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Broadening and anomalous infrared activity of the H_g-derived phonons in the metallic fullerides

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It is pointed out that broadening of the Raman-active H_g-derived phonons in the fulleride superconductors is due to *inter*band electron-phonon interaction and that orientational disorder can render these phonons infrared active. The long-wavelength A_g phonons are left completely unrenormalized by the electron-phonon interaction.

The metallic fullerides have formula A_3C_{60} where A denotes an alkali-metal atom.[1] Each of the latter has donated an electron to a partially filled complex of three narrow overlapping conduction bands derived from intermolecular interaction of the threefold degenerate t_{1u} molecular orbitals $\phi_v(r)$ ($v=1,2,3$) of the C_{60} molecule.[2] In these states the conduction electrons couple to phonons derived from the Raman-active H_g and A_g vibrations of the C_{60} molecular ion. This electron-phonon coupling is relevant[3] to the remarkable occurrence of superconductivity[4] in these compounds at relatively high temperatures. Experimental information on the magnitude of this coupling is available from Raman-[5] and inelastic neutron-[6] scattering spectroscopies.

In this paper we make the following points with regard to the observability of the electron-phonon interaction via optical probes. First, the *long-wavelength* ($q\rightarrow 0$) H_g-derived phonons are renormalized by their coupling to *inter-*t_{1u}*-band* excitations but not by their coupling to *intra-*t_{1u}*-band* excitations. This is because the intra-t_{1u}-band electronic polarizability is negligible at the optical wave vectors q and H_g phonon frequencies ω_α of interest ($qv_F/\omega_\alpha \ll 1$). Thus, Raman spectroscopy provides information only on the *inter*band electron-phonon interaction and not on the intraband electron-phonon interaction as has been previously supposed.[3] The main consequence of the former is to dampen the H_g phonons whose frequencies overlap those of the inter-t_{1u}-band excitation continuum. Second, the long-wavelength A_g phonons couple neither to intra- or inter-t_{1u}-band excitations and are, therefore, left unrenormalized by the electron-phonon interaction. Third, we point out that the H_g phonons can become weakly infrared (IR) active due to the breaking of the usual selection rules by orientational disorder.[7] The observation of this effect would provide an additional channel for obtaining experimental information on the electron-phonon interaction. A simplified model calculation is introduced to illustrate these results.

In a tight-binding band description[3] of A_3C_{60} the frequency-dependent conductivity $\sigma(\omega)$ in the region of the low-lying excitations of the solid can be derived to be of the following form:

$$\sigma(\omega)=\frac{e^2}{3}\sum_n N_F(n)v_{F,n}^2\tau_n/(1-i\omega\tau_n)-[i\omega\Omega_0^{-1}\chi(\omega)]\ . \tag{1}$$

The first term is the Drude contribution from the intraband excitations while the second term arises from the electronic polarizability $\chi(\omega)$ of the crystal. Since the crystal is cubic we have taken $\sigma(\omega)=\sigma_{xx}(\omega)$. In the Drude term, $N_F(n)$ is the density of states at the Fermi level contributed by the band n, $v_{F,n}^2$ is an average over the Fermi surface n of the square of the Fermi velocity, and τ_n are phenomenological transport lifetimes. Ω_0 denotes the volume of the solid. $\chi(\omega)$ consists of two parts,

$$\chi(\omega)=\chi_e(\omega)+\sum_{\alpha\beta}V_\alpha(\omega+i\delta)D_{\alpha\beta}(\omega)V_\beta^*(\omega-i\delta)\ . \tag{2}$$

