k(t)$ coefficients in the superposition. For example, the equations contain the following factor

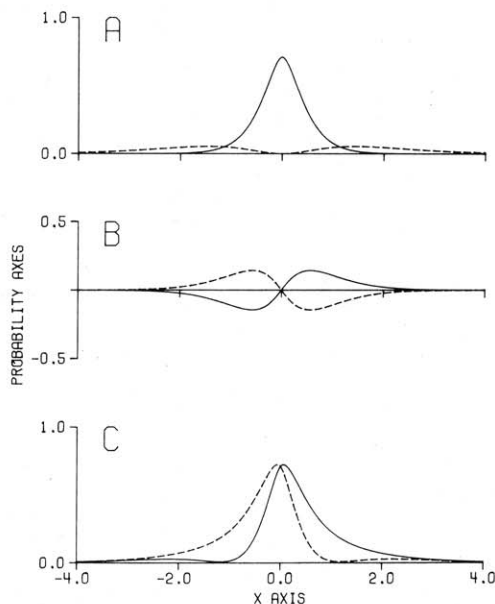


Figure 3. The $P(x,t)$ function for a superposition Ψ of the 1s and $2p_x$ states; A: $0.75 P(x)$ for the 1s state (—), $0.25 P(x)$ for $2p_x$ (---); B: $2\sqrt{0.75 \cdot 0.25} P(x,t)$ for the interference term between 1s and $2p_x$ with the cosine term = +1 (—) and = -1 (---); C: $P(x,t)$ for $\Psi\Psi^*$ when the cosine is = +1 (—) and = -1 (---).

$$\int (\psi_k')^* x \psi_0' d\tau$$

If the integral vanishes, the superposition of ψ_k and ψ_0 does not exhibit fluctuating electric dipole character in the x -direction, and the transition is forbidden. In addition the expressions derived for the coefficients have factors which show that the coefficient associated with a particular excited state is very small unless the energy associated with the exciting radiation matches the separation between that state and the ground state. (See Kauzmann).

Fortunately, for most purposes we do not have to evaluate these coefficients. As discussed earlier, whether or not a particular superposition involves fluctuating electric dipole character depends only on the nature of the spatial functions of the stationary states involved, and not on the relative magnitudes or the dynamical nature of the coefficients. *Therefore to ascertain whether a particular transition may be excited by the electric dipole mechanism, all we need to do is to examine an arbitrary superposition of the two stationary states involved and determine whether the superposition exhibits fluctuating electric dipole character.* If so the transition is orbitally allowed and should be induced in the presence of light of the proper frequency.³

The Hydrogen Atom

The ground state of the hydrogen atom is the $1s$ state. To determine whether a transition from the $1s$ state to an excited state is allowed we may simply superpose the excited state on the $1s$ state and see if the superposition exhibits fluctuating dipole character. To be specific, we restrict attention to plane polarized light with the electric vector oscillating along the x -axis.

As noted earlier, Figure 2C shows that a superposition of the $1s$ state and the $2s$ state gives rise to an oscillating charge cloud, but one which lacks fluctuating electric dipole character. Thus we would predict that this transition would not be excited by electromagnetic radiation, and our prediction agrees with experiment.

Next we consider the superposition of the $1s$ and $2p_x$ states given by eqn. (6). Again, the coefficients chosen are arbitrary except

$$\psi = \frac{\sqrt{3}}{2} \psi_{1s} e^{-iE_1 t/\hbar} + 1/2 \psi_{2p_x} e^{-iE_2 p_x t/\hbar} \quad (6)$$

for the normalization requirement. In Figure 3C the plot of $P(x,t)$ for this superposition is presented for two different times. It may be seen that the center of negative charge for this superposition oscillates about the nucleus and thus the fluctuating charge cloud has oscillating dipole character.

In Figures 3A and 3B the component functions of $P(x,t)$ are presented. The interference term, plotted in Figure 3B, contains the time dependence. As can be seen from eqn. (4), the interference term is a product of a function involving the spatial coordinates and a cosine function involving the time coordinate. For the state described by eqn. (6) the spatial factor is negative for $x < 0$ and positive for $x > 0$, because ψ_{1s} is positive for all x and ψ_{2p_x} is negative if $x < 0$, but positive if $x > 0$. Therefore at a given time the contribution to $P(x,t)$ of the interference term indicates there is enhanced electron density on one side of the nucleus and depleted electron density on the other; i.e., the electron density is skewed, or displaced, to one side of the nucleus. In time the charge displacement oscillates at the "beat" frequency of the two states. The conclusion is that a superposition of the $1s$ state and the $2p_x$ state involves fluctuating electric dipole character and that the $1s \rightarrow 2p_x$ transition is allowed. Experiment agrees with this prediction.

