Phonon line shape in disordered A₃C₆₀ (A = K, Rb)

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We present a calculation of the H₉ phonon self-energy for a model of A₃C₆₀ (A = K, Rb). The orientational disorder of the C₆₀ molecules is included, and the lowest order self-energy diagram is considered. The calculations illustrate that due to the violation of momentum conservation by the orientational disorder, Raman scattering can measure the decay of a phonon in an electron-hole pair, allowing the estimate of the electron-phonon coupling from such experiments. Comparison with experimental line shapes further provides support for a local correlation of the molecular orientations, with neighboring molecules preferentially having orientations differing by a 90° rotation.

I. INTRODUCTION

It is essential for the understanding of the alkali-doped fullerences A₃C₆₀ (A = K, Rb) to obtain reliable estimates of the strength λ of the electron-phonon interaction. In metallic systems, such as A₃C₆₀, a phonon can decay in an electron-hole pair. This decay leads to an extra width of the phonon. It was pointed out by Allen that λ can be estimated from the average of this extra width (γₚₗ) over all q-vectors. This width can be measured, e.g., by neutron scattering. It is, however, not easy to extract accurate values of λ from such experiments for C₆₀. Raman scattering provides an interesting alternative, since it gives a high resolution and since the Raman active modes (A₁ and H₃) are the modes which couple to the electrons in the partly filled t₁ᵤ band.

In the context of the fullerences, it was early pointed out that for the ordered system energy and momentum conservation forbids the decay of a q = 0 intramolecular phonon in an intraband electron-hole pair excitation. Due to the long wave length of the photons used in Raman scattering, this experiment would then not be appropriate for extracting λ, since q ≈ 0 phonons are excited. A₃C₆₀ has, however, strong orientational disorder, with each molecules taking essentially randomly one out of two preferred directions. Schlüter et al. therefore emphasized that decay of a H₉ phonon is nevertheless possible, since q-conservation is violated, while the decay of a q = 0 A₁ phonon is not possible. It was later assumed that the violation of q-conservation is so efficient, that Raman scattering actually measures an average of λ over all q-vectors, as assumed in the Allen formula. Recently, however, the applicability of Allen’s formula was anew put into question. It was concluded that for a q-independent interaction, there is no broadening of the q = 0 H₉ mode, and that the broadening of this mode is entirely due to the q-dependence of the coupling. This led to a drastic reinterpretation of the coupling constants derived from earlier Raman measurements. Explicit calculations have been performed for orientationally disordered systems, but the broadening of the q = 0 modes was not studied. Therefore, although Allen’s formula is the basis for deductions of λ from Raman data, its validity for disordered A₃C₆₀ has to our knowledge never been explicitly tested. The purpose of this paper is to perform such a test.

In Sec. II we present our model and the formalism, the results are presented and discussed in Sec. III and we give a summary in Sec. IV.

II. MODEL AND FORMALISM

We consider a model which includes the partly occupied t₁ᵤ band. There are three t₁ᵤ orbitals on each C₆₀ molecule i, which are connected by hopping matrix elements tᵢμₗ. We want to describe the coupling to the intramolecular five-fold degenerate H₉ Jahn-Teller modes. To describe the electron-phonon interaction, we use the Hamiltonian

\[
H^{cl} - ph = \varepsilon_{t_{1u} \sigma} n_{i \sigma} + \sum_{\langle ij \rangle \sigma \sigma'} t_{ij \sigma \sigma'} \psi_{i \sigma}^{\dagger} \psi_{j \sigma'}
\]

The orientational disorder has been built into the matrix elements tᵢμₗ. We describe the coupling to the intramolecular five-fold degenerate H₉ Jahn-Teller modes. To describe the electron-phonon interaction, we use the Hamiltonian

\[
H^{cl} = \sum_{i, \mu=1}^{5} (b_{i \mu}^{\dagger} b_{i \mu} + \frac{1}{2}) + \sum_{\mu=1}^{5} \sum_{\sigma m=1}^{3} V_{\mu \sigma}^{(i)} \psi_{i \sigma}^{\dagger} \psi_{im} (b_{i \mu} + b_{i \mu}^{\dagger}),
\]

