# Phonons, electron-phonon and electron-plasmon coupling in $C_{60}$ compounds

V.P. Antropov,* O. Gunnarsson, and A.I. Liechtenstein
*Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart-80, Germany*
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We have performed *ab initio* calculations for the $A_g$ and $H_g$ intramolecular phonon frequencies, using a full-potential LMTO method. The deviation from experiment is typically 5 %. We have further calculated the electron-phonon coupling for these modes, as well as for some alkali and libration modes, using both tight-binding and *ab initio*, full potential LMTO methods. The tight-binding calculations illustrate that for the intramolecular modes the tedious Brillouin zone sums can be replaced by calculations for a free molecule, while for the libration modes a simplification of this type is not possible. The *ab initio* calculations show a strong coupling to the two highest and, to a lesser extent, to the second lowest $H_g$ intramolecular modes, while the coupling is weak to the librations and the studied alkali modes. The total coupling to the $H_g$ intramolecular modes is $\lambda = 0.068N(0)$, where N(0) is the density of states per eV, spin and ball, which corresponds to $\lambda \sim 0.6-0.7$ for the alkali doped $C_{60}$ compounds. The difference in coupling between superconductivity and photoemission, where the molecule is charged during the emission process, is studied for the $A_g$ modes. Furthermore, the electron-plasmon coupling is calculated in a tight-binding formalism. This coupling $(g/\omega_p)^2 \sim 1$ is found to be substantial. The calculated electron-phonon couplings are finally tested by calculating the superconductivity transition temperature using the Eliashberg equation and the temperature dependent resistivity. These calculations show that the calculated couplings are of the right order of magnitude, but probably somewhat small, and that the coupling to librations and intermolecular modes should be weak.

## I. INTRODUCTION

There is a substantial amount of evidence that phonons and electron-phonon interactions play an important role in $C_{60}$. In particular, the electron phonon-interaction provides a likely mechanism for the superconductivity in doped $C_{60}$ compounds.[1-4] However, the electron-phonon interaction also influences the electronic structure more generally. This is for instance seen in photoemission, where the coupling to phonons gives rise to important satellites,[5,6] which leads to a broadening of the photoemission spectrum seen in angular integrated photoemission. The electron-phonon coupling should, however, also modify the band structure, and it may, for instance, result in a reduced dispersion of the bands. Coupling to plasmons[6] and other many-body effects[7] may, however, also play an important role for the electronic structure.

There are several empirical phonon models,[8,9] where the parameters are adjusted to fit the experimentally observed phonon frequencies. While many of these models give good fits of the frequencies, it is less clear how good the eigenvectors are. Since the eigenvectors play an important role for the electron-phonon coupling, it is interesting to perform *ab initio* calculations, where the eigenvectors may be more reliable. Only a few *ab initio* phonon calculations have been performed so far.[10-12] One purpose of this paper is to present an *ab initio* calculation of the phonon frequencies based on the local density approximation (LDA)[13] and the linear-muffin-tin-orbital formalism (LMTO)[14] in the full-potential version of Methfessel.[15]

Doped $C_{60}$ compounds have several types of phonons. There are high energy phonons in the range 270-1600 $cm^{-1}$, which correspond to essentially intra molecular vibrations, and which have a small dispersion.[16,17] At substantially lower energies there are optical phonons of essentially alkali atom character, inter molecular, acoustical phonons of mainly $C_{60}$ character and $C_{60}$ librations. There have been several calculations of the electron-phonon interaction[1-3] for the intra molecular phonons. These calculations have been based on a semi-empirical (MNDO) formalism,[1] a tight-binding or an LDA calculation together with empirical phonon models[2] or a rigid-muffin-tin approximation together with an empirical phonon model.[3] In this paper we present *ab initio* calculations of the electron-phonon interaction for $K_3C_{60}$. We focus on the $C_{60}$ intra molecular phonons, which are usually believed to be most important for the value of the superconductivity transition temperature $T_c$.[1-3] However, it has also been argued that the alkali optical phonons provide the main coupling.[18] Finally, it has been argued that low energy phonons, e.g., librations, could be important for certain superconductivity properties, such as the reduced gap.[19] We therefore also consider the electron-phonon coupling for some alkali optical phonons and librations.

