

## Spectral narrowing and rotational diffusion of molecular impurities in a deformable lattice

S. D. Mahanti

*Physics Department, Michigan State University, East Lansing, Michigan 48824*

G. Kemeny

*College of Natural Science, Michigan State University,**East Lansing, Michigan 48824*

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Oriental dynamics of a single diatomic molecular impurity in a deformable lattice is investigated using the Mori technique, and results are compared to the rigid-lattice case studied by de Raedt and Michel. The rotation-translation coupling, in addition to modifying the single-site cubic potential, suppresses librational motion, enhances diffusive motion, and narrows the width of the diffuse central peak.

The orientational structure and dynamics of simple diatomic molecular impurities in cubic host lattices have been a problem of considerable interest over the past several years.<sup>1-5</sup> Typical systems are  $(\text{CN})^-$  and  $\text{O}_2^-$  ions in alkali-halide crystals. Recently<sup>6</sup> these systems, in particular  $(\text{CN})^-$  in KCl and NaCl, have been explored in great detail in order to understand how the structure and dynamics evolve from a single-impurity limit to the molecular crystal limit, with special focus on orientational glass phase<sup>7</sup> observed in the intermediate concentration range.

A necessary starting point for understanding the dynamic properties of the glass phase in these systems is a proper study of the single-impurity limit. This latter problem is interesting in its own right as it forms a prototype of a problem of a single molecular impurity described by its orientational degrees of freedom coupled strongly to a polarizable medium, a problem similar to the polaron problem. Therefore, as in the polaron case, one expects to find here effects similar to effective-mass enhancement and self-trapping.

In this Rapid Communication, we discuss briefly the effect of rotation-translation coupling on the orientational dynamics of a single impurity in a cubic host. The dynamics in a rigid host was studied in great detail by de Raedt and Michel<sup>5</sup> using the Mori projection-operator technique. We have reexamined the physical origins of some of their interesting observations and apply the same procedure to the case of a deformable host.

The Hamiltonian  $H$  for a single diatomic molecule of moment of inertia  $I$  interacting with a cubic host is given by

$$H = H_R + H_T + H_{RT} \quad (1)$$

where

$$H_R = \frac{\bar{L}^2}{2I} + V_0(\theta, \phi) \quad (2a)$$

$$H_T = \sum_{j, \bar{k}} \hbar \omega_{j\bar{k}} (b_{j\bar{k}}^\dagger b_{j\bar{k}} + \frac{1}{2}) \quad (2b)$$

and

$$H_{RT} = i \sum_{\alpha, j, \bar{k}} Y_\alpha(\Omega) V_{\alpha j}(\bar{k}) (b_{j\bar{k}} + b_{b-\bar{k}}^\dagger) \quad (2c)$$

In the above equations,  $\bar{L}$  is the angular momentum operator,  $V_0(\theta, \phi) = V_0(\Omega)$  the cubic potential associated with a rigid lattice,  $\omega_{j\bar{k}}$  the phonon frequency of the pure host lattice ( $j$  the branch index and  $\bar{k}$  the wave vector),  $b_{j\bar{k}}$  and  $b_{j\bar{k}}^\dagger$  the phonon destruction and creation operators, and

$Y_\alpha(\Omega)$  the properly symmetrized spherical harmonic of order two. The rotation-translation coupling constants  $V_{\alpha j}(\bar{k})$  have been given in detail in Ref. 8. It should be pointed out that since molecules undergo large amplitude motions,  $(\theta, \phi)$  cannot be expanded about the minima with any justification (except at very low temperatures) and the proper dynamic variables are  $Y_\alpha(\theta, \phi)$ .

