Superallowed Electric-Quadrupole Transitions of Ions in Crystals

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A collective, many-electron response of a host crystal to the electric field of a photon can enhance the oscillator strength for a quadrupole transition of an ion (imbedded in the crystal) by 8 orders of magnitude, e.g., from 10^{-5} to 10^3.

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We show that optical transitions which are ordinarily very weak in a free ion because they are electric quadrupole can be enhanced by many orders of magnitude whenever the ion is in an appropriate crystalline environment. The effect we study is *not a consequence of configuration mixing* (caused by a ligand field of low symmetry), but is rather a many-electron contribution to the transition matrix element.

In order to simplify the presentation we shall focus attention on an idealized ion substituting for a Zn^{2+} ion in ZnS. The idealized ion will be taken to have one electron in a three-dimensional harmonic-oscillator potential, i.e., $V(\mathbf{r}) = \frac{1}{2} m\omega_0^2 r^2$. The electronic energy levels are then $(n+\frac{3}{2})\hbar\omega_0$. An advantage of this model is that the oscillator strength of the electric-dipole transition, $n=0\rightarrow 1$, is unity (by definition). Furthermore, all relevant optical matrix elements can be evaluated easily. Let the vector potential of the electromagnetic field be

$$\mathbf{A} = A\hat{\mathbf{x}}\cos(qz-\omega t)\,, \tag{1}$$

where $q = q_0\epsilon^{1/2}$. q_0 is the wave vector of the photon (in vacuum) and ϵ is the *optical* dielectric constant of ZnS. The square matrix element of the $n=0\rightarrow 1$ transition for the electron-photon interaction, $e\mathbf{A}\cdot\mathbf{p}/mc$, is (in the dipole approximation, $qz \ll 1$)

$$|m_{10}|^2 = \frac{e^2A^2\hbar\omega}{8mc^2}\,. \tag{2}$$

We have replaced ω_0 by ω, as is appropriate for this transition.

A one-photon transition from $n=0\rightarrow 2$ can result from the term linear in qz, obtained by expanding Eq. (1). This term in the interaction Hamiltonian is

$$H' = \frac{eqA}{mc} z p_x \sin\omega t\,, \tag{3}$$

and can excite the state with $n=2$ having one "vibrational" quantum in the $\hat{\mathbf{x}}$ mode and one in the $\hat{\mathbf{z}}$ mode. The square matrix element for this transition is

$$|m_{20}|^2 = \left(\frac{eA\hbar q}{4mc}\right)^2\,. \tag{4}$$

Since Eq. (2) corresponds to unit oscillator strength, the oscillator strength of the $n=0\rightarrow 2$ transition is the ratio of (4) to (2):

$$f_{0\rightarrow 2} = \frac{\hbar q_0 \epsilon}{2mc}\,. \tag{5}$$

For a transition that absorbs light having a (vacuum) $\lambda = 5000$ Å, and for $\epsilon = 5.6$ (as in ZnS), Eq. (5) becomes

$$f_{0\rightarrow 2} = 1.4\times 10^{-5}\,. \tag{6}$$

(The same transition in a free ion would be weaker by the factor ϵ, i.e., $f = 2.5\times 10^{-6}$.)

We now turn to the collective motion of the M-shell electrons in the S^{2-}-ion lattice. This negative-ion lattice is a face-centered cubic with lattice constant $a = 5.41$ Å. The charge density ranging from the M shells is

$$\rho(\mathbf{r}) = \sum_{\mathbf{L}} \rho_0(\mathbf{r}-\mathbf{L})\,, \tag{7}$$

where $\rho_0(r)$ is the (spherical) charge density of the eight electrons in each negative-ion M shell. $\{\mathbf{L}\}$ are the S^{2-} lattice sites. Equation (7) may be written as a Fourier sum

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r})\,, \tag{8}$$

where $\{\mathbf{G}\}$ are the reciprocal-lattice vectors of the fcc lattice, i.e., $2\pi(h,k,l)/a$, hkl either all odd or all even, and

$$\rho_{\mathbf{G}} = N\rho_0(G)\,. \tag{9}$$

$N = 4/a^3$, the number of molecules per cm^3, and $\rho_0(G)$ is the Fourier transform of $\rho_0(r)$. The electrostatic potential arising from the M-shell lattice is

$$\phi(\mathbf{r}) = \sum_{\mathbf{G}} \frac{4\pi\rho_{\mathbf{G}}}{G^2} \exp(i\mathbf{G}\cdot\mathbf{r})\,. \tag{10}$$

(The term for $G=0$ is omitted.)

