

SCATTERING FROM JAHN-TELLER IMPURITIES IN IONIC SOLIDS

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Introduction

Light scattering has been a providential tool in the study of impurities in solids. This is clear from the wealth of contributions in this field to the previous Light Scattering Conferences ¹ as well as to the present one.

Jahn-Teller impurities form a subclass of impurities distinct in at least three respects : First, symmetry considerations introduce special selection rules. Secondly, characteristically J-T-centres possess a set of low lying, discrete excitations whose spacing is of the order of 10^{-1} - 10^1 wavenumbers, being inversely proportional to the J-T stabilization energy E_{JT} . Thirdly, almost inevitably there exists a strong coupling between the host crystal and the impurity ion which is the nucleus of the J-T centre.

It is this last circumstance which has made theoretical progress in the field slow (or suspect) for some time. However, in the course of the last few years a transformation-method of the vibrational modes of the solid has been developed in several papers ²⁻⁴, which simplified the situation considerably. For many purposes we can view the vibronic interaction as concentrated in a single (or a few) set of modes while the rest of the modes (here called quasi-phonons or the bath) are subject to residual interaction only. Utilizing this simplification phonon scattering from J-T centres has been studied previously ^{4,5}; in this work we delineate how the not dissimilar problem of light-scattering is treated. Our work is in chronological conjunction with the Raman scattering studies on Cu^{2+} in CaO by Guha and Chase ⁶, who present extensive

theoretical argumentations. We rely in this work on their assignment of their spectra but concern ourselves with their linewidths, a subject not covered by them.

Another conjunction of the present study is with the recent progress made ^{7,8} in the theory of molecular light scattering (or lineshapes) through the application of tetradic operator formalism. This is based on the ideas of Zwanzig ⁹ and Fano ¹⁰ that dynamical variables are to be expanded in double or Liouville space (so that the operators in this space have tetradic labeling) and projected onto a subspace of single-molecule excitation modes. Considerable generality is achieved in this formalism ⁸. In particular, one can treat in a very straightforward way the case when only one subsystem has fully specified states whereas the rest can at best be described by a stationary distribution function. Since the transformation mentioned earlier achieves an equivalent separation to the vibronic subsystem and the rest, the molecular scattering formalism is readily adapted to our case.

This work starts by defining the system, reviewing the transformation applied to it (next section), goes on to introduce the tetradic formalism in the present context, evaluates the broadening of the vibronic transition lines due to the (residual) coupling to the quasi-phonon continuum and compares the calculations to the observed widths ⁶.

The Transformation

We write down the Hamiltonian for the material system, the radiation field and the (weak) interaction between the two.

Our material system is $E \otimes \epsilon$, i.e. an orbital doublet electronic state of an impurity ion, linearly coupled with a large number of vibrational modes of the crystal, whose frequencies ω_1 start from zero and reach some maximum frequency ω_D . In the basis of the degenerate electronic wavefunction $|\theta\rangle, |\epsilon\rangle$ which transform according to the irreducible representation E of a point group, the Hamiltonian has the form

$$H = \sum_i \kappa \omega_i \left(\frac{1}{2} \vec{p}_i^2 + \frac{1}{2} \vec{q}_i^2 + k_i \vec{q}_i \cdot \vec{\sigma} \right) + H_r + V \quad (1)$$

Here the components $q_{i\mu}$ ($\mu=\theta, \epsilon$) of q_i are the coordinates of an ϵ -type set of degenerate modes of frequency ω_i , $p_{i\mu}$ are their conjugate momenta and k_i are coupling coefficients - all written in reduced, dimensionless form. The symbol i refers to what we shall call symmetry phonons, which are linear combinations of degenerate plane-wave phonons so chosen as to span E representations of the point group at the impurity site. The components $\sigma_\theta, \sigma_\epsilon$ of $\vec{\sigma}$ are the Pauli spin matrices $-\sigma_z$ and σ_x , respectively. H_r is the Hamiltonian for the radiation field and V represents the interaction of light with the material system.