$\chi_e(\omega)$ is the direct inter-t_{1u}-band polarizability

$$\chi_e(\omega)=\sum_{\mathbf{k}}\sum_{n'n}{}'\frac{|\mu_{n'n}(\mathbf{k})|^2\nu_{n'n}(\mathbf{k})}{\omega_{n'n}(\mathbf{k})-(\omega+i\delta)} \tag{3}$$

which has already been investigated in Ref. 8. The second term represents the phonon polarizability and is induced by the electron-phonon interaction. The function

$$V_\alpha(\omega)=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}\sum_{n'n}{}'\frac{\mu_{n'n}(\mathbf{k})g_{n'n}^\alpha(\mathbf{k})^*\nu_{n'n}(\mathbf{k})}{\omega_{n'n}(\mathbf{k})-\omega} \tag{4}$$

determines the effective charge acquired[9] by the H_g or A_g phonon mode labeled α. In Eqs. (3) and (4), $\mu_{n'n}(\mathbf{k})$ is the transition dipole moment between Bloch states. It may be expressed as $\mu_{n'n}(\mathbf{k})=i\hbar e v_{n'n}(\mathbf{k})/\omega_{n'n}(\mathbf{k})$, where $v_{n'n}(\mathbf{k})$ is the x component of the interband matrix element of the one-electron velocity, and $\hbar\omega_{n'n}(\mathbf{k})=\varepsilon_{\mathbf{k},n'}-\varepsilon_{\mathbf{k},n}$ is the energy of an interband transition. The quality $\nu_{n'n}(\mathbf{k})=f_{\mathbf{k},n}-f_{\mathbf{k},n'}$, where $f_{\mathbf{k},n}$ denotes the Fermi-Dirac occupation function for the Bloch state of energy $\varepsilon_{\mathbf{k},n}$. In Eq. (2) $D_{\alpha\beta}(\omega)$ is the phonon propagator given by the Dyson equation

$$(1/D)_{\alpha\beta}=(1/D^{0}_{\alpha\alpha})\delta_{\alpha\beta}-\Pi_{\alpha\beta} \tag{5}$$

in which

$$\Pi_{\alpha\beta}(\omega)=\frac{1}{N}\sum_{\mathbf{k}}\sum_{n'n}{}' \frac{g^{\alpha}_{n'n}(\mathbf{k})g^{\beta}_{n'n}(\mathbf{k})^{*}\nu_{n'n}(\mathbf{k})}{\omega_{n'n}(\mathbf{k})-(\omega+i\delta)} \tag{6}$$

is the phonon self-energy and $D^{0}_{\alpha\alpha}=(2\omega_{\alpha})/[\omega_{\alpha_2}-(\omega+i\delta)^2]$ defines the unperturbed phonon propagator. N denotes the number of C_{60} molecules in the solid. Finally, $g^{\alpha}_{n'n}(\mathbf{k})$ is the long-wavelength limit $(\mathbf{k}'=\mathbf{k})$ of the interband $(n'\neq n)$ or intraband $(n'=n)$ electron-phonon coupling constant $g^{\alpha}_{n'n}(\mathbf{k}',\mathbf{k})$.[3] Specifically,

$$g^{\alpha}_{n'n}(\mathbf{k})=\sum_{\nu'\nu} g^{\alpha}_{\nu'\nu}A_{n'\nu'}(\mathbf{k})A_{n\nu}(\mathbf{k}) \tag{7}$$

where $g^{\alpha}_{\nu\nu'}$ is the local electron-molecular-vibration (EMV) coupling constant for the vibration α, and $A_{n\nu}(\mathbf{k})$ is the Bloch state amplitude for finding an electron in a molecular orbital ν. For the A_g modes it follows from the orthogonality of the Bloch states that $g^{\alpha}_{n'n}(\mathbf{k})=0$ for $n'\neq n$.

It is important to note that in Eqs. (3), (4), and (6), the prime over the summation symbol indicates that terms corresponding to $n'=n$ are to be excluded from the sums over the band indices. This is because at the frequencies (ω_{α}) and wave vectors $(q\rightarrow 0)$ of interest, the intraband contributions have the form

$$\lim_{\mathbf{q}\rightarrow 0}\sum_{\mathbf{k}n}\frac{(\partial f_{\mathbf{k},n}/\partial\varepsilon_{\mathbf{k},n})(\mathbf{q}v_{F,n})^{2-s}}{(\mathbf{q}v^{2}_{F,n})^{2}-(\omega+i\delta)^{2}} \tag{8}$$

