

## Moments of absorption- and emission-band shapes of impurities in solids

C. Stuart Kelley

Harry Diamond Laboratories, Adelphi, Maryland 20783

(Received 28 November 1977)

General expressions are reviewed and explicitly presented for determining all quantum-mechanical moments of absorption- and emission-band shapes that originate from electronic transitions in a defect whose vibrational interaction contains, in the Condon and adiabatic approximations, terms both linear and quadratic in a single configuration coordinate. The zeroth through fourth absorption and emission moments are presented, the fourth moments for the first time. The band shapes, proportional to transition probabilities, have moments that differ from those of experimentally measured absorption coefficients and emission rates.

### I. INTRODUCTION

The method of moments provides a powerful means for determining the values of theoretical parameters from experimental optical absorption- and emission-band shapes due to defects in solids. This method is powerful because the moments can be calculated precisely from theory and can be readily compared to experimental results that are amenable to calculation from the data by the use of simple computer programs. The method of moments was originally developed by Lax,<sup>1</sup> and extended by others,<sup>2</sup> for optical absorption-band shapes originating from vibrationally assisted electronic transitions. Lax gave general expressions for the first five quantum-mechanical moments without introducing explicit expressions for the vibrational interaction terms. A method for explicit calculation of all quantum-mechanical moments was given by O'Rourke.<sup>2</sup>

The present work uses the approach of O'Rourke, reiterating his general expressions for calculating absorption and emission moments, and presents the calculational results for the zeroth through fourth moments.

### II. THEORETICAL DEVELOPMENT

The experimentally measured absorption coefficient and the emission probability per unit time per unit energy interval are, respectively,<sup>1</sup>

$$\alpha(E) = (4\pi^2/3\hbar c)(F_e/F)^2(nN/\epsilon_s)EI_\alpha(E), \quad (1)$$

$$\epsilon(E) = (4/\hbar^4 c^3)(F_e/F)^2(n^3N/\epsilon_s)E^3I_\epsilon(E), \quad (2)$$

where the  $I_\alpha(E)$  and  $I_\epsilon(E)$  are the band-shape functions. The defect concentration is  $N$ , the index of refraction of the host lattice is  $n$ , and the dielectric constant is  $\epsilon_s$ . The factor  $(F_e/F)^2$  occurs because the effective field ( $F_e$ ) at the defect may differ from that ( $F$ ) of the host lattice.

### A. Moments of $I_\alpha$ and $I_\epsilon$

The absorption-band shape  $I_\alpha(E)$  for electric-dipole transitions from the ground-state  $a\alpha$  to the excited-state  $b\beta$  of the defect (where the electronic-ground-state quantum number is  $a$ , and  $\alpha$  is the vibrational-ground-state quantum number) is

$$I_\alpha(E) = \sum_{\beta} av_\alpha |\langle \Psi_{a\alpha} | e\vec{r} | \Psi_{b\beta} \rangle|^2 \delta(E - E_{b\beta} + E_{a\alpha}), \quad (3)$$

where  $av_\alpha$  designates a thermal average over the ground-state vibrational levels of the product of the square of the matrix element of the electric dipole operator  $e\vec{r}$  and the  $\delta$  function that locates the energy of the  $a\alpha - b\beta$  transitions. We now replace the  $\delta$  function by its Fourier transform, integrate Eq. (3) over  $E$ , recognize the definition of the  $n$ th moment

$$M_n \equiv \int_{-\infty}^{\infty} dE I_\alpha(E)(E - E_0)^n \quad (4)$$

taken about an offset energy  $E_0$  (see below), and make two approximations.<sup>3</sup> The adiabatic approximation is that  $\Psi$  can be written as the product  $\chi\phi$ , where  $\chi$  represents the vibrational part of the wave function and  $\phi$  represents the electronic part. The Condon approximation is that the electric dipole operator  $e\vec{r}$  is independent of the nuclear coordinates. With these approximations,

$$M_n/M_0 = \{ [d^n/d(it/\hbar)^n] g(t) \}_{t=0}, \quad (5)$$

where

$$g(t) \equiv \sum_{\beta} av_\alpha \exp\left(\frac{it(E_{b\beta} - E_{a\alpha} - E_0)}{\hbar}\right) |\langle \chi_\alpha | \chi_\beta \rangle|^2, \quad (6)$$

and

$$M_0 \equiv |\langle \phi_a | e\vec{r} | \phi_b \rangle|^2. \quad (7)$$

The wave functions characterizing simple harmonic vibrational motion of the ground state (frequency  $\omega$ ) and excited state (frequency  $R\omega$ ) are<sup>4</sup>