The Laporte selection rule is often invoked to explain the fact that an s to p type transition is allowed whereas an s to s type transition is forbidden. Essentially the rule states that transitions do not occur between states that have the same symmetry with respect to the inversion operation. With the discussion above we can understand the physical basis of this

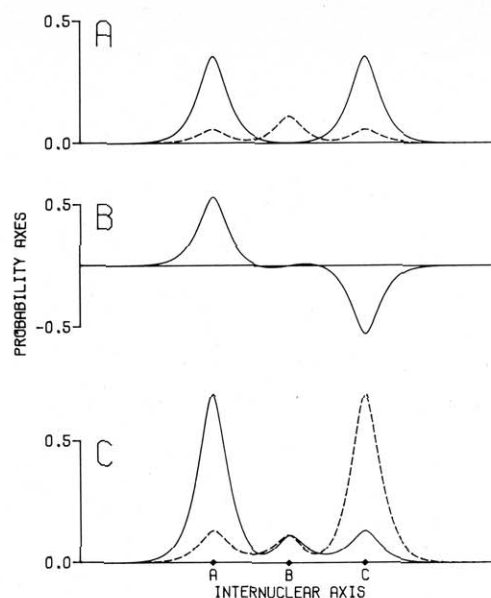


Figure 4. The $P(x,t)$ functions for a superposition Ψ of Ψ_2 and Ψ_3 of eqn. (7); A: $0.75 P(x)$ for Ψ_2 (—), $0.25 P(x)$ for Ψ_3 (---); B: $2\sqrt{0.75 \cdot 0.25} P(x,t)$ for the interference term between Ψ_2 and Ψ_3 with the cosine term = $+1$ (—); C: $P(x,t)$ for $\Psi\Psi^*$ when the cosine term is $+1$ (—) and -1 (---).

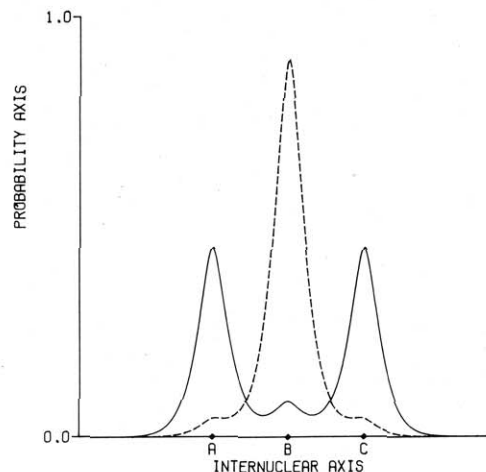


Figure 5. The $P(x,t)$ function for the superposition Ψ of Ψ_1 and Ψ_3 of eqn. (7) when the cosine term is $+1$ (—) and -1 (---).

rule: *the states which are strongly mixed into the ground state under the influence of radiation are those which interfere asymmetrically with the ground state, permitting fluctuating electric dipole character. In order to interfere asymmetrically, the states involved must have opposite inversion symmetry.* The same ideas carry over to molecules, and there some new considerations arise.

A One-Electron Molecule

We will consider a particularly simple system which consists of three protons arranged in a linear fashion and a single electron. If the nuclei are labelled A, B, and C, according to simple Huckel theory, the three molecular orbitals derived from the $1s$ orbitals are

³ We are ignoring multiple-photon processes as well as spin selection rules. The latter are important for many electron atoms.