where εₜ₁ᵤ is the phonon frequency, bᵢ₁μ annihilates a phonon with quantum number μ on site i, g is an overall coupling strength and Vᵢₖₖ⁽¹⁾, are dimensionless coupling
constants given by symmetry;
\[
V^{(\mu)} = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -2
\end{pmatrix}, \sqrt{3} \begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 0
\end{pmatrix},
\]
\[
\sqrt{3} \begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}, \sqrt{3} \begin{pmatrix}
0 & 0 & 0 \\
0 & 1 & 0 \\
1 & 0 & 0
\end{pmatrix}, \sqrt{3} \begin{pmatrix}
0 & 0 & 1 \\
0 & 0 & 0 \\
1 & 0 & 0
\end{pmatrix}, \quad (3)
\]
for \( \mu = 1, \ldots, 5 \) respectively. The electron-phonon coupling constant \( \lambda \) is then given by
\[
\lambda = \frac{5}{3} N(0) g^2 \frac{\omega_{\text{ph}}}{\omega_{\text{ph}}}, \quad (4)
\]
where \( N(0) \) is the density of states (DOS) per spin at the Fermi energy. We have assumed that the \( H_g \) modes are local Einstein modes with a local coupling to the electrons. Since these modes are intramolecular and since the interaction between the \( C_60 \) molecules is very weak, these assumptions should be very good. Actually, explicit calculations of the phonon dispersion curves for the \( H_g \) modes find that the dispersion is extremely small.

To describe the broadening of the phonon, we calculate the phonon self-energy due to the electron-phonon interaction. We consider the lowest order self-energy, expressed in terms of the zeroth order electron and phonon Green’s functions. This is the formalism used by Allen.

In the present case, the phonon energy is not much smaller than the bandwidth and the validity of Migdal’s theorem is therefore questionable. Contributions beyond the lowest order self-energy diagram may therefore be important. The on-site Coulomb interaction is large in these systems, which are believed to be close to a Mott transition. For simplicity, we have here nevertheless neglected corrections to Migdal’s theorem and effects of the Coulomb interaction.

We diagonalize the electronic part \( H^{el} \) of the Hamiltonian. The eigenstates are labelled by \( n \), the eigenvalues are \( \varepsilon_n \), and the corresponding zeroth order electron Green’s function is \( G^0_n(\omega) \). The phonon self-energy is then
\[
\Pi_{\alpha,\alpha'}(\omega) = -i \sum \sum \int_{\omega'} \frac{d\omega'}{2\pi} g^0_{nm} g^0_{nm} G^0_n(\omega') G^0_m(\omega + \omega'), \quad (5)
\]
where \( \alpha = (i\mu) \) labels a combined site and phonon degeneracy index and \( g^0_{nm} \) is the matrix element of the coupling to the phonon \( \alpha \) between the one-particle states \( n \) and \( m \). The frequency integral can be performed analytically, giving
\[
\Pi_{\alpha,\alpha'}(\omega) = 2 \sum g^0_{nm} g^0_{nm} \frac{f_m - f_n}{\varepsilon_m - \varepsilon_n - \omega + i\eta}, \quad (6)
\]
where \( f_n = f(\varepsilon_n) \) is the Fermi function, \( \eta \) an infinitesimal positive number. In the present calculation, we used \( \eta = 0.0004 \) eV, comparable to experimental resolution and much smaller than \( \omega_{\text{ph}} \) and \( \gamma_{\text{ph}} \).

The phonon Green’s function \( D \) is given by
\[
D^{-1} = [D^0]^{-1} - \Pi, \quad (7)
\]
where a matrix notation is understood and the noninteracting phonon Green’s function is given by
\[
D^0_{\alpha\alpha'}(\omega) = \frac{2 \omega_{\text{ph}}}{\omega^2 - \omega_{\text{ph}}^2 + i\eta} \delta_{\alpha\alpha'}. \quad (8)
\]
We introduce the reduced Green’s function in momentum space
\[
\tilde{D}_{\mu,\mu'}(\mathbf{q}, \omega) = \frac{1}{N} \sum_{ij} \sum_{\nu} e^{i \mathbf{Q}_i (\mathbf{R}_i - \mathbf{R}_j)} c^{ij}_{\mu,\nu} D_{\nu,\nu'}(\omega), \quad (9)
\]
where \( N \) is the number of molecules in the cluster, \( c^{ij}_{\mu,\nu} \) the scattering coefficients with proper symmetry factors corresponding to the specific experiment, as discussed in the Appendix.