$$\chi_\alpha = [(\omega/\pi\hbar)^{1/2}/2^\alpha \alpha!]^{1/2} \times \exp(-\omega q^2/2\hbar) H_\alpha[(\omega/\hbar)^{1/2}q], \quad (8a)$$

$$\chi_\beta = [(R\omega/\pi\hbar)^{1/2}/2^\beta \beta!]^{1/2} \times \exp\{-\frac{1}{2}[(R\omega/\hbar)^{1/2}q + (2S)^{1/2}]^2\} \times H_\beta[(R\omega/\hbar)^{1/2}q + (2S)^{1/2}] \quad (8b)$$

for motions characterized by a single configuration coordinate  $q$ , where the force constants of the two oscillators differ, indicative of quadratic coupling (the vibrational Hamiltonian contains terms quadratic in  $q$ ), and the equilibrium coordinates differ, indicative of linear coupling (the vibrational Hamiltonian contains terms linear in  $q$ ), the strength of which is measured by  $S$ , the Huang-Rhys factor. The  $H_k$  are Hermite polynomials. The energies are

$$E_{b\beta} = E_0 + (\beta + \frac{1}{2})R\hbar\omega, \quad (9a)$$

$$E_{a\alpha} = (\alpha + \frac{1}{2})\hbar\omega. \quad (9b)$$

One then defines the thermal average  $\text{av}_\alpha(\xi)$  and applies the Slater sum, as was done by O'Rourke, to find that

$$M_n/M_0(\hbar\omega)^n = [A^{1/2}(\tau)(d^n/d\tau^n)g(\tau)]_{\tau=0}, \quad (10)$$

where  $\tau = i\omega t$ , and

$$g(\tau) = A^{-1/2}(\tau)B(\tau), \quad (11)$$

$$A(\tau) = 2R \cosh\lambda \cosh\mu - 2R + (R^2 + 1) \sinh\lambda \sinh\mu, \quad (12a)$$

$$B(\tau) = \exp\{-2S[R \coth(\frac{1}{2}\mu) + \coth(\frac{1}{2}\lambda)]^{-1}\}. \quad (12b)$$

For absorption

$$\lambda = -R\tau, \quad (13a)$$

$$\mu = \theta/T + \tau, \quad (13b)$$

$$\theta = \hbar\omega/k. \quad (14)$$

Equations (10)–(13) were used to calculate the first five moments for absorption. For simplicity, the central moments  $m_n$  are presented. They are evaluated about  $M_1$ , which has been evaluated about  $E=0$ :

$$M_0 = |\langle \phi_a | e^{\mathbf{r}} | \phi_b \rangle|^2, \quad (15a)$$

$$\frac{M_1}{M_0\hbar\omega} = \frac{E_0}{\hbar\omega} + SR + \frac{1}{4}(R^2 - 1) \coth\left(\frac{\theta}{2T}\right), \quad (15b)$$

$$\frac{m_2}{M_0(\hbar\omega)^2} = SR^3 \coth\left(\frac{\theta}{2T}\right) + \frac{1}{8}(R^2 - 1)^2 \coth^2\left(\frac{\theta}{2T}\right), \quad (15c)$$

$$\frac{m_3}{M_0(\hbar\omega)^3} = SR^3 + \frac{1}{4}(R^2 - 1)^2 \coth\left(\frac{\theta}{2T}\right) + \frac{3}{2}SR^3(R^2 - 1) \coth\left(\frac{\theta}{2T}\right) + \frac{1}{8}(R^2 - 1)^3 \coth^3\left(\frac{\theta}{2T}\right), \quad (15d)$$

$$\begin{aligned} \frac{m_4}{M_0(\hbar\omega)^4} &= \frac{1}{4}(R^2 - 1)^2 + SR^3(4R^2 - 3) \coth\left(\frac{\theta}{2T}\right) \\ &+ [3S^2R^6 + \frac{1}{4}(R^2 - 1)^2(2R^2 - 1)] \coth^2\left(\frac{\theta}{2T}\right) \\ &+ \frac{15}{4}SR^3(R^2 - 1)^2 \coth^3\left(\frac{\theta}{2T}\right) \\ &+ \frac{15}{64}(R^2 - 1)^4 \coth^4\left(\frac{\theta}{2T}\right). \end{aligned} \quad (15e)$$