The calculation of the electron-phonon coupling $\lambda$ entering in superconductivity involves complicated Fermi surface integrals. For $C_{60}$, the inter molecular hopping $t_{inter}$ is much smaller than the intra molecular hopping $t_{intra}$. In the limit when $t_{inter}/t_{intra} \to 0$, it is possible to perform the Fermi surface integrals analytically.[2] We consider a simple tight-binding model where all the Fermi surface integrals can be carried out, even for $t_{inter}/t_{intra} > 0$, and compare the results with results for the limit $t_{inter}/t_{intra} \to 0$. We conclude that the accuracy of the assumption $t_{inter}/t_{intra} = 0$ is satisfactory for the doped $C_{60}$ compounds, and use this assumption in the *ab initio* calculations.

To calculate the $\lambda$ entering superconductivity, we consider how the excitation of a phonon shifts and couples the electronic levels, assuming that the system stays neutral. In photoemission, however, the system is ionized in the photoemission process. Thus the electron-phonon coupling in photoemission may not only be due to the fact that a certain level is depopulated, but also to the fact that the molecule is charged. We calculate how this influences the electron-phonon coupling for the $A_g$ modes.

In photoemission for doped, metallic $C_{60}$ compounds, there is also an important coupling to low-lying (0.5 eV) plasmons,[6] which essentially correspond to charge oscillations of the $t_{1u}$ electrons. We show how this coupling can be calculated, and present results for a tight-binding model.[4] The coupling strength is found to be substantial, $((g/\omega_p)^2 \sim 1)$.

As a test of the calculated coupling strengths, we have calculated the superconductivity transition temperature $T_c$ using the Eliashberg equations. Using earlier estimates of the Coulomb pseudopotential $\mu^* \sim 0.4$,[4] we find that our calculated coupling constants have to be increased by about 30 % to reproduce experimental values of $T_c$. Alternatively $\mu^*$ can be reduced to about 0.20 to 0.25. We have further calculated the temperature-dependence of the resistivity $\rho(T)$. We find that the calculated values of coupling constants are of the right order of magnitude, and can conclude that the coupling to the librations and inter molecular modes should not be very strong, in agreement with the calculations.

The details of the *ab initio* LMTO calculations are given in Sec. II and the phonon calculations in Sec. III. The tight-binding formalism is presented in Sec. IV. The results for the electron-phonon coupling for the intra molecular modes and the libration and alkali modes are given in Sec. V and VI, respectively. The difference between the coupling in superconductivity and photoemission is discussed in Sec. VII The electron-plasmon coupling is calculated in Sec. VIII. $T_c$ and $\rho(T)$ are calculated in Sec. IX, and we give some concluding remarks in Sec. X.

## II. LMTO-CALCULATIONS

$K_3C_{60}$ forms a fcc lattice with the K atoms on the octahedral and tetrahedral positions. The $C_{60}$ molecules have their three-fold axes along the (1,1,1) directions. This allows two possible orientations of the $C_{60}$ molecule, where the double bond with the largest $z$-coordinate is along the $x$-axis or along the $y$-axis, i.e., an $x$-oriented or $y$-oriented $C_{60}$ molecule. X-ray diffraction experiment have been interpreted to mean that both orientations occur randomly at room temperature.[20] It has recently been argued that at low temperatures, the orientations are ordered "anti-ferromagnetically" in two dimensions and disordered in the third dimension,[21] and that electronically, this structure is similar to a "bi-directional" structure,[22–24] with one x-oriented and one y-oriented $C_{60}$ molecule per unit cell. Here we for simplicity consider a fcc structure containing one $C_{60}$ molecule per cell with a fixed orientation (uni-directional), say x-oriented. The experimental lattice parameter $a$ = 14.24 Å was used. For the $C_{60}$ molecule the bond lengths measured for undoped $C_{60}$[25] have been used, i. e., $b_h$=1.391 Å for the double bond and $b_p$=1.455 Å for the single bond.