where, on using the relation between $\mu_{n'n}(\mathbf{k})$ and $v_{n'n}(\mathbf{k})$, $s=2$, 1, and 0 for the right-hand sides of Eqs. (3), (4), and (6), respectively. Thus the *intra*band contributions to the effective phonon charge $V_{\alpha}(\omega)$ and phonon self-energy $\Pi_{\alpha\beta}(\omega)$ both vanish[10] while the intraband contribution to $\chi_{e}(\omega)$ survives, and has, in fact, been factored out as the Drude contribution in Eq. (1) [in which we carried out the replacements $\delta\rightarrow(\frac{1}{2}\tau_n)$]. Consequently, unlike the corresponding situation in a conventional metal $(qv_F/\omega)\sim v_F/s\gg 1$, where s is the sound velocity,[11] the renormalization of the H_g phonons is due entirely to their coupling to *inter-t_{1u}*-band excitations. Equations (5) and (6) show that the dampings of the H_g phonons are determined by the strength of the interband electron-phonon coupling constants and the density of the inter-t_{1u}-band *transitions*, $N(\omega)$, where

$$\begin{aligned}\pi N(\omega)&=\mathrm{Im}N^{-1}\sum_{k,n'n}{}' \nu_{n'n}(\mathbf{k})/[\omega_{n'n}(\mathbf{k})-(\omega+i\delta)]\\&\equiv\mathrm{Im}F(\omega)\,,\end{aligned} \tag{9}$$

rather than the density of states at the Fermi surface, N_F. Significant damping arising from a high value of $N(\omega)$ is probably the reason why the highest-frequency H_g modes are apparently absent from the observed Raman spectra[5] of the A_3C_{60} compounds. We expect essentially the same conclusion for orientationally disordered A_3C_{60} since in the region of the H_g frequencies interband scattering will remain the dominant form of electron-phonon coupling in the disordered material. By contrast, we note that the A_g modes remain entirely unrenormalized since for $n'\neq n$ $g^{\alpha}_{n'n}(\mathbf{k})=0$ for these modes. The A_g phonons should therefore appear as sharp Lorentzian features in the Raman spectrum.

For the H_g modes to become IR active the effective charge $V_{\alpha}(\omega)$ defined in Eq. (4) must be nonvanishing. Since for the crystal we have the symmetry properties $g^{\alpha}_{n'n}(-\mathbf{k})=g^{\alpha}_{n'n}(\mathbf{k})^{*}$ and $v_{n'n}(-\mathbf{k})=-v_{n'n}(\mathbf{k})^{*}$, $V_{\alpha}(\omega)$ is nonvanishing only if the product $v_{n'n}(\mathbf{k})g^{\alpha}_{n'n}(\mathbf{k})^{*}$ has an *imaginary* part. However, both $\nu_{n'n}(\mathbf{k})$ and $g^{\alpha}_{n'n}(\mathbf{k})$ are real if the conduction bands are derived purely from t_{1u} orbitals, in which case $V_{\alpha}(\omega)=0$. This selection rule, however, is broken by orientational disorder which can be regarded to introduce imaginary contributions to $\nu_{n'n}(\mathbf{k})$ and $g^{\alpha}_{n'n}(\mathbf{k})$. A presumably weak IR activity of the H_g phonons can therefore be expected in orientationally disordered A_3C_{60}.