The corresponding moments for emission are found in the same fashion as for absorption. The result is still given by Eqs. (10)–(12), but with

$$\lambda = R\theta/T - R\tau, \quad (16a)$$

$$\mu = \tau, \quad (16b)$$

and  $\theta$  replaced by  $R\theta$  in the thermal average. The first five moments are

$$M_{e0} = |\langle \phi_b | e^{\mathbf{r}} | \phi_a \rangle|^2 = M_0, \quad (17a)$$

$$\begin{aligned} \frac{M_{e1}}{M_{e0}(\hbar\omega)} &= \frac{E_0}{\hbar\omega} - \frac{S}{R} \\ &+ \frac{1}{4R}(R^2 - 1) \coth\left(\frac{R\theta}{2T}\right), \end{aligned} \quad (17b)$$

$$\begin{aligned} \frac{m_{e2}}{M_{e0}(\hbar\omega)^2} &= \frac{S}{R^2} \coth\left(\frac{R\theta}{2T}\right) \\ &+ \frac{1}{8R^2}(R^2 - 1)^2 \coth^2\left(\frac{R\theta}{2T}\right), \end{aligned} \quad (17c)$$

$$\begin{aligned} \frac{m_{e3}}{M_{e0}(\hbar\omega)^3} &= -S/R - \frac{1}{4R}(R^2 - 1)^2 \coth\left(\frac{R\theta}{2T}\right) \\ &+ \frac{3S}{2R^3}(R^2 - 1) \coth^2\left(\frac{R\theta}{2T}\right) \\ &+ \frac{1}{8R^3}(R^2 - 1)^3 \coth^3\left(\frac{R\theta}{2T}\right), \end{aligned} \quad (17d)$$

$$\begin{aligned} \frac{m_{e4}}{M_{e0}(\hbar\omega)^4} &= \frac{1}{4}(R^2 - 1)^2 + \frac{S}{R^2}(4 - 3R^2) \coth\left(\frac{R\theta}{2T}\right) \\ &+ \left(\frac{3S^2}{R^4} + \frac{1}{4R^2}(R^2 - 1)^2(2 - R^2)\right) \coth^2\left(\frac{R\theta}{2T}\right) \\ &+ \frac{15S}{4R^4}(R^2 - 1)^2 \coth^3\left(\frac{R\theta}{2T}\right) \\ &+ \frac{15}{64R^4}(R^2 - 1)^4 \coth^4\left(\frac{R\theta}{2T}\right). \end{aligned} \quad (17e)$$

The first four absorption and emission moments agree with the results of Fonger and Struck,<sup>5</sup> who did not calculate  $m_4$ . Elsewhere,<sup>6</sup> however, they did give an expression for  $m_4$  for the linear interaction ( $R=1$ ) that agrees with the above results. They include a translation of their nomenclature to those of others.<sup>5</sup> For comparison purposes, Table I gives a notational correspondence between the present nomenclature and theirs.

Because of the symmetry involved in going from absorption to emission, the absorption moments

TABLE I. Notational correspondence between the present work and that of Fonger and Struck (Ref. 5).

This work	Fonger and Struck (Ref. 5)
$q$	$M_0^{1/2}\chi$
$(2S)^{1/2}$	$-(M_0\omega_v/\hbar)^{1/2}a$
$S^{1/2}$	$-(S_v)^{1/2}$
$\hbar\omega$	$\hbar\omega_u$
$R$	$\tan^2\theta = \omega_v/\omega_u = S_v/S_u$
$-(2S)^{1/2}[(1+R)/R]^{1/2}$	$a_{uv}$
$[R/(1+R)]^{1/2}$	$\sin\theta$
$(1-R^2)/4R$	$k_\theta$
$\coth(\theta/2T)$	$\langle 2n+1 \rangle_u$
$\coth(R\theta/2T)$	$\langle 2m+1 \rangle_v$

can be transformed to give the emission moments. Four steps are required to convert Eqs. (15) to Eqs. (17): (i) replace  $\theta$  with  $R\theta$ , (ii) replace  $\hbar\omega$  with  $-R\hbar\omega$ , (iii) replace  $S$  with  $S/R$ , and (iv) replace  $R$  with  $1/R$ . These steps are similar to those found by Fonger and Struck.<sup>5</sup> The moments calculated by Fonger and Struck are phonon moments, and are different from Eqs. (15) and (17) which are photon moments. The photon moment  $M_1$  for absorption represents the band centroid as measured from  $E=0$ . On the other hand, the phonon moment that corresponds to  $M_1$  represents the band centroid as measured from  $E=E_0$ . Thus, the two values of  $M_1$  are related simply by the energy displacement  $E_0$ . The central photon moments are the same as the central phonon moments.