The *ab initio* calculations have been performed using the linear-muffin-tin method[14] in the full potential version of Methfessel.[15] Thus there are no assumptions about the shape of the potential. This method has been shown to be an efficient and accurate method for calculating the band structure, total energies, structural properties and phonon frequencies.[15,26] In this method all atoms are surrounded by spheres and additional interstitial spheres are added in large empty regions. A basis set is constructed, where the basis functions are derived from the solutions of the radial Schrödinger equation inside the spheres, and joined continuously and differentiably to tails obtained from Hankel functions outside the spheres. The C atoms were surrounded by 60 spheres with the radii 1.21 Å. On the octahedral (one sphere per cell with the radius 3.25 Å) and tetrahedral (two spheres per unit cell with radii 2.8 Å) sites further spheres were introduced. 8 additional spheres (radii 2.7 Å) were added between the tetrahedral and octahedral spheres. A large (radius 3.3 Å) sphere was put in the center of the $C_{60}$ molecule. Smaller spheres (1.4 Å) were introduced in two shells inside and outside the C atoms and located above and below the pentagons and hexagons, except above the hexagons in the (1,1,1)-directions, which would have led to an overlap with the tetrahedral spheres. The spheres are chosen so that they do not overlap for the distortions considered in the frozen phonon calculations. For the doped compounds, the alkali atoms are located in the tetrahedral and octahedral spheres. The total number of spheres is 128. For all spheres containing (carbon or alkali) atoms, basis functions with $l$ = 0 and 1 were constructed, while for the empty spheres only $l$ = 0 functions were included. For each $l$ quantum number two basis functions were used with tails corresponding to the kinetic energies $\kappa^2$ =-0.4 Ryd and -1.2 Ryd, respectively, except on the central sphere where a third basis state with $\kappa^2 = -2.3$ Ryd was added. As a test, basis functions with $\kappa^2 = -0.7$ Ryd and -1.5 Ryd were also considered. This led to a change of the energy of the $H_g(8)$ by 45 cm$^{-1}$. The inclusion of a third set of basis states with $\kappa^2 = -2.3$ Ryd, in addition to $\kappa^2 = -0.4$ Ryd and -1.2 Ryd, lead to a change of the energy of the $H_g(8)$ phonon by 40 cm$^{-1}$. The calculations used 5 **k**-points in the irreducible Brillouin zone together with the tetrahedron method. Increasing the number of **k**-points to 18, changed the frequency of the $H_g(8)$ phonon by about 30 cm$^{-1}$. To calculate the electrostatic potential, the charge density is fitted by functions centered in the spheres.[15]

We used functions with $l = 0, 1, 2, 3$ in the carbon, octahedral and tetrahedral spheres and $l = 0, 1$ in the other spheres. Including also $l = 4$ functions in the spheres containing atoms increased the frequency of the $H_g(8)$ phonon by 35 $cm^{-1}$. These tests suggest that the calculations are reasonably well converged. Further details about the calculations are published elsewhere.[24]

As discussed in the introduction, for the calculation of the electron-phonon interaction, one needs the splitting of the $t_{1u}$ levels for a molecule which has been disconnected from its surrounding, i.e., in the limit $t_{inter} = 0$. Thus we perform a self-consistent calculation for $K_3C_{60}$ with $C_{60}$ distorted by a phonon eigenvector. In the last iteration the bulk structure constants are then replaced by the structure constants calculated in real space for a free $C_{60}$ molecule, including all the empty spheres which can be assigned uniquely to a given molecule. Thus the $C_{60}$ self-consistent potential is obtained for bulk $K_3C_{60}$, but the splittings are calculated for molecule without hopping to the surrounding. Since the potential derived from the solid state calculation has a lower symmetry than the icosahedral symmetry there are three inequivalent carbon spheres. The potentials of these different spheres are averaged to essentially restore the icosahedral symmetry. In these "molecular" calculations, the basis functions have rather long-ranged tails sticking out in the vacuum region, with a kinetic energy which is less appropriate for this region. This reduces the accuracy of the calculation, and may for instance lead to states with an incorrect spatial extent. In these calculations, we are, however, only interested in the splitting of the $t_{1u}$ level. The errors due to the long-ranged tails cannot induce such a splitting, and can therefore only influence the splitting indirectly. Below (Table III) this calculation is referred to as FP (full potential).

As a further check, we have also performed calculations with a large number of empty spheres, arranged in two "shells" outside the $C_{60}$ molecule. The arrangement of these empty spheres has been described in detail elsewhere[7]. The additional shell allows for a better description of the vaccum region, and the behavior of the tails outside the outermost shell becomes less important. In this latter calculation we have used the atomic-sphere-approximation (ASA). This calculation is referred to as ASA in Table III.