From the point of view of experiments with J-T impurity ions in solids it is the limit of strong vibronic coupling (for which $\sum k_i^2 \gg 1$) that turns out to be of major interest. We shall transform the symmetry-phonon coordinates in such a way that one pair of transformed modes behaves as though subject to a molecular J-T effect, while the rests are only weakly coupled to the electronic states. As shown earlier ⁴ the validity of this method depends on the coupling being concentrated in a narrow frequency range. Applying an orthogonal transformation

$$\vec{q} = \sum_i A_{ji} q_i \quad (2)$$

the Hamiltonian (1) can be separated into the following four parts :

$$\begin{aligned} H &= \tilde{H}_{JT} + \tilde{H}_{\text{quasi-ph}} + H' + H'' + H_r + V, \quad (3) \\ \tilde{H}_{JT} &= \kappa \Omega \left(\frac{1}{2} \vec{p}_1^2 + \frac{1}{2} \vec{q}_1^2 + \kappa \vec{q}_1 \cdot \vec{\sigma} \right), \\ \tilde{H}_{\text{quasi-ph}} &= \frac{1}{2} \sum_{j \neq 1} \kappa \Omega \left(\vec{p}_j^2 + \vec{q}_j^2 \right), \\ H' &= \sum_{j \neq 1} \left\{ c_j \kappa \vec{q}_j \cdot \vec{\sigma} + d_{j1} \left(\vec{p}_j \cdot \vec{p}_1 + \vec{q}_j \cdot \vec{q}_1 \right) \right\}, \\ H'' &= \frac{1}{2} \sum_{j \neq 1} \sum_{j' \neq 1, j} d_{jj'} \left(\vec{p}_j \cdot \vec{p}_{j'} + \vec{q}_j \cdot \vec{q}_{j'} \right). \end{aligned}$$

The various parameters appearing in this rearranged form of the Hamiltonian are defined as follows :

$$\left. \begin{aligned} \Omega &= \sum_i \omega_i A_{1i}^2, & K &= \frac{1}{\Omega} \sum_i \omega_i k_i A_{1i}, & \Omega_j &= \sum_i \omega_i A_{ji}^2 \quad (j \neq 1), \\ c_j &= \frac{1}{K} \sum_i \omega_i k_i A_{ji} \quad (j \neq 1), \\ d_{jj'} &= \sum_i \omega_i A_{ji} A_{j'i} \quad (j \neq 1, j \neq j'). \end{aligned} \right\} (4)$$

The first two terms in (3) describe a molecular J-T coupling for the mode \tilde{q}_1 and an uncoupled phonon Hamiltonian for all the rest. In order to reduce the effects of the residual interaction (H' and H'') as far as possible, a variational solution for the total Hamiltonian has been postulated in the form of a product of wavefunctions which are the lowest eigenstates of H_{JT} and H_{quasiph} .

The elements of the first row of the transformation matrix in (2) have been given before^{3,4}. To evaluate the expressions in Eq.(4) some approximating assumptions have to be made⁴. In particular a Debye type distribution has been chosen for the frequencies, that is the density of vibrational levels

$$\rho(\omega) \propto \omega^2.$$

Moreover, for the coupling constants k_i in (1) two possibilities have been envisaged, namely

$$k(\omega) \propto \omega^{-1/2}, \quad (5)$$

$$k(\omega) \text{ independent of } \omega. \quad (6)$$

The Formalism.

We regard the system as consisting of the material system and of the radiation field. Following the transformation described in the previous section, the material system is subdivided into the vibronic system and the quasi-phonons. The radiation field interacts with the vibronic system, which is coupled (by the "residual" interaction) to the bath of quasi-phonons, providing damping and broadening mechanisms. The three systems, their main physical characteristics, as well as the notation to be used with respect to them are displayed in Table 1.

Table 1

Subsystem	1 Radiation field	2 Vibronic	3 Quasi-phonons =bath	2 + 3 Material
Nature of levels	Continuous	Discrete	Cont.	Cont.
Symbols for states	$ \text{vac}\rangle$ $ \vec{k}\rangle$	a, b, \dots or $\tilde{a}, \tilde{b}, \dots$ *	α β	$a\alpha, b\beta$
Hamiltonian	H_r	H_{JT}	H_b	H^M
Liouvillian	\mathcal{L}_r	\mathcal{L}_{JT}	\mathcal{L}_b	\mathcal{L}^M
Interaction operator	(with 2:) V	(with 1:) V (with 3:) H'	(with 2:) H'	(with 1:) V
Interaction Liouvillian	\mathcal{U}	\mathcal{U} \mathcal{L}'	\mathcal{L}'	\mathcal{U}

* the tilde is used for the product of a vibronic state and a one-phonon state $|\tilde{a}\rangle |\vec{k}\rangle$

The natural theoretical tool to handle such a combined system is the tetradic scattering formalism. Its advantage is due to the circumstance that it describes the evolution of the density matrix and thus leads directly to probabilities (cross-sections) rather than amplitudes. The formalism incorporates the Fano-Zwanzig projection operator technique, and this enables us to concentrate on a chosen set of degrees of freedom (in our case the vibronic subsystem) and take account of the other degrees of freedom, in a less rigorous way, notably by "bath averaging" 7,9,10.