The presence of the photon's macroscopic electric field, which from Eq. (1) is

$$\mathbf{E} = -\frac{\omega A}{c}\hat{\mathbf{x}}\sin(qz-\omega t)\,, \tag{11}$$

causes the M shells to collectively oscillate relative to their ion cores according to Newton's law. Accordingly the displacement at $z=0$ is $b\hat{\mathbf{x}}\sin\omega t$, having an amplitude

$$b=\frac{e\omega A}{mc(\omega_M^2-\omega^2)}. \tag{12}$$

$m\omega_M^2$ is the spring constant of the restoring force between an M-shell electron and its ion core. The optical polarization, $-8eNb\hat{\mathbf{x}}\sin\omega t$, leads to a simplified expression for the optical dielectric constant

$$\epsilon=1+\frac{32\pi Ne^2}{m(\omega_M^2-\omega^2)}. \tag{13}$$

From Eqs. (12) and (13) it follows that,

$$b=\frac{\omega A(\epsilon-1)}{32\pi Nec}. \tag{14}$$

(We have attributed $\epsilon-1$ entirely to the response of the S^{2-} M shells.)

In the presence of the dynamic electric field (11) the M-shell potential near $\mathbf{r}=0$ will be

$$\phi(\mathbf{r},t)=\sum_{\mathbf{G}}\frac{4\pi\rho_{\mathbf{G}}}{G^2}\exp[i\mathbf{G}\cdot(\mathbf{r}-b\hat{\mathbf{x}}\sin\omega t)]. \tag{15}$$

Since this potential now has a time-dependent term with the photon frequency ω, it will contribute to the matrix elements for optical transitions. *$\nabla\phi$ terms will supplement the usual dipole operator in important ways and must always be included in a complete theory.* However, our goal here is to call attention to the surprisingly large enhancement of quadrupole transitions arising from the second derivatives of Eq. (15), i.e., from the dynamic electric field gradients.

We will suppose that our idealized "harmonic" ion is located at a Zn site, e.g., at $\boldsymbol{\tau}=(a/4,a/4,a/4)$, and will calculate the quadratic terms in $\phi(\mathbf{r})-\phi(\boldsymbol{\tau})$. It turns out that for the ZnS lattice only $\mathbf{G}$ families having h,k,l odd contribute. The $\{111\}$ family is the most important one because the M-shell Fourier transform, $\rho_0(111)$, is near its maximum value, $\rho_0(0)=-8e$. (The next contributing family is $\{311\}$; and we shall neglect it, and also the higher ones, because for them $[\rho_0(G)]^2$ is much smaller.) On evaluating the second derivatives of Eq. (15) for all eight $\mathbf{G}$'s of the $\{111\}$ family, we find only one quadratic contribution to $\phi(\mathbf{r})-\phi(\boldsymbol{\tau})$:

$$\phi_2(\mathbf{r},t)=\frac{512\pi^2Ne}{3a}byz\sin\omega t. \tag{16}$$

(All eight $\mathbf{G}$'s contribute equally to the numerical coefficient.) Had the photon polarization vector been $\hat{\mathbf{y}}$ or $\hat{\mathbf{z}}$, then the quadratic product yz (y,z relative to the Zn site) would have been zx or xy.

The dynamic perturbation, $-e\phi_2$, will obviously cause an $n=0\rightarrow 2$ transition of the harmonic ion at the zinc site. The square matrix element of $-e\phi_2$ for this transition is

$$|m_{0\rightarrow 2}|^2=\left(\frac{128\pi^2Ne^2\hbar b}{3m\omega_0 a}\right)^2. \tag{17}$$

Here it is important to note that $\omega_0=\frac{1}{2}\omega$. (Matrix-element comparisons are relevant only for transitions having the same ω.) The oscillator strength can be found by substituting (14) for b in (17) and dividing by (2)

$$f_{0\rightarrow 2}=\frac{512\pi^2\hbar(\epsilon-1)^2}{9ma^2\omega}\sim 1240. \tag{18}$$

This value exceeds the oscillator strength of Eq. (5) by 9×10^7 (and the free-ion value by 5×10^8).