As discussed in the introduction, we also consider the electron-phonon coupling for the $A_g$ modes appropriate for photoemission. As shown below (Sec. VII) we need to calculate the change of the bond lengths of a $C_{60}$ molecule when an electron is removed. Since we have to consider a charged molecule, it is not possible to periodically repeat the molecule. As in the previous paragraph, we consider a free molecule, with two shells of empty spheres outside the $C_{60}$ molecule.[7] Since the ASA may not be sufficiently accurate for the calculation of total energies, needed to determine the bond lengths, we have in Sec. VII used a more accurate approach. Thus the ASA was first iterated to self-consistency. The total energy was then calculated without shape approximations for the charge or potential. Finally the lengths of the single and double bonds were varied until the energy was minimized.

## III. PHONON CALCULATION

The 60 C atoms in $C_{60}$ give rise to 3*60-6=174 modes. Of these modes, the $t_{1u}$ level only couples to modes with $A_g$ and $H_g$ symmetry.[2] There are two modes of $A_g$ symmetry and eight, five-fold degenerate modes of $H_g$ symmetry. For the doped compounds, in addition to these pure $C_{60}$ intra molecular modes, there are also modes involving the alkali atoms. These modes mix with the pure $C_{60}$ modes, but since they have a much lower energy than the $C_{60}$ intra molecular modes, we neglect this coupling.

To calculate the phonon frequencies, we need a complete basis set of atomic displacements of $A_g$ and $H_g$ symmetry. These basis states were obtained by solving the dynamical matrix corresponding to the force constant model of Wu et al,[9] using the parameters suggested by Weeks and Harter.[9] Among the solutions, we identified the 2 modes of $A_g$ symmetry and 40 modes of $H_g$ symmetry, which provide a complete basis set for the $A_g$ and $H_g$ modes, respectively. The basis states for the $H_g$ modes are, however, arbitrary mixtures of the five degenerate modes of a given energy. To obtain convenient linear combinations, we have calculated the electron-phonon coupling matrix elements between the $t_{1u}$ orbitals, using the TB-formalism described below. We then required that for a free molecule, the matrices should have simple forms,[27] where the matrices corresponding to two modes are diagonal, and the matrices corresponding to the other modes have only two nonzero off diagonal elements. In particular, the matrix corresponding to the $\theta$-mode is a diagonal matrix with the diagonal matrix elements -$\delta\epsilon$, -$\delta\epsilon$ and $2\delta\epsilon$. Due to the small dispersion of these phonons,[16,17] we can focus on $\mathbf{q} = 0$. In the solid there is also a small splitting of a few $cm^{-1}$ of the $H_g$ modes,[16] which is neglected here.

For the $H_g$ modes we obtain distortions $e^0_{\nu\tau}(i,k)$, where $\nu$ labels the eight sets $H_g$ modes and $\tau$ the five degenerate modes (partner functions). For such a mode the $k$th coordinate of the $i$th atom is displaced by $e^0_{\nu\tau}(i,k)$. The distortions are normalized as $\sum_{i=1}^{60}\sum_{k=1}^{3}|e^0_{\nu\tau}(i,k)|^2 = 1$. Because of symmetry, we only need to consider $\tau$= 1, i.e., the $\theta$-mode. We then perform calculations of the change in the total energy due to the 8 "diagonal" displacements $\gamma e^0_{\nu\tau}(i,k)$ and due to the 28 "non diagonal" distortions $\frac{1}{2}\gamma(e^0_{\nu\tau}(i,k) + e^0_{\nu'\tau}(i,k))$, where $\gamma$ is some appropriate constant. The corresponding energy changes are then expressed as

$$\Delta E = \frac{1}{2}\sum_{\nu=1}^{8}\sum_{\nu'=1}^{8} A_{\nu\nu'}\gamma_{\nu\tau}\gamma_{\nu'\tau} \tag{1}$$

where $\gamma_{\nu\tau}$ refers to the magnitude of the distortion $e^0_{\nu\tau}$. The eigenvalues, $M\omega_\nu^2$, and eigenvectors, $c$, of $A$ are then obtained, where $\omega_\nu$ is the phonon frequency. In the calculations, we use distortions which are small enough to ensure that $\Delta E$ is quadratic and the splitting of the band at the $\Gamma$-point is linear in the displacement. Within this constraint, the displacements were chosen as large as possible to increase the numerical accuracy. Depending on the mode, we have found it convenient to use distortions of the order $\gamma_{\nu\tau}$ ~0.07-0.28 Å. The coefficients $A_{\nu\nu'}$ were then obtained from a least square fit to the (harmonic) terms in Eq. (1), using distortions of different magnitudes.