The orientational dynamics is contained in the Kubo's relaxation function  $\Phi_{\alpha\alpha}(Z)$  associated with the dynamic variable  $Y_\alpha(\Omega)$  and can be calculated by using Mori technique<sup>9</sup> which gives

$$\Phi_{\alpha\alpha}(Z) = X_{\alpha\alpha}(T) \left[ Z + \frac{\langle \omega^2 \rangle_\alpha}{Z + \Sigma_\alpha(Z)} \right]^{-1} \quad (3)$$

where  $Z$  is a complex frequency and  $X_{\alpha\alpha}(T) = \beta \langle Y_\alpha; Y_\alpha \rangle$  the isothermal susceptibility. The memory function  $\Sigma_\alpha(Z)$  has been calculated in the de Raedt-Michel approximation<sup>5</sup> which neglects the effect of  $H_{RT}$  on the dynamics of the host, i.e.,

$$\Sigma_\alpha(Z) = - \frac{1}{\langle \omega^2 \rangle_\alpha} \frac{\langle \omega^4 \rangle_\alpha - \langle \omega^2 \rangle_\alpha^2}{Z + i(\langle \omega^4 \rangle_\alpha / \langle \omega^2 \rangle_\alpha)^{1/2}} \quad (4)$$

In Eqs. (3) and (4),  $\langle \omega^{2n} \rangle$  is the  $2n$ th moment given by

$$\langle \omega^{2n} \rangle_\alpha = \langle Y_\alpha^{(n)}; Y_\alpha^{(n)} \rangle / \langle Y_\alpha; Y_\alpha \rangle \quad (5)$$

$Y_\alpha^{(n)}$  being the  $n$ th time derivative of  $Y_\alpha$ . It should be pointed out that Eq. (4), though not exact, has the nice feature that the spectral function

$$S_\alpha(\omega) = - \frac{1}{\pi} \text{Im} \phi_{\alpha\alpha}(\omega + i\epsilon) |_{\epsilon \rightarrow 0}$$

satisfies desirable sum rules.<sup>10</sup>

To have a better physical understanding of the spectral function, we note that  $\phi_{\alpha\alpha}(Z)$  has three poles in the complex  $Z$  plane which results in a spectral function having three quasi-Lorentzian components. In the following we drop  $X_{\alpha\alpha}(T)$  and the suffix  $\alpha$  for the sake of convenience. We find

$$S(\omega) = \frac{1}{\omega_0} \left[ A \frac{\Gamma}{\bar{\omega}^2 + \Gamma^2} + \frac{1}{2} \frac{X\gamma - Y(\bar{\omega} + \delta)}{(\bar{\omega} + \delta)^2 + \gamma^2} + \frac{1}{2} \frac{X\gamma + Y(\bar{\omega} - \delta)}{(\bar{\omega} - \delta)^2 + \gamma^2} \right] \quad (6)$$

where  $\omega_0 = \langle \omega^2 \rangle^{1/2}$  sets the frequency scale, i.e.,  $\bar{\omega} = \omega/\omega_0$  and all other parameters appearing in Eq. (6), namely,  $A$ ,  $X$ ,  $Y$ ,  $\Gamma$ ,  $\gamma$ , and  $\delta$  depend upon a single dimensionless variable  $R$ , where

$$R = (\langle \omega^4 \rangle / \langle \omega^2 \rangle^2)^{1/2}. \quad (7)$$

Equation (6) gives a diffusive central peak of weight  $A$  and two librational peaks of total weight  $X$  centered around frequencies  $\pm \omega_0 \delta$ . The most important parameter in the study of orientational dynamics is  $R$  which depends upon the symmetry of the dynamic variable  $Y_\alpha(\Omega)$  and the nature of the Hamiltonian  $H$ . The detailed equations relating the spectral parameters to  $R$  are rather complicated and will be published elsewhere.<sup>11</sup> Instead, we show their  $R$  dependence in Fig. 1.

From Fig. 1 we can see several important features. First,  $R \geq 1$  which can be proven easily, and is a necessary condition for spectral stability. The weight of the central peak  $A = 1 - X$  is zero when  $R = 1$  (oscillator or librational limit) and is one when  $R = \infty$  (central peak limit). The weight of the libration peak  $X$  is one for  $R = 1$  and zero for  $R = \infty$ . Also the width of the central peak  $\Gamma$  decreases with increasing  $R$ , indicating a narrowing of the diffusive central peak. The parameters  $\delta$  and  $\gamma$  which give the position and width of the librational peak  $\rightarrow \infty$  as  $R \rightarrow \infty$ , but the products  $\delta\omega_0$  and  $\gamma\omega_0$  remain finite.