The above conclusions regarding the phonon renormalization and the IR activity can be explicitly illustrated by the introduction into Eqs. (6) and (4) of the simpliciations $g^{\alpha}_{n'n}(\mathbf{k})=g_{\alpha}$, $\mathrm{Re}\mu_{n'n}(\mathbf{k})=\delta\mu$, where g_{α} and $\delta\mu$ are real constants independent of the labeling of the band states. The Dyson equation (5) may then be solved, resulting in the phonon contribution to $\sigma(\omega)$

$$\sigma_{\mathrm{ph}}(\omega)=-(i\omega/\Omega_0)N\delta\mu^{2}[F(\omega)^{2}/F(0)]\lambda D_{\mathrm{ph}}(\omega)\,. \tag{10}$$

Here, $D_{\mathrm{ph}}(\omega)$ is the composite phonon propagator satisfying $D_{\mathrm{ph}}(\omega)^{-1}=D_0(\omega)^{-1}-\lambda\tilde{F}(\omega)$ where

$$D_0(\omega)=\sum_{\alpha}(\lambda_{\alpha}\omega^{2}_{\alpha}/\lambda)\{\omega^{2}_{\alpha}/[\omega^{2}_{\alpha}-(\omega+i\delta)^{2}]\}\,, \tag{11}$$

$F(\omega)$ is the interband density-density response function defined in Eq. (9), and $\tilde{F}(\omega)=F(\omega)/F(0)$. The quantities $\lambda_{\alpha}=(2g^{2}_{\alpha}/\omega_{\alpha})F(0)$ denote the dimensionless interband electron-phonon coupling constants while $\lambda=\sum_{\alpha}\lambda_{\alpha}$. The frequencies Ω_m of the renormalized H_g phonons are given by the solution of $\mathrm{Re}D_{\mathrm{ph}}(\omega)^{-1}=0$. If only the coupling of the H_g phonons to the inter-t_{1u}-band excitations is considered in the Raman process, the Raman spectrum is proportional to $\lambda\,\mathrm{Im}D_{\mathrm{ph}}(\omega)$. This line shape is suppressed as $1/N(\Omega_m)$ in the region of Ω_m. On the other hand, Fano-like indentations in $\mathrm{Re}\sigma(\omega)$ arise from dominant (negative) contributions in $\sigma_{\mathrm{ph}}(\omega)$ which are proportional to $-N(\omega)^{2}\lambda\,\mathrm{Im}D_{\mathrm{ph}}(\omega)$. Thus, the renormalized H_g modes may be observed in the infrared spectrum. This situation would be similar to that which occurs for the A_g molecular vibrations of tetracyanoquinodimethane (TCNQ) in the semiconducting TCNQ charge-transfer salts.[12] We also note that since $\mathrm{Re}F(\omega)$ will be small when $N(\omega)$ is large the frequencies Ω_m of the renormalized phonons that are strongly damped will be only slightly shifted from their unrenormalized values.

Illustrative calculations of $\lambda\,\mathrm{Im}D_{\mathrm{ph}}(\omega)$ and $\mathrm{Re}\sigma(\omega)$

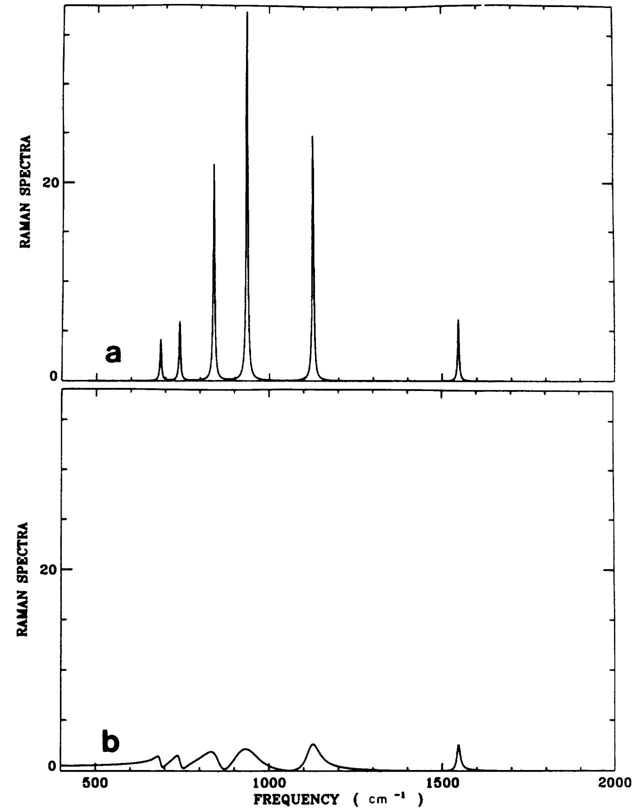

FIG. 1. H_g Raman spectrum (arbitrary units) calculated for (a) no coupling and (b) coupling to interband excitations.