The results for the frequencies for $K_3C_{60}$ are shown in Table I, and compared with the results of two other *ab initio* calculations for undoped $C_{60}$ by Adams et al[10] and by Kohanoff et al[11] and by experimental results by Zhou et al[28] for $K_3C_{60}$, by Mitch et al[29] for $Rb_3C_{60}$ and by Bethune et al,[30] (in parentheses) for undoped $C_{60}$. For the doped compounds several frequencies were not observed. Our results agree with experiment to within typically 5 %. For the two highest $H_g$ modes our energies are somewhat to low, as in the calculation of Adams et al,[10] while the results of Kohanoff et al[11] are a bit too high. For the lower $H_g$ modes our energies are generally somewhat too high.

Table I also shows the radial character of the phonons. The lowest three phonons have primarily radial character, with a substantial tangential character mixed in, while the five highest phonons have mainly tangential character. The two highest phonons are almost purely tangential.

The results for the new phonon displacements $e_{\nu\tau}$

$$e_{\nu\tau}=\sum_{\nu'=1}^{8} c_{\nu\nu'}e^0_{\nu'\tau} \tag{2}$$

are expressed in terms of the displacements $e^0_{\nu\tau}$ of the Wu model[9] and the coefficients $c_{\nu\nu'}$, given in Table II. We can see that our $H_g$ eigenvectors differ substantially from the eigenvectors in the model of Wu et al.[9] The $A_g(1)$ eigenvector contains 0.975 of the Wu $A_g(1)$ and -0.224 of the Wu $A_g(2)$ eigenvectors. The $A_g(2)$ eigenvector is given by orthogonality.

## IV. TIGHT-BINDING CALCULATIONS AND ELECTRON-PHONON INTERACTION

The information about the electron-phonon coupling is contained in the matrix elements between states $|n\mathbf{k}>$ with a band index $n$ and a wave vector $\mathbf{k}$

$$g_{n\mathbf{k},m(\mathbf{k}+\mathbf{q})}(\nu)=<n\mathbf{k}|\Delta V_{\nu\mathbf{q}}|m(\mathbf{k}+\mathbf{q})>\frac{1}{\sqrt{2M\omega_{\nu\mathbf{q}}}} \tag{3}$$

where

$$\Delta V_{\nu\mathbf{q}}(\mathbf{r})=\sum_{ik}E_{\nu\mathbf{q}}(i,k)\frac{\partial V(\mathbf{r})}{\partial R_{i,k}} \tag{4}$$

is the change in the potential $V(\mathbf{r})$ due to a phonon with band index $\nu$ and wave vector $\mathbf{q}$ and $1/\sqrt{2M\omega_{\nu\mathbf{q}}}$ is the amplitude of the phonon vibration. Here $M$ is the mass of a carbon atom and $\omega_{\nu\mathbf{q}}$ is the phonon frequency. The sum over $i$ runs over all atoms, the sum over $k$ over the three Cartesian coordinates, and $E_{\nu\mathbf{q}}(i,k)$ is the phonon eigenvector, which gives the displacements of the different atoms, and which is normalized to the whole system. We have dropped the partner index $\tau$, since we will only consider the $\theta$-mode ($\tau=1$). The electron-phonon coupling $\lambda$ entering in superconductivity is then given by[47]

$$\lambda=\frac{2}{N(0)}\sum_{\nu\mathbf{q}}\frac{1}{\omega_{\nu\mathbf{q}}}\sum_{n,m,\mathbf{k}}|g_{n\mathbf{k},m(\mathbf{k}+\mathbf{q})}(\nu)|^2$$
$$\times\,\delta(\epsilon_{n\mathbf{k}})\delta(\epsilon_{m(\mathbf{k}+\mathbf{q})}-\epsilon_{n\mathbf{k}}-\omega_{\nu\mathbf{q}}). \tag{5}$$