We will now discuss our results of the calculation of different spectral parameters with and without the inclusion of rotational-translation coupling,  $H_{RT}$  [see Eq. (1)] in the calculation of  $\langle \omega^4 \rangle$  and  $\langle \omega^2 \rangle$ . When  $H_{RT} = 0$ , the spectra depend primarily on the nature of  $V_0(\theta, \phi)$ .<sup>5</sup> For  $(\text{CN})^-$  ion in KBr, an example we have studied in this paper,  $V_0$  consists of two parts, i.e.,

$$V_0 = V_0^R + rV_0^H, \quad (8)$$

where  $V_0^R$  is the short-range repulsion and  $V_0^H$  is the hexadecapole moment contribution to  $V_0$ . For the  $\text{CN}^-$  ion, these two contributions tend to oppose each other. Therefore, for the calculations that follow, we use a parameter  $r$  ( $0 \leq r \leq 1$ ) which can be varied to change the location of the minima and the height of barrier of  $V_0$  (see Fig. 2).

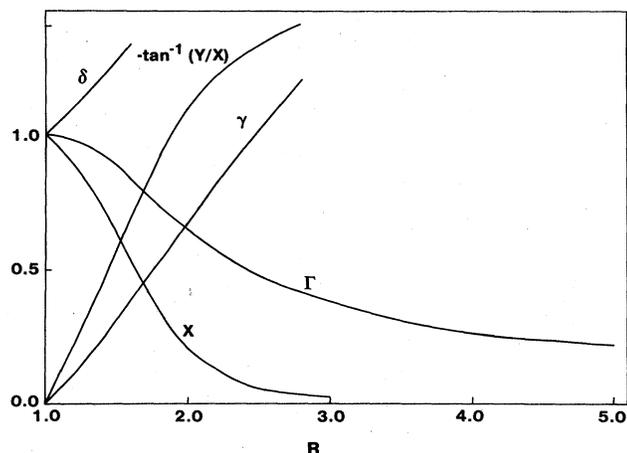


FIG. 1.  $R$  dependence of the parameters of reduced spectral weight  $\omega_0 S(\omega/\omega_0)$  where  $\omega_0 = \langle \omega^2 \rangle^{1/2}$  and  $R = (\langle \omega^4 \rangle / \langle \omega^2 \rangle^2)^{1/2}$ .

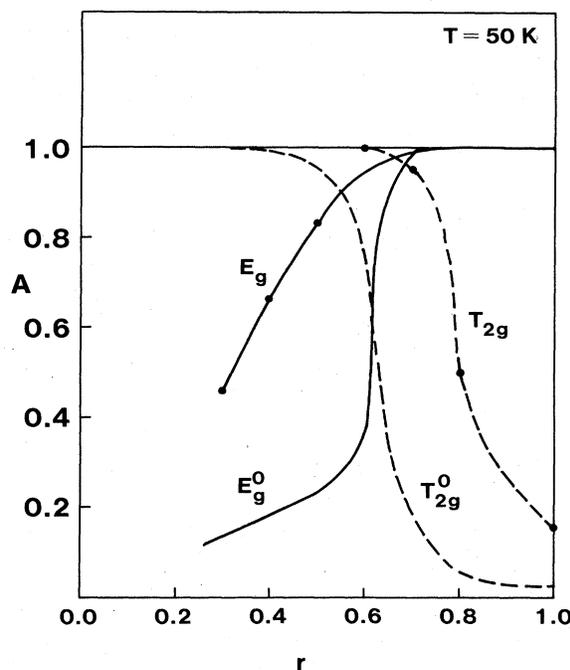


FIG. 2. Central peak weight  $A$  for a rigid ( $E_g^0$  and  $T_{2g}^0$ ) and a deformable ( $E_g$  and  $T_{2g}$ ) lattice as a function of the parameter  $r$  [see Eq. (8)] which controls the strength of  $(\text{CN})^-$  ion hexadecapole moment ( $V = V_0$ ).