It is now evident that the induced collective oscillation of negative-ion valence electrons can lead to extraordinary enhancement of *parity-forbidden* transitions. No doubt Eq. (18) provides a somewhat exaggerated result on account of the simplified model we have embraced for this initial presentation. Several possible refinements can be easily entertained. We note, however, that Eq. (18) does not depend on the number of electrons assumed for each M shell. That number (taken herein to be eight) cancels out when the final result is expressed in terms of $\epsilon-1$.

The simplicity of the derivation given above can be attributed to use of the shell model[1] for describing the negative-ion electronic response. An analogous theory[2] for collective contributions to interband transitions in metals was presented several years ago. An unexpected and strong absorption band, observed in metallic potassium[3] at $\hbar\omega=8$ eV, was quantitatively explained by a dynamic term in the interband matrix element stemming from photon-induced oscillation of the potassium M shells.[2] The same phenomenon was also found in metallic Rb and Cs.[3] We remark that interpretations of solid-state optical spectra must recognize the collective-electron phenomena emphasized in this work.

An interesting question is how the f sum rule can be reconciled with the oscillator strength of Eq. (18), especially since the sum rule is already exhausted by the $n=0\rightarrow 1$ transition. The answer is, of course, that $f_{0\rightarrow 2}$ arises from the oscillator-strength "budget" of the $8N$ negative-ion M-shell electrons, with which the photons interact directly.

Application of the present theory can be envisaged for transition-metal, rare-earth, and actinide ions in wide band-gap crystals. The accessible electronic excitations of such ions are frequently alternative states of the *same* configurations, e.g., $(3d)^m$ or $(4f)^m$. Accordingly, many observed (or possible) transitions are both spin forbidden and parity forbidden. Spin-orbit coupling can relax somewhat the first selection rule; but a ligand field lacking inversion symmetry cannot ordinarily lead to *considerable* configuration mixing of opposite parity states into *tightly bound* orbits, since the electric field at an ion must be zero (a requirement of equilibrium). Our induced quadrupole mechanism not only negates completely the parity selection rule, it provides a superstrong matrix element that will partially compensate remaining weakness caused by the (spin-orbit relaxed) spin selection rule. The recently studied Mn^{2+} absorption spectrum[4] in $Zn_{1-x}Mn_xSe$ is unexpectedly strong and may exemplify the present theory.

Rare-earth ions in solvents have exhibited quadrupole transitions too large by several orders of magnitude, a behavior attributed[5] to dynamic electric field gradients associated with inhomogeneity of the surrounding dielectric (which is an idea having some similarity to our present treatment). Oscillator strength increases up to 10^3 have been observed for 3D impurity ions in MgF_2 following γ radiation.[6] However, these changes were attributed to reduction of the spin forbiddenness arising from exchange interactions with F centers. Anomalously strong forbidden transitions in americium halides have been reported[7] and are hypersensitive to the crystalline environment.

Zn^{2+} in ZnS has a tetrahedral environment. Had the site symmetry been cubic, enhancement of the impurity ion's quadrupole transition would not have occurred since ϕ_2, Eq. (16), would then be nil. An interesting possibility suggested by our theory involves impurity substitution in (for example) a cubic-perovskite ferroelectric. Quadrupole transitions would then not be visible at temperatures above T_F, when the site symmetries are cubic. However, the large positive-ion displacements (~0.5 Å) below T_F will reduce the site symmetry and activate otherwise hidden quadrupole transitions. Ambient temperatures very near T_F might reveal critical behavior in electrochromic or piezochromic response, phenomena which may have some service in optical devices.

Finally, we noted above that $\nabla\phi$ terms from Eq. (15) would contribute significantly to (allowed) dipole transitions. The first derivative terms arising from the {200} family enhance the $n=0\rightarrow 1$ transition and, by themselves, lead to

$$f_{0\rightarrow 1}=4(\epsilon-1)^2\sim 80\,. \qquad (19)$$

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