Let us briefly sketch the tetradic formalism. A tetradic operator \mathfrak{F} (represented by a capital curly letter) is defined by its operational property on an ordinary (diadic) operator A, leading to another diadic operator B. $B = \mathfrak{F}A$. We can formally characterize \mathfrak{F} by the tetradic matrix elements having four indices $B_{ij} = \sum \mathfrak{F}_{ij,kl} A_{kl}$. The Liouvillian is a (special) tetradic operator defined by $\mathcal{L}A = [H, A]_{kl}$ where H is the total Hamiltonian of the system. Comparing the last two equations, we are led to

$$\mathcal{L}_{ij,kl} = H_{ik} \delta_{jl} - H_{jl}^* \delta_{ik}$$

A scattering problem may be described in Liouville space by means of the tetradic S matrix and the density matrix ρ , as follows :

$$\rho_{ij}(t \rightarrow \infty) = \sum_{kl} S_{ij,kl} \rho_{kl}(-\infty) \quad (7)$$

It has been shown that we can write ^{7,9} :

$$S_{ij,kl} = \delta_{ik} \delta_{jl} - 2\pi i \tau_{ij,kl}(\omega_{ij}) \delta(\omega_{ij} - \omega_{kl}) \quad (8)$$

where τ is the tetradic T-matrix :

$$\tau = \mathcal{V} + \mathcal{V}G\mathcal{V} \quad , \quad (9)$$

G is the tetradic Green's function :

$$G(\omega) = (\mathcal{H}\omega - \mathcal{L} + iE)^{-1} \quad (10)$$

and \mathcal{V} is the tetradic light-material interaction (Table 1).

The attenuation cross-section for a photon \mathbf{K} is in terms of the τ -matrix

$$(8) : \quad \sigma_{\mathbf{K}} = \frac{iL^3}{\hbar c} \sum_{\tilde{\alpha}\tilde{c}} \langle \tau_{\tilde{c}\tilde{c},\tilde{\alpha}\tilde{\alpha}} \rangle \rho_{\alpha} \quad (11)$$

where L^3 is the photon box-normalization volume, $\rho_{\alpha} \equiv \rho_{\alpha\alpha}$ and the argument ω_{ij} in Eq.(8) is zero ($\omega_{ij} = \omega_{\alpha\alpha,\alpha\alpha} = \omega_{\alpha\alpha} = 0$). The sum in the above equation runs over the states of the vibronic subsystem (Table 1) weighted by its density operator. The bath-average $\langle \rangle$ defined by

$$\langle Z_{\tilde{c}\tilde{c},\tilde{\alpha}\tilde{\alpha}} \rangle \equiv \sum_{\alpha\beta} Z(\tilde{c}\beta)(\tilde{c}\beta), (\tilde{\alpha}\alpha)(\tilde{\alpha}\alpha) \rho_{\alpha} \quad (12)$$

enters in Eq.(11), since regarding the phonon-scattering by vibronic system the state of the bath is only statistically important.

Evaluating now τ from Eq.(9) where the first term vanishes for the diagonal matrix element, we find ⁸ :

$$\tau_{\tilde{c}\tilde{c},\tilde{\alpha}\tilde{\alpha}} \rho_{\alpha} = 2 \operatorname{Im} \sum V_{\tilde{\alpha}b} V_{\tilde{c}d} G_{\tilde{c}d,\tilde{\alpha}b}(0) (\rho_{\alpha} - \rho_b)$$

where the b, d states involve two or zero photon-, $\tilde{\alpha}$, \tilde{c} one-photon states.