We compute the coefficients \( c^{ij}_{\mu,\nu} \) for Raman scattering experiments. We consider electronic transitions within the \( t_{1u} \) and \( t_{1g} \) bands, assuming that the photon energy is larger than the \( t_{1u} - t_{1g} \) splitting. To obtain a simple result, we make the approximation that the hopping matrix elements are small. Calculations using realistic hoppings give qualitatively similar results. Details of the derivation are given in the Appendix. Then, we have an expression for \( c^{ij}_{\mu,\nu} \) which only depends on \( \mu, \nu \) and molecular orientations \( o(i) \) at sites \( i, j \), \( o(i) = \pm 1 \).

Between molecules with the same orientation, \( i.e., o(i) = o(j) \),
\[
c^{ij}_{\mu,\mu} = 1 \quad (\text{all } \mu), \quad (10)
\]
For \( o(i) = 1, o(j) = -1 \),
\[
c^{ij}_{11} = -c^{ij}_{22} = -c^{ij}_{33} = -c^{ij}_{45} = -c^{ij}_{54} = 1, \quad (11)
\]
and for \( o(i) = -1, o(j) = 1 \),
\[
c^{ij}_{11} = -c^{ij}_{22} = -c^{ij}_{33} = c^{ij}_{45} = -c^{ij}_{54} = 1. \quad (12)
\]
Finally,
\[
c^{ij}_{\mu,\mu} = 0, \quad \text{otherwise.} \quad (13)
\]

In the following we are interested in \( \tilde{D}_{\mu,\mu}(\mathbf{q} = 0, \omega) \), since in Raman scattering the coupling is to \( \sum_{\mu} \tilde{D}_{\mu,\mu}(\mathbf{q} = 0, \omega) \), and in
\[
D^\text{local}(\omega) = \frac{1}{N} \sum_{\mathbf{q}} \sum_{\mu} \tilde{D}_{\mu,\mu}(\mathbf{q}, \omega). \quad (14)
\]
In the \( \mathbf{q} = 0 \) phonon Green’s function momentum conservation is considered, to the extent that it survives the
orientational disorder. On the other hand, the usage of \( D_{\text{local}} \) instead implies an assumption that the orientational disorder has completely destroyed momentum conservation and that we therefore can average over all momenta as in neutron scattering. The spectral functions are defined as the imaginary part of the Green’s functions, i.e., \( \rho_{\mu}(q, \omega) = -(1/\pi) \text{Im} D_{\mu,\mu}(q, \omega) \).

Allen’s formula for the phonon broadening \( \gamma_{ph} \) (full width at half maximum (FWHM)), can be derived from Eq. (6) in the limit of \( w_{ph} \ll W \) and by ignoring the momentum conservation, and it is given by

\[
\gamma_{ph} = \frac{2\pi}{3} g^2 \omega_{ph} N(0)^2 = \frac{2\pi}{5} \lambda \omega_{ph}^2 N(0). \tag{15}
\]

The phonon level shift estimated from the real part of the self-energy can be expressed as

\[
\Delta \omega_{ph} = \left(-2 \ln 2 + \frac{7}{9} (w_{ph} N(0))^2\right) g^2 N(0), \tag{16}
\]

for a flat DOS. The second term in the bracket is the correction of order \((\omega_{ph}/W)^2\).

III. RESULTS

We have performed calculations for clusters with 256 atoms on an fcc lattice and with periodic boundary conditions. We take into account the fact that neighboring molecules tend to anti-align due to the jumping integral being stronger for such configurations. We control the randomness of orientation by introducing an Ising-type nearest neighbor antiferromagnetic interaction for the two preferred orientations, i.e., \( E_{\text{rot}} = N^{-1} \sum_{<i,j>} o(i)o(j) \) with \( N \) the number of nearest neighbor pairs. First we start from a truly random orientation and then anneal the system to any desired randomness by using a ficticious temperature. Since the fcc lattice is frustrated, there are many “antiferromagnetic” (AFM) states which minimize \( E_{\text{rot}} \) at \( E_{\text{rot, min}} = -1/3 \). Therefore even a perfectly annealed system retains a certain disorder, as can be seen in the electron density of states. Then the phonon spectral functions are averaged over many sets of orientational configurations.