When  $r = 0$ , the minima are along the [111] directions and we find that at low  $T$ , spectral function associated with  $E_g$  symmetry shows librational behavior [ $R(E_g) \rightarrow 1$ ] whereas that associated with  $T_{2g}$  symmetry shows diffusive behavior [ $R(T_{2g}) \rightarrow \infty$ ]. If, on the other hand, we choose  $r = 1$ , which corresponds to using the full strength of the  $(\text{CN})^-$  ion hexadecapole moment, the minimum shifts towards the (100) directions. In this case,  $E_g$  symmetry shows diffusive and  $T_{2g}$  symmetry shows librational behaviors. This point was realized by de Raedt and Michel<sup>5</sup> who used a simple Devonshire model<sup>4</sup> for  $V_0(\theta, \phi)$ , i.e.,  $V_0(\theta, \phi) = \pm KV_D(\theta, \phi)$ ,  $K$  being the strength of the potential. Experimentally, similar behavior has been seen in the Raman scattering measurements of Callender and Pershan<sup>1</sup> for  $\text{CN}^-$  in KCl and NaCl.

The reason behind this rather remarkable behavior is the following: At low  $T$ , the potential  $V_0(\theta, \phi)$  can be expanded about its minimum  $(\theta_0, \phi_0)$  leading to terms  $(\theta - \theta_0)^2$ ,  $(\phi - \phi_0)^2$ , and  $(\theta - \theta_0)(\phi - \phi_0)$  in the Hamiltonian. If the dynamic variable  $Y_\alpha(\theta, \phi)$  is such that it goes to zero linearly at  $(\theta_0, \phi_0)$ , then it behaves like an oscillator variable and  $R \rightarrow 1$  for this case. If, on the other hand,  $Y_\alpha(\theta, \phi)$  has maximum or is finite at  $(\theta_0, \phi_0)$ , then  $R \rightarrow \infty$  for this variable. Thus, depending on the direction of the potential minima, dynamic variables of different symmetry can exhibit drastically different spectral characteristics at low  $T$ .

Now we discuss how  $R$  and  $\omega_0$  and, hence,  $S_\alpha(\omega)$  change when we include the effect of the rotational-translational coupling. We find that the inclusion of  $H_{RT}$  changes  $\phi_{\alpha\alpha}(Z)$  at three places, each having a different physical interpretation.

First, the isothermal susceptibility changes because

$V_0(\theta, \phi)$  gets modified to  $V(\theta, \phi)$  where

$$V(\theta, \phi) = V_0(\theta, \phi) + V_s(\theta, \phi) = A_{11} + A_{21}V_D(\theta, \phi) + \dots, \quad (9)$$

where the self-energy contribution  $V_s(\theta, \phi)$  to the single-site potential is given by<sup>12</sup>

$$V_s(\theta, \phi) = - \sum_{\alpha, j, \vec{k}} \frac{|V_{\alpha j}(\vec{k})|^2}{\hbar \omega_j \vec{k}} |Y_{\alpha}(\Omega)|^2 = A_{11}^s + A_{21}^s V_D(\theta, \phi). \quad (10)$$

This modification of  $V_0(\theta, \phi)$  is equivalent to a constant shift in the energy of a polaron in a translationally invariant system. For  $(\text{CN})^-$  in KBr, we<sup>11</sup> find that  $A_{21}^s \approx 820$  K,  $A_{21}^R = 2351$  K, and  $A_{21}^H = -4110$  K. Thus, the self-energy contribution to  $V$  is quite important, particularly because the repulsion and hexadecapole contributions oppose each other.

Second, the second moment  $\langle \omega^2 \rangle = \omega_0^2$ , which provides the frequency scale and strength of the librational frequency  $\omega_0 \delta$  of the appropriate symmetry mode, changes. This change is brought about only through the modification of the single-site potential by  $V_s(\theta, \phi)$ . Physically this is equivalent to a change in effective moment of inertia of the molecule (similar to the effective mass enhancement of a polaron).

Third, the fourth moment and, hence, the quantity  $R$  gets modified in two distinctly different ways. One is again a change from  $V_0$  to  $V_0 + V_s$ , and the second is a new contribution to the torque acting on the molecule associated with the noncubic distortion of the surrounding cage caused by the rotational-translational coupling. We will denote this extra contribution to the fourth moment as  $\langle \omega^4 \rangle_{nc}$ , i.e.,

$$\langle \omega^4 \rangle = \langle \omega^4 \rangle_c + \langle \omega^4 \rangle_{nc}, \quad (11)$$