We now return to Eq.(10), the definition of G and amend this by excluding from \mathcal{L} the field Liouvillian. Invoking the rotating wave approximation (there being zero-photon (vacuum)-excited material states and one photon-deexcited material states only) we get in terms of the material Liouvillian \mathcal{L}^M and its Green's function G^M :

$$G(0) \simeq (\mathcal{H}\omega_{\mathbf{K}} - \mathcal{L}^M + i\epsilon)^{-1} = G^M(\omega_{\mathbf{K}}) \quad .$$

At last we obtain for the photon attenuation cross-section ⁸ :

$$\sigma_{\mathbf{K}} = - \frac{2L^3}{c} \text{Im} \sum_{abcd} V_{dc}^* V_{ba} (\rho_a - \rho_b) \langle G_{dc,ab}^M(\omega_{\mathbf{K}}) \rangle .$$

Using now the subdivision of the Liouvillian in Table 1 and a result by Zwanzig ⁹, we rewrite the angular brackets (which, we recall, denote an averaging over the bath, i.e. the quasi-phonons) ⁷⁻¹⁰ :

$$\langle G^M(\omega_{\mathbf{K}}) \rangle = (\hbar\omega_{\mathbf{K}} - \mathcal{L}_{\text{JT}} - \langle \mathcal{R} \rangle)^{-1} \quad (13)$$

where \mathcal{R} is the Liouvillian self-energy operator :

$$\mathcal{R}(\omega_{\mathbf{K}}) = \mathcal{L}' + \mathcal{L}' D (\hbar\omega_{\mathbf{K}} - \mathcal{L}_{\text{JT}} - D\mathcal{L}'D)^{-1} D\mathcal{L}' \quad , \quad (14)$$

D being a (diadic) projection operator defined by $DZ\rho_{\alpha} = Z\rho_{\alpha} - \rho_{\alpha} \langle Z\rho_{\alpha} \rangle$.

Physically, D removes (annihilates) systems which have the undisturbed distributions in accordance with ρ_{α} . Diagrammatically, only connected parts can appear in the diagrammatic representation of the self-energy, Eq.(14).

We note that \mathcal{R} , whose real and imaginary parts give the frequency shift and the inverse lifetime Γ respectively, is a tetradic operator in the vibronic subsystem which does not commute with \mathcal{L}_{JT} . Having averaged out the bath continuum, one is merely left with the task of inverting a discrete (and, occasionally, even finite) matrix :

$$[\hbar\omega_{\mathbf{K}} - (E_a - E_b) \delta_{cb} \delta_{da} - \langle \mathcal{R}_{cd,ba} \rangle] \quad . \quad (15)$$

One may wish to approximate the matrix-inversion by ignoring off-diagonal terms, i.e. writing $cd = ba$, thereby neglecting interference between transitions and replacing the inverse of the matrix by the matrix of the inverses. (Such was in fact the procedure adopted in the paper of two of the authors ⁴, based on Zubarev's Green's function method and on a decoupling). Interference in the self-energy operator is not neglected, however.

The Lineshape Widths.

The width has been calculated ⁴ with the above-mentioned approximation, namely replacing the inverse of the matrix (15) by the matrix of the inverse,

for the transition between the vibronic states $M' \rightarrow M$. The result is

$$2\pi^2 \pi^{-1} \text{Im } R_{M',M}(\omega) = \sum_k \frac{1}{2} \{ \coth[\frac{1}{2} \beta \hbar(\omega + \omega_{kM'})] - 1 \} \\ \times \{ [c^2 \rho(-\omega - \omega_{kM'}) - c^2 \rho(\omega + \omega_{kM'})] X_{Mk,kM} + [c^2 \rho(-\omega - \omega_{kM'}) + c^2 \rho(\omega + \omega_{kM'})] Y_{Mk,kM} \\ + \sum_k \frac{1}{2} \{ \coth[\frac{1}{2} \beta \hbar(\omega + \omega_{Mk}) + 1 \} \{ [c^2 \rho(-\omega - \omega_{Mk}) - c^2 \rho(\omega + \omega_{Mk})] X_{M',k,kM'} \\ - [c^2 \rho(-\omega - \omega_{Mk}) + c^2 \rho(\omega + \omega_{Mk})] Y_{M',k,kM'} \} \quad (16)$$

where the argument of c^2 , defined in Ref.4, has been suppressed, it being understood that it is the same as in its accompanying cofactor ρ (ρ , the density of vibrational levels and not the density operator of the previous section, vanishes for negative arguments so that only one of the two terms in each square bracket will survive. The bath averaging introduced in the previous section reappears here through the presence of ρ). Further definitions are