The phonon spectral functions for the scattering vector \( q=0 \) and the local (summed over all \( q \)) spectral function are plotted in Fig. 1 for different orientational disorders. The phonon line widths for \( q=0 \) (solid lines) and local (dashed lines) spectral functions are about the same over a large range of disorder (different values of \( E_{\text{rot}} \)). This shows that the orientational disorder effectively breaks momentum conservation, and it supports the assumption that the Raman scattering experiment can give an estimate of the electron-phonon coupling. On the other hand, a calculation for a periodic “ferro-magnetically” ordered system gave two unbroadened peaks due to energy and momentum conservation, as will be discussed later.

The validity of Allen’s formula, Eq. (15), is explicitly tested by changing the phonon frequency \( w_{ph} \). Since the self-energy is trivially proportional to \( g^2 \), we concentrated on the linear dependence of \( \gamma_{ph} \) on \( w_{ph} \) for a fixed \( g \). The numerical estimates for the broadening \( \gamma_{ph} \) and the level shift \( \Delta \omega \) are computed by fitting the \( q=0 \) spectral functions to a single-pole phonon spectral function

\[
\rho_{\text{fit}}(\omega) = -\text{Im} \frac{A/\pi}{\left(\omega^2 - \omega_{ph}^2\right)^2 - \Delta \omega + i\gamma_{ph}}, \tag{17}
\]

where \( A \) is the total spectral weight. Although the numerical spectral functions are far from being single-pole structured, the peak position and the FWHM, \( \gamma_{ph} \), can be understood in an average sense.

The widths and shifts obtained from these fits are compared with the results of Allen’s formula in Table I. In Allen’s formula we have used \( N(0) = 6.2eV^{-1} \), which is the appropriate value for our model of \( A_3\text{C}_{60} \). The coupling constant \( g \) was set to 0.03 eV. We find that Allen’s formula is reasonably well reproduced from the \( q=0 \) spectral functions. The discrepancies between the numerical and Allen’s estimated values range within 20-40 %, which we attribute mainly to finite size effects. The phonon broadening decreased as the number of sites was increased. Also note that \( \gamma_{ph} \) shows a poorer agreement for small values of \( \omega_{ph} \), where finite size effects become more pronounced due to the small number of particle-hole pairs with excitation energy less than \( \omega_{ph} \). Due to computational limitations, we have considered a maximum number of 256 sites although the convergence with respect to the system size is not good enough for a systematic finite size scaling analysis.
We have calculated the Raman scattering spectra for systems close to the local minima of antiferromagnetically ordered orientations by using realistic parameters for the coupling constant $g$ obtained from the photoemission spectra analysis. We then discuss the relevance of our calculation to Raman scattering experiments. We have performed the calculations for the first two $H_g$-modes at frequencies of 0.0336 and 0.0542 eV (270, 432 cm$^{-1}$, respectively) and have taken average over 10 sets of rotational configurations for $E_{rot} = -0.323$, close to the AFM minima at $E_{rot} = -0.333$.

For the first two $H_g$ modes the fitted $\gamma_{ph}$'s are 13, 47 cm$^{-1}$ for $\omega_{ph}=270$, 432 cm$^{-1}$, respectively. These values differ by almost a factor of 2 from the experimental estimates at 20 and 21 cm$^{-1}$, respectively. This illustrates the fact that photoemission and Raman scattering give rather different estimates of the distribution of the coupling strength for the low-lying phonons. The calculated Raman spectrum for $H_g(2)$ mode is shown in Fig. 2. The total spectrum can be resolved into two major peaks from the first two ($\mu = 1, 2$ at $A$) and the last three ($\mu = 3, 4, 5$ at $B$) modes of the phonon. This leads to a spectrum which agrees reasonably well with the low-energy part of the spectrum in Ref. 2 in the sense that the spectrum is strongly skewed towards higher energies and has additional structures. This provides support for the belief that there is a local 'antiferromagnetic' correlation, since the agreement with experiment is better than for the random orientation. The two narrow high frequency peaks in the experimental spectrum seem, however, to be beyond our treatment.