where  $c$  and  $nc$  refer to cubic and noncubic components of the local distortion. We have found that  $\langle \omega^4 \rangle > \langle \omega^4 \rangle_c$ . Thus, an explicit effect of  $H_{RT}$  is to enhance the fourth moment without changing the second moment (disregarding the implicit effect of changing  $V_0$  to  $V$ ). This behavior is similar to the exchange narrowing of the spin-resonance spectral function where the exchange interaction contributes to the fourth moment and not to the second.<sup>13</sup> The increase in the fourth moment results in an enhancement of  $R$  and, consequently, an increase in the spectral weight of the central peak irrespective of the symmetry of the dynamic variable. This is clearly seen in Fig. 2, where we plot the weight of the central peak without (curves  $E_g^0$  and  $T_{2g}^0$ ) and with (curves  $E_g$  and  $T_{2g}$ ) the inclusion of  $\langle \omega^4 \rangle_{nc}$  of Eq. (11). The parameter  $r$  determines whether [111] or [100] is the direction of minimum of  $V_0(\theta, \phi)$ . In Figs. 2 and 3, we have used  $V = V_0$  to bring out the significance of  $\langle \omega^4 \rangle_{nc}$ . This figure shows that over a large range of  $r$  values ( $0.3 < r < 0.8$ ), about 50% of the spectral weight is in the

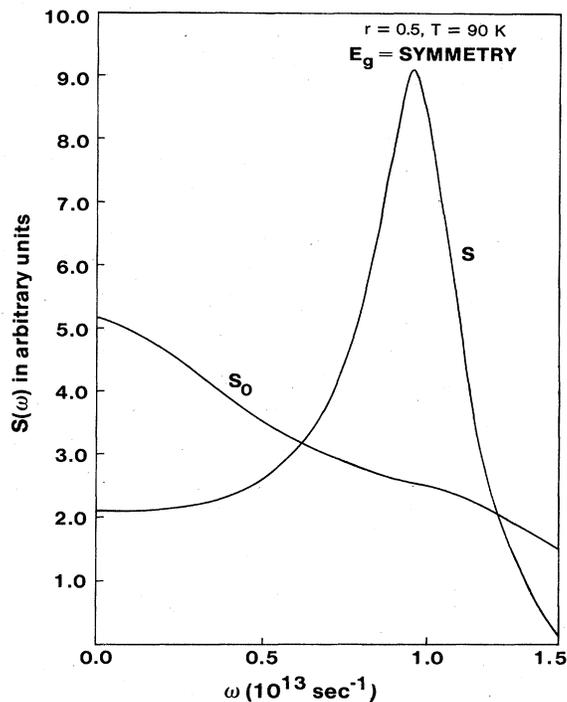


FIG. 3. Frequency dependence of the reduced spectral function for a rigid (curve  $S$ ) and a deformable (curve  $S_0$ ) lattice;  $E_g$  symmetry;  $T = 90$  K;  $r = 0.5$ ;  $V = V_0$ .

diffuse central peak for both  $E_g$  and  $T_g$  symmetries irrespective of the direction of potential minimum.

These results indicate that when the cubic potential is sufficiently flat, the noncubic part of the lattice distortion caused by the rotation-translation coupling has a tendency to self-trap the molecule at low enough temperature. The additional torque caused by the noncubic deformation increases  $\langle \omega^4 \rangle$  without affecting  $\langle \omega^2 \rangle$ . The net result of this is to enhance the weight of the central peak at the cost of the librational peak. The transfer of weight from libration to diffusive peak is shown in Fig. 3 for  $E_g$  symmetry for  $r = 0.5$  and  $T = 90$  K. The  $T$  dependence of this spectral weight shift will be discussed in a more detailed version of this paper.<sup>11</sup>

In summary, we find that coupling to a deformable lattice strongly affects the rotational dynamics. However, for a better understanding, one has to include the explicit dynamics of translation on the calculation of memory function  $\Sigma(Z)$  of Eq. (4) which goes beyond the approximation used in this paper. But we believe that the general conclusion of our work will be valid in this case also.

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<sup>9</sup>For a detailed list of references for the application of Mori's projection operator technique to molecular solids, see Ref. 5 above.

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<sup>12</sup>D. Sahu and S. D. Mahanti, Phys. Rev. B **29**, 340 (1984); a factor  $\frac{1}{2}$  is missing on the right-hand side of Eq. (2.8) of this paper.

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