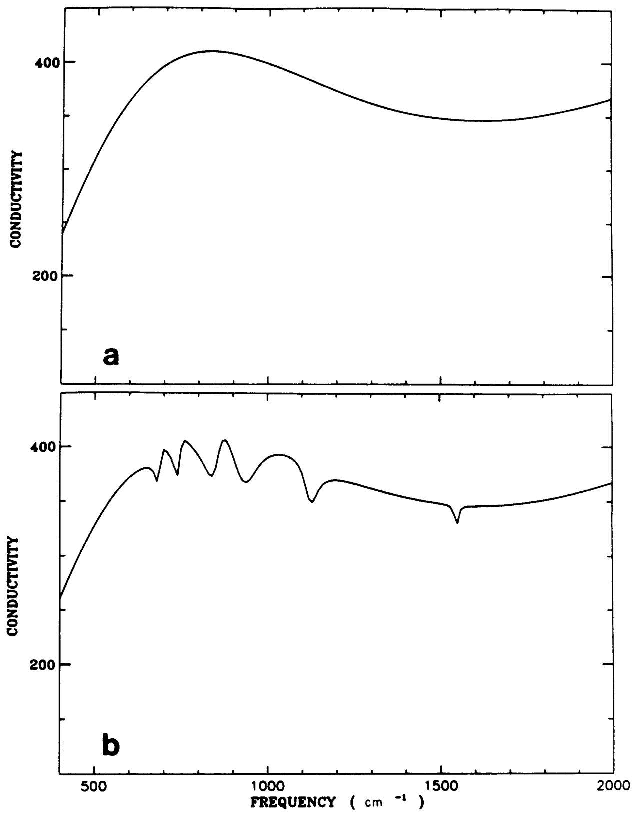

FIG. 2. Re$\sigma(\omega)$ vs ω (arbitrary units) calculated for (a) $\delta\mu=0$ and (b) $\delta\mu\neq0$.

(excluding the Drude contribution) as a function of ω are shown in Figs. 1 and 2, respectively. We have taken representative values[13] for the frequencies ω_α of the six highest-frequency $C_{60}H_g$ vibrations and assumed $\lambda_\alpha=0.1$ for all α. $\chi_e(\omega)$ is expressed simply as $\mu^2F(\omega)$ where μ is a constant interband transition dipole moment and $F(\omega)$ taken to be the sum of two broadened Lorentz oscillators centered at 780 and 3000 cm^{-1}, respectively. These model the inter-t_{1u}-band excitation continuum recently reported by Pichler, Matus, and Kuzmay[13] for K_3C_{60}. We have assumed the value $(\delta\mu/\mu)^2=0.1$.

A preliminary measurement of Re$\sigma(\omega)$ for Rb_3C_{60}, which reveals a broad absorption band centered at 0.1 eV with no vibrational features resolved, has been recently reported.[14] During the preparation of this paper, however, we have been informed of measurements[13] of Re$\sigma(\omega)$ for K_3C_{60}, which suggest that the Raman-active H_g-derived phonons may well be present in the IR spectrum in accordance with the discussion of this paper.

In conclusion, we note that our main results are straightforwardly generalized to the case that the "crystal" is composed of a periodic sequence of supercells each containing the same arbitrary number of merohedrally disordered C_{60} ions. When carried out numerically, this type of calculation, in principle, treats the problem of disorder exactly. The observation of the IR activity in the fullerides would provide the opportunity to use such calculations to deduce "experimental" values of the underlying H_g EMV coupling constants $g^{\alpha}_{\nu\nu'}$. We have made progress with calculations of this type and these will be presented in a forthcoming paper.[15,16]

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