To discuss the phonon level splitting into a doublet ($\mu = 1, 2$) and a triplet ($\mu = 3, 4, 5$), we define the reduced phonon self-energy at $q=0$ in analogy to the reduced phonon Green's function $\tilde{D}_{\mu,\mu'}(q=0,\omega)$ as

$$\tilde{\Pi}_{\mu,\mu'}(q=0,\omega) = \frac{1}{N} \sum_{ij} \sum_{\nu} \epsilon^{ij}_{\mu\nu} \tilde{\Pi}_{i\nu,j\mu'}(\omega),$$

which is the corresponding self-energy for $\tilde{D}_{\mu,\mu'}(q=0,\omega)$. (See Appendix.) The real part of $\tilde{\Pi}_{\mu,\mu}(0,\omega_{ph})$ agrees very well with the phonon level shift previously obtained by fitting the spectral function for $\tilde{D}_{\mu,\mu}(0,\omega)$. The level shifts are better understood by investigating the imaginary part of $\tilde{\Pi}_{\mu,\mu}(0,\omega)$, which, related to the real part by the Kramers-Kronig relation, gives the excitation spectrum responsible for the perturbational level shift. Spectra of $\text{Im}\tilde{\Pi}_{\mu,\mu}(0,\omega)$ extend from 0 to the bandwidth and show different shapes for the doublet and triplet. For orientational configurations close to the AFM minima, those for the doublet are skewed to higher energy giving the smaller contribution to the level shift while those for triplets are skewed to lower energy leading to the larger level shift. For random orientations, the two spectra show essentially the same shape as the system size is increased.

The imaginary part of $\tilde{\Pi}_{\mu,\mu}(0,\omega)$ represents the spectral distribution of coupling of $\mu$-th phonon to electron-hole pair excitations. More specifically, $\tilde{\Pi}_{\mu,\mu}(0,\omega)$ can be written as the energy spectrum of the state for the uniformly distorted field, $|\phi(\mu)\rangle$, due to $\mu$-th Jahn-Teller phonon mode;

$$\text{Im}\tilde{\Pi}_{\mu,\mu}(0,\omega) = \frac{q^2}{4} \sum_{\sigma,\alpha,\beta} \left| \langle \alpha, \beta | \phi(\mu) \rangle \right|^2 \delta(\omega - \epsilon_\alpha + \epsilon_\beta),$$

where the summation is over the electron-hole pair states $|\alpha, \beta\rangle$ ($\epsilon_\alpha > \epsilon_F$, $\epsilon_\beta < \epsilon_F$ with the Fermi energy $\epsilon_F$) and

$$|\phi(\mu)\rangle = \sum_{imn,\sigma} \tilde{\psi}_{imn\sigma} V_{mn} \psi_{imn'\sigma} |0\rangle,$$

with the non-interacting Fermi sea $|0\rangle$. $\tilde{\psi}_{imn\sigma}$ is the annihilation operator for the orbital pointing along the $m$-th principal axis, not along the molecular orientation, i.e., $\tilde{\psi}_{imn\sigma} = \psi_{imn\sigma}$ for $o(i) = 1$ and $\tilde{\psi}_{imn\sigma} = \psi_{imn\sigma}, \tilde{\psi}_{imn\sigma} = -\psi_{imn\sigma}$ and $\tilde{\psi}_{imn\sigma} = \psi_{imn\sigma}$ for $o(i) = -1$. The energy expectation value of the distorted field can be related to the first moment of $\text{Im}\tilde{\Pi}_{\mu,\mu}(0,\omega)$ as

$$\frac{\langle \phi(\mu) | H^d | \phi(\mu) \rangle}{\langle \phi(\mu) | \phi(\mu) \rangle} = E_0 + \int_0^{\infty} \omega \text{Im}\tilde{\Pi}_{\mu,\mu}(0,\omega)d\omega / \int_0^{\infty} \text{Im}\tilde{\Pi}_{\mu,\mu}(0,\omega)d\omega,$$

where $E_0$ is the ground state energy of non-interacting electrons. As expected near the AFM local minima, $\langle \phi(\mu) | H^d | \phi(\mu) \rangle / \langle \phi(\mu) | \phi(\mu) \rangle$ has smaller value for the doublet and larger value for the triplet.