In an experimental measurement, the absorption and emission-band shapes have a qualitative mirror symmetry about the zero-phonon line (for example, the  $\alpha=0 \rightarrow \beta=6$  transition in absorption is on the high-energy side of the zero-phonon line, whereas the  $\beta=0 \rightarrow \alpha=6$  transition in emission is on the low-energy side). Fonger and Struck employ a generalized methodology that uses positive energy scales for both absorption and emission (for example, both the  $\alpha=0 \rightarrow \beta=6$  transition in absorption and the  $\beta=0 \rightarrow \alpha=6$  transition in emission lie on the same side of the zero-phonon line). As a result of this, the odd emission moments presented by Fonger and Struck have a sign reversal from those presented here. All absorption moments and the even emission moments, of course, agree.

<sup>1</sup>M. Lax, J. Chem. Phys. **20**, 1752 (1952).

<sup>2</sup>(a) R. C. O'Rourke, Phys. Rev. **91**, 265 (1953); (b) R. Kubo and Y. Toyozawa, Prog. Theor. Phys. **13**, 160 (1955); (c) H. J. G. Meyer, Physica (Utr.) **21**, 253 (1955); (d) J. T. Ritter, J. Chem. Phys. **53**, 3461 (1970).

<sup>3</sup>D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 6, p. 353.

### B. Moments of $\alpha$ and $\epsilon$

An experimentally obtained absorption coefficient  $\alpha(E)$  differs from the absorption-band shape  $I_\alpha(E)$  by a multiplicative factor proportional to the energy  $E$ ; in emission, that factor is proportional to the cube of the energy [see Eqs. (1) and (2)]. It is found experimentally that the  $E$  correction to the moments in absorption is much less critical than the  $E^3$  correction in emission.<sup>7</sup> Both factors should, however, be considered when interpreting experimental data by moments techniques. From Eqs. (1) and (2),

$$M_n(\alpha) = K_\alpha M_{n+1}(I_\alpha), \quad (18a)$$

$$M_{\epsilon n}(\epsilon) = K_\epsilon M_{\epsilon n+3}(I_\epsilon). \quad (18b)$$

Mistaking  $\alpha(E)$  for  $I_\alpha(E)$  in the linear interaction introduces a mild temperature dependence in the band centroid,

$$\frac{M_1(\alpha)}{M_0(\alpha)} = E_0 + S\hbar\omega + \frac{S(\hbar\omega)^2}{E_0 + S\hbar\omega} \coth\left(\frac{\theta}{2T}\right), \quad (19)$$

a mistake that suggests the presence of weak quadratic coupling (the centroid shift is only  $\sim 0.01E_0$  over  $0 < T < 300$  K). The presence of quadratic coupling would also be inferred from the temperature dependence of the second central moment. Corresponding relations for  $\epsilon$  are more complex. The leading terms for the centroid,

$$\frac{M_{\epsilon 1}(\epsilon)}{M_{\epsilon 0}(\epsilon)} \approx E_0 - S\hbar\omega + \frac{6S(\hbar\omega)^2}{E_0 - S\hbar\omega} \coth\left(\frac{\theta}{2T}\right), \quad (20)$$

give a sixfold larger shift than in absorption, the result of the stronger dependence in  $\epsilon(E)$ .

### III. SUMMARY

The O'Rourke technique is used to establish a procedure for calculating all moments of the  $I_\alpha$  and  $I_\epsilon$  band-shape functions when there are both linear and quadratic vibrational interaction terms. This procedure is used to find the explicit forms of the  $I_\alpha$  and  $I_\epsilon$  moments  $M_0$  through  $m_4$ . Experimental  $\alpha$  and  $\epsilon$  moments differ from those of  $I_\alpha$  and  $I_\epsilon$ . In the linear vibrational interaction, for example, the  $I_\alpha$  and  $I_\epsilon$  centroids are temperature independent, whereas the  $\alpha$  and  $\epsilon$  centroids contain temperature dependences that are similar to those in the  $I_\alpha$  and  $I_\epsilon$  centroids that are induced by the addition of quadratic coupling.

<sup>4</sup>C. S. Kelley, Phys. Rev. B **6**, 4112 (1972); R. C. O'Rourke, Ref. 2(a).

<sup>5</sup>W. H. Fonger and C. W. Struck, J. Chem. Phys. **60**, 1994 (1974).

<sup>6</sup>C. W. Struck and W. H. Fonger, J. Chem. Phys. **60**, 1988 (1974).

<sup>7</sup>W. Gebhart and H. Kühnert, Phys. Status Solidi **14**, 157 (1966).