$$X_{nm,1k} \equiv (K\vec{\sigma}_{nm} + \vec{Q}_{nm}) \cdot (K\vec{\sigma}_{1k} + \vec{Q}_{1k}) + (\vec{P}_{nm} \cdot \vec{P}_{1k}), \\ Y_{nm,1k} = i(K\vec{\sigma}_{nm} + \vec{Q}_{nm}) \cdot \vec{P}_{1k} - i\vec{P}_{nm} \cdot (K\vec{\sigma}_{1k} + \vec{Q}_{1k}), \\ \vec{Q}_{nm} \equiv \langle n | \vec{q}_1 | m \rangle,$$

where n, m represent vibronic eigenstates and the tilda refers to the transformed coordinates of Eq.(2). The summation index k in Eq.(16) runs over all intermediate states, which for the vibronic system $E \otimes \epsilon^{11}$ comprise the following: (a) Rotational states of the ground radial level, (b) Excited radial states (on which rotational levels are superimposed) associated with the lower potential surface, (c) States on the upper potential surface. The relative importance of these depend on the particular transition $M \rightarrow M'$ and associated parameters (temperature, etc.) in question. We exemplify our calculations by reference to $\text{CaO}:\text{Cu}^{2+}$ at 4.2 K⁶.

The prominent transitions are shown on Table 2.

$\omega_{nn'}$, in cm^{-1}	4	26	39
Γ_1	E	E	E
Γ'	A ₁	A ₂	E*
$ M' $	1/2	1/2	1/2
$ M $	3/2	3/2	5/2

Table 2. Transitions observed in $\text{CaO}:\text{Cu}^{2+}$ (Ref.6)

In the table the second and third rows give the assignments ⁶ in cubic symmetry (whose deviation from the spherical symmetry is given by the anisotropy parameter β/α whose value is ~ 4 Ref.6) whereas the fourth and fifth rows give the approximate assignments in terms of rotational quantum numbers appropriate to spherical symmetry and consistent with our calculations that include linear vibronic coupling only.

It turns out ⁴ that at low temperatures the dominant contribution to the linewidth is due to intermediate states of type (a), i.e. to the neighbouring rotational levels. At temperatures low compared to ω_D the resonance width goes as E_{JT}^{-2} for the model in Eq.(5) and as E_{JT}^{-3} for the model in Eq.(6).

Considering the latter we find for the two transitions :

$$|\text{Im } R_{3/2,1/2}| = \frac{1}{2} \frac{\Omega^2}{K^6} (\pi/2K^2) 3c^2 N \omega_D^{-3} = \frac{1}{3} \Omega^2 \pi K^{-6} \omega_D^{-1} \sim \omega_D K^{-6}, \quad (17)$$

$$|\text{Im } R_{5/2,1/2}| = 32 \frac{\Omega^2}{K^6} (\pi/2K^2) 3c^2 N \omega_D^{-3} = \frac{64}{3} \Omega^2 \pi K^{-6} \omega_D^{-1} \sim 64 \omega_D K^{-6}, \quad (18)$$

where in each line we have utilized an approximation for c^2 derived in App. B of Ref.4 and $\Omega \sim \omega_D K^2$ ($= 2E_{JT}/K\Omega$) is variously given in Ref.6 as 5 or 30 and $\omega_D \sim 300 \text{ cm}^{-1}$. The experimental half widths at half heights ($\sim |\text{Im } R|$, assuming that they are predominantly due to interactions with the phonon-bath) are about $\Delta\omega_{1/2 \rightarrow 3/2} = 2.5 \text{ cm}^{-1}$, $\Delta\omega_{1/2 \rightarrow 5/2} = 7 \text{ cm}^{-1}$. The alternative $K^2 = 5$ yields from Eq.(17) 2.4 cm^{-1} for $\Delta\omega_{1/2 \rightarrow 3/2}$ and from Eq.(18) 150 cm^{-1} for $\Delta\omega_{1/2 \rightarrow 5/2}$. [The alternative $K^2 = 30$ leads to values (0.01 cm^{-1} and 0.7 cm^{-1}) which are much too low]. We conclude that a qualitative agreement is indicated between our calculation based on linear coupling and the experimental values for $\text{CaO}:\text{Cu}^{2+}$. The lineshapes at elevated temperatures are insufficiently resolved, already at 20 K, to afford comparison with our results.

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