The Jahn-Teller phonon couples to the distortion of the electronic density. For the doublet modes, the phonons couple to the density distortion along the principal axes, e.g., for $\mu = 1, (b_{11}^1 + b_{12}^1)$ couples to $(n_{xx} + n_{yy} - 2n_{zz})$, the distortion elongated or squeezed along $z$-axis. Similarly, the triplet phonons couple to distortions along diagonal directions in $xy, xz, yz$-planes e.g., for $\mu = 3, (b_{31}^3 + b_{33}^3)$ couples to $(n_{xy} - n_{yz})$ where $\hat{x}, \hat{y}$ axes are rotated from $x, y$-axes by $45^\circ$ along $z$-axis. Therefore, the distortion for $\mu = 3, 4, 5$ tend to distribute more electrons along the in-plane diagonal directions, which are the strongest bonding directions for $t_{1u}$-orbitals in the fcc lattice. Furthermore, upon the inter-site coherence close to AFM minima, the distortions from neighbors add up constructively along the strongest bonding direction to give the energy gain for the triplet phonons, leading to the skewedness toward the low energy.

It has been suggested that the locally broken cubic symmetry, due to the orientational disorder, could lead to a splitting of all five levels in the $H_g$ modes. However within our model, it seems unlikely that the local energy splittings survive after averaging over all sites. Rather, the calculation indicates that the local energy splittings contribute to the broadening of levels, not to collective $q=0$ modes which survive disorder. We observe that the first two peaks in the experiment of Winter et al. could
reflect states in isolated $C_{60}$, since their observed energy shifts from the undoped $C_{60}$ values are too small compared to estimates of the phonon self-energy from the lowest order diagram and sometimes even have different signs. Considering the narrowness of these peaks, they could result from a many-electron molecular states, due to effects neglected an this study, and with a very weak coupling to the surrounding.

Our results are in strong contrast to the results of Aksenov and Kabanov. They studied the problem in a model where the orientational disorder was described by a relaxation rate, leading to an imaginary self-energy in the electron Green’s function. However, the breaking of the translational symmetry was not explicitly included, and momentum conservation was assumed in evaluating various diagrams. The orbital degeneracy was also neglected. It was concluded that for a $q$-independent electron-phonon coupling there is no broadening of a $H_{g}(2)$ phonon and that the broadening is entirely due to the dependence of the coupling on the angle of $q$. This is in strong contrast to the results above, where we find that a $q$-independent coupling gives a substantial broadening, provided that the violation of the translational symmetry is included explicitly. As was discussed in Sec. II, the $q$-dependence of the coupling should be very weak, and the effect discussed in Ref. 8 not very important.

Aksenov and Kabanov were not able to obtain the angular dependence of the coupling constants and therefore they could not deduce the absolute magnitude of the coupling constants from Raman experiments, but instead estimated the relative coupling constants from Raman experiments. To obtain absolute estimates, they used coupling constants deduced from photoemission for a free $C_{60}$ molecule and arbitrarily assumed that the coupling constant to the lowest mode is correct. Had they instead, equally arbitrarily, assumed that the coupling to the third mode is correct, all values of $\lambda_{p}$ would have been about a factor of two larger and if they had assumed that the deduced coupling to the eighth mode is correct, all couplings would have been zero.

\section{IV. SUMMARY}

We have demonstrated that because the orientational disorder breaks the momentum conservation, Raman measurements of the $H_{g}$ modes in the $A_{3}C_{60}$ should see a broadening due to the decay in electron-hole pairs. This enables Raman scattering experiments to derive electron-phonon coupling strengths. Furthermore, the explicit calculation shows that the width of this $q=0$ mode is not very different from the $q$-averaged width, where the latter is described by Allen’s formula. We further find that the local “anti-ferromagnetic” correlation of the molecular orientation is important for obtaining the non-symmetric line-shape seen experimentally. This provides support for such a local correlation actually taking place in the real system. This leads to a large splitting between a two-fold and a three-fold degenerate component. Experimentally additional structures are seen which are not reproduced by the present calculations. It would therefore be interesting to include corrections to Migdal’s theorem beyond the present calculations, and effects of the Coulomb interaction.