⁴ For the multi-nuclear system the integration over y and z was performed using cylindrical coordinates. Integrals involving functions centered on the same nucleus were handled analytically. Integrals involving functions centered on different nuclei were performed numerically in part.

$$\psi_3 = (1s_A - \sqrt{2} 1s_B + 1s_C)/2 \quad (7)$$

$$\psi_2 = (1s_A - 1s_C)/\sqrt{2} \quad (8)$$

$$\psi_1 = (1s_A + \sqrt{2} 1s_B + 1s_C)/2 \quad (9)$$

First consider the transition $\psi_2 \rightarrow \psi_3$. As seen in Figure 4 a superposition of ψ_2 and ψ_3 gives rise to an oscillating charge cloud whose center is alternately near A and then C. Evidently, the $\psi_2 \rightarrow \psi_3$ transition would readily occur by the electric dipole mechanism.⁴

It is apparent that the oscillation of the electron cloud associated with the superposition of ψ_2 and ψ_3 is confined along the internuclear axis. Therefore if the electric vector were oscillating along an axis perpendicular to the internuclear axis, it could not couple to the fluctuating electric dipole. As a consequence the transition is only induced if the electric vector of the light wave has a non-zero component along the internuclear axis.

In Figure 5 the analogous plot is presented for a superposition of ψ_1 and ψ_3 and it can be seen that the transition $\psi_1 \rightarrow \psi_3$ would be forbidden because there is no net dipole character in the fluctuation of the charge cloud. Again our conclusions are consistent with the Laporte selection rule because the $\psi_2 \rightarrow \psi_3$ transition is from an asymmetric to a symmetric orbital whereas $\psi_1 \rightarrow \psi_3$ involves two symmetric orbitals.

The Effect of Nuclear Motion

The fluctuation in Figure 5 has no electric dipole character, but does have electric quadrupole character. The quadrupole may be regarded as two oppositely directed dipoles placed end to end. The fluctuation in one dipole is exactly balanced by a fluctuation in the opposite dipole and there is no change in the center of charge. Thus, the $\psi_2 \rightarrow \psi_3$ transition is forbidden so long as the bond distances are rigidly fixed. If, on the other hand, the bond distances between the central nucleus B and the two outer nuclei A and C are not identical, the charge displacements associated with the two oppositely directed dipoles do not exactly balance and the system may exhibit an electric dipole. The nuclei undergo just this type displacement during an asymmetric stretching vibration, and consequently, the electronic transition $\psi_1 \rightarrow \psi_3$ is allowed if it occurs in conjunction with excitation of the asymmetric stretching mode. Such a transition is called a vibronic transition.

Summary

Knowing the properties of the wavefunctions which are associated with the various energy levels of a system, one can use the principles described to determine if a transition is allowed and what polarization would be observed for the transition. In addition one can ascertain what types of vibrations would allow electronically forbidden transitions to occur as vibronic transitions.

To be accurate, we computed the $P(x,t)$ functions for Figures 1–5 exactly by integrating the appropriate expressions. After a little practice, however, for qualitative purposes the $P(x,t)$ functions can be sketched freehand, and formal integration is unnecessary.

The approach presented does not serve as an alternative to a rigorous mathematical theory of absorption. Rather, it serves

as a pictorial aid which helps to provide a physical appreciation for the way in which atoms and molecules respond to electromagnetic radiation. Moreover, it helps to bridge the gap between the classical-mechanical and the quantum-mechanical theory of absorption.

Acknowledgment

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Appendix

The following exercises suggest ways in which the model may be extended.

- 1) Sketch $P(y,t) = P(y)$ for the $2p_x$ state of the hydrogen atom.
- 2) Show that the $1s \rightarrow 4f$ transition of the hydrogen atom is forbidden, though it does not violate the Laporte Selection rule.
- 3) Describe a distortion of our 3 atom molecule that would enable the $\Psi_1 \rightarrow \Psi_3$ transition to occur by the electric dipole mechanism in y polarization.
- 4) In charge transfer spectra the intensity of the charge transfer band depends on the extent to which there is overlap between the orbitals of the two centers, and if the centers are so far removed that their orbitals do not overlap, the intensity of the band goes to zero. Explain why, keeping in mind the nature of the interference term.
- 5) Why are the so-called *d-d* transitions of transition metal complexes usually extremely weak?
- 6) Consider the system in Figure 5 having the electric quadrupole. Explain why the energy of the system is affected if a non-uniform electric field, which is stronger in the region between B and C than in the region between A and B, is impressed on the molecule. Owing to this effect, a transition may occur by the electric quadrupole mechanism. The effect is weak because the magnitude of the electric vector of visible or even ultraviolet light is nearly constant over the dimensions of atoms and molecules because the latter dimensions are so small in comparison to the wavelength of the light.

General References

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