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\begin{table}[h]
\begin{tabular}{cccccc}
$\omega_{ph}$ & $\Delta \omega_{ph}$ & $\gamma_{ph}$ & $\Delta \omega_{Allen}$ & $\gamma_{Allen}$ \\
0.03 & -0.0076 & 0.00328 & -0.0076 & 0.00217 \\
0.04 & -0.0064 & 0.00402 & -0.0074 & 0.00229 \\
0.05 & -0.0063 & 0.00460 & -0.0073 & 0.00362 \\
0.06 & -0.0062 & 0.00560 & -0.0071 & 0.00435 \\
\end{tabular}
\caption{Phonon level shifts and broadening from numerical estimates and Allen’s formula. The numerical estimates are from fitting of $q=0$ spectral function (see text) and the estimates from Allen’s formula use Eqs. (15-16) with $N(0) = 6.2$ per eV and $g = 0.03$ eV.}
\end{table}
V. APPENDIX: COEFFICIENTS $c^{ij}_{\mu \nu}$ FOR RAMAN SCATTERING

In the Raman scattering experiment ($q = 0$), the incoming light with energy $\omega_i$ is scattered by losing the energy of $\omega_{ph}$ to the phonon in solid. Following Quang et al., we treat the photon classically. The scattering rate $I_p(\omega_i, \omega_{ph})$ with a polarization vector $p$ can then be expressed as

$$I_p(\omega_i, \omega_{ph}) \propto \sum_{\alpha, \alpha'} \text{Im} D_{\alpha, \alpha'}(\omega_{ph}) h^p_\alpha(w_i, \omega_{ph}) h^\dagger_{\alpha'}(w_i, \omega_{ph}),$$

where $h^p_\alpha(w_i, \omega_{ph})$ is given by, as depicted in Fig. 3.

$$h^p_\alpha(w_i, \omega_{ph}) = \sum_{n, m, l} g^p_{\alpha, mn} P^p_{nl} P^p_{ml}$$

$$\times \int d\omega G^0_{\alpha}(\omega) G^0_{m}(\omega + \omega_{ph}) G^0_{i}(\omega + \omega_i),$$

(23)

with matrix elements $P^p_{nl}$ of the dipole moment operator at the polarization $p$ between non-interacting electronic eigenstates $n$ and $m$. Since a typical frequency of the light source is a few eV, and the $t_{1u} - t_{1g}$ splitting is only about $\Delta_1 \sim 1$ eV, transitions to higher states may, however, also play a role.

![Fig. 3. Effective photon-phonon interaction vertex. The incoming photon (dashed lines) with frequency $\omega_i$ scatters to a photon with frequency $\omega_i - \omega_{ph}$ by losing its energy to the $\alpha$-th phonon mode (wavy line) with energy $\omega_{ph}$. The interaction is mediated by the electrons (thick lines labelled as $n, m, l$) in the partially filled $t_{1u}$ band and in the empty $t_{1g}$ band in the solid. The filled dot represents the electron-phonon interaction with strength $g^p_{\alpha, mn}$, and the empty dots represent the electron-photon dipole interaction.](image)

The matrix elements $P^p_{nl}$ of the dipole moment operator at the polarization $p$ are expressed as $\langle \alpha|\mu|n\rangle \langle n|\nu|l\rangle$ with the bandwidth $W \sim 0.5$ eV, we ignore the $w_i, \omega_{ph}$ dependency in $h^p_\alpha(w_i, \omega_{ph})$. Now factoring out the integral, we have

$$h^p_\alpha(w_i, \omega_{ph}) = \frac{g}{2} \sum_{i, m, l} V^{(ij)}_{im} P^p_{i, ml} P^p_{i, ml},$$

(24)

where the matrix elements $P^p_{i, ml}$ in Eq. (23) are reduced to matrix elements between local orbitals $n, l$ at site $i$, $P^p_{i, ml}$. We denote the three $t_{1u}$ and $t_{1g}$-molecular orbitals as $x, y, z$, as in Ref. [24]. For the first type of orientation, we can easily understand from symmetry of C$_{60}$ molecules that

$$P^p_{i, xy} = p_z, P^p_{i, yz} = p_x, P^p_{i, zx} = p_y \text{ (orient. 1)}$$

(25)

for a polarization direction $p = (p_x, p_y, p_z)$ with $|p| = 1$. Similarly for the second type of orientation, we only need to rotate the molecule 90 degree along z-axis, which gives

$$P^p_{i, xy} = p_z, P^p_{i, yz} = -p_y, P^p_{i, zx} = p_x \text{ (orient. 2)}.$$  

(26)

Note that $P^p_{i, nn} = 0$. Therefore, leaving out common factors, we can write using Eq. (3),

$$h^p_{i1}(w_i, \omega_{ph}) = p_x^2 + p_y^2 - 2p_x^2, p_y^2 - 2p_y^2$$

(27)

$$h^p_{i2}(w_i, \omega_{ph}) = \sqrt{3}(p_y^2 - p_x^2), -\sqrt{3}(p_y^2 - p_x^2)$$

(28)

$$h^p_{i3}(w_i, \omega_{ph}) = 2\sqrt{3}p_x p_y, -2\sqrt{3}p_x p_y$$

(29)

$$h^p_{i4}(w_i, \omega_{ph}) = 2\sqrt{3}p_y p_z, 2\sqrt{3}p_y p_z$$

(30)

$$h^p_{i5}(w_i, \omega_{ph}) = 2\sqrt{3}p_x p_z, -2\sqrt{3}p_x p_z,$$

(31)

where the first expressions on the right hand side are for molecules of orientation of type 1 and the second for type 2.

Finally, we take average of $h^p_{i1} h^p_{i1'}$ over the polarization directions, i.e., $< h^p_{i1} h^p_{i1'} > = \int dt D_{i1} D_{i1'}$. Defining $c^{ij}_{\mu \nu} = \frac{5}{4} < h^p_{i\mu} h^p_{i\nu} >$, we obtain $c$ as given in Eqs. (32). Then

$$< I_p(\omega_i, \omega_{ph}) > \propto \sum_{\alpha} \text{Im} \tilde{D}_{\alpha, \alpha}(\omega_{ph}),$$

(32)

with $\tilde{D}_{\alpha, \alpha}$ defined in Eq. (33).

Now, we look for the Dyson equation corresponding to the reduced Greens function $\tilde{D}_{\alpha, \alpha}(q, \omega)$ at $q=0$. We can rewrite $\tilde{D}_{i\mu, j\nu}$ by splitting the coefficient matrix $c^{ij}_{\mu \nu}$ as

$$\tilde{D}_{i\mu, j\nu} = \sum_{\mu'} c^{ij}_{\mu \mu'} D_{i\mu', j\nu} = \sum_{\nu', \mu'} \tilde{\tau}^{ij}_{\mu \nu'} D_{i\mu', j\nu'}\tilde{\tau}^{ij}_{\nu' \mu},$$

(33)
and \( \tilde{\tau}^i = (\tau^i)^{-1} \). Now employing the matrix notation for the orbital indices,

\[
\tilde{D}_{ij} = \tilde{\tau}^i \left( D^0 \delta_{ij} + D^0 \sum_k \Pi_{ik} D_{kj} \right) \tau^j \tag{34}
\]

\[
= D^0 \delta_{ij} + D^0 \sum_k \tilde{\tau}^i \Pi_{ik} \tilde{\tau}^k D_{kj} \tau^j \tag{35}
\]

\[
= D^0 \delta_{ij} + D^0 \sum_k \tilde{\Pi}_{ik} \tilde{D}_{kj}, \tag{36}
\]

with the reduced self-energy \( \tilde{\Pi}_{\mu, j\nu}(\omega) \) defined as

\[
\tilde{\Pi}_{\mu, j\nu}(\omega) = \sum_{\nu'} c^i_{\mu \nu'} \Pi_{\nu' j\nu}. \tag{37}
\]

Finally by taking the summation over site indices \( i, j \), we obtain the reduced phonon self-energy \( \tilde{\Pi}_{\mu \nu}(q = 0, \omega) \) for \( \tilde{D}_{\mu \nu}(q = 0, \omega) \) as Eq. (36).

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