We first want to illustrate how the calculation of $\lambda$ is simplified for $t_{inter}/t_{intra}=0$.[2,27] We further assume that the phonon frequencies and eigenvectors are independent of $\mathbf{q}$, which should be a good approximation for $C_{60}$.[16,17] We write the states $|n\mathbf{k}>$ as

$$|n\mathbf{k}>=\sum_\alpha c_\alpha(n\mathbf{k})|\alpha\mathbf{k}> \tag{6}$$

where $|\alpha\mathbf{k}>$ is a Bloch sum over the molecular orbital $|\alpha>$ of a free $C_{60}$ molecule. We introduce

$$g_{\alpha\alpha'}(\nu)=<\alpha\mathbf{k}|\Delta V_{\nu\mathbf{q}}|\alpha'(\mathbf{k}+\mathbf{q})>\frac{1}{\sqrt{2M\omega_{\nu\mathbf{q}}}} \tag{7}$$

where we have assumed[27] that $g_{\alpha\alpha'}$ is independent of $\mathbf{k}$ and $\mathbf{q}$, as follows for the assumptions introduced above. If Eq. (3,6,7) are inserted in Eq. (5), the sums over $\mathbf{k}$ and $\mathbf{k}'=\mathbf{k}+\mathbf{q}$ become independent and can be trivially carried out. This leads to

$$\lambda=\frac{2}{N(0)}\sum_\nu\frac{1}{\omega_\nu}$$
$$\times\sum_{\alpha\alpha'}\sum_{\alpha_1\alpha_2}\rho_{\alpha\alpha_1}(0)g_{\alpha\alpha'}(\nu)\rho_{\alpha'\alpha_2}(0)g_{\alpha_1\alpha_2}(\nu) \tag{8}$$

where

$$\rho_{\alpha\alpha'}(0)=\sum_{n\mathbf{k}}c^*_\alpha(n\mathbf{k})c_{\alpha'}(n\mathbf{k})\delta(\epsilon_{n\mathbf{k}}) \tag{9}$$

is a density of states matrix at the Fermi energy (= 0). In Eq. (8) and in the following, we assume that the phonon energy is small compared with the electronic energy scale and use the energy argument 0 for $\rho$. This assumption is not essential for the present argument, but it ought to be reconsidered in actual calculations of $\lambda$. If we only consider indices $\alpha$ corresponding to the $t_{1u}$ orbital, the partial density of states matrix is diagonal and $\rho_{\alpha\alpha}(0)=N(0)/3$. Then one obtains[2]

$$\lambda = \frac{2}{9}N(0)\sum_\nu \frac{1}{\omega_\nu}\mathrm{Tr}\ g(\nu)g^\dagger(\nu) \equiv \sum_\nu \lambda_\nu \tag{10}$$

Here Tr $g(\nu)g(\nu)$ is independent of the partner index of the mode. For the $\theta$-mode, where the displacements of the $t_{1u}$ levels is -$\delta\epsilon$, $-\delta\epsilon$ and $2\delta\epsilon$, respectively, the Tr gives $6\delta\epsilon^2$.

We now consider the effects of the approximation in Eq. (7), namely that $g_{\alpha\alpha'}(\nu)$ is independent of $\mathbf{q}$, which follows if we neglect the hopping of the electrons between the $C_{60}$ molecules and the $\mathbf{q}$-dependence of the phonon eigenvectors. Here we restore the $\mathbf{q}$-dependence of $g_{\alpha\alpha'}(\nu)$ by including the hopping between the molecules. We still assume, however, that the forces between the molecules are sufficiently weak to allow us to neglect the dispersion of the phonons and the $\mathbf{q}-$dependence of the corresponding eigenvectors, which is supported by experiment.[16,17] We study a tight-binding (TB) model[22] of $C_{60}$,which is sufficiently simple to allow us to perform all the Fermi surface integrals without assuming that $g$ is $\mathbf{q}$-independent. The TB-model has one 2p-orbital per C atom, pointing radially out from the $C_{60}$ molecule. These p-orbitals provide the essential contributions to the states close to the Fermi energy, which are the important ones in this context. The parameters of the TB-representation are obtained from our earlier work.[22,23]

We can then assume that the distortions $E$ and $e$ (referring to $\mathbf{q}=0$ and normalized to one molecule) are related as

$$E_{\nu\mathbf{q}}(j\gamma,k) = \frac{1}{\sqrt{N}}e_{\nu 1}(j,k)e^{i\mathbf{q}\cdot\mathbf{R}_\gamma}, \tag{11}$$

where $\mathbf{R}_\gamma$ gives the position of the molecule $\gamma$ and $j$ refers to an atom in a $C_{60}$ molecule with the position $\mathbf{R}_j$ relative to the center of the molecule. We now calculate the changes of the electronic Hamiltonian matrix $H_{j\gamma,l\mu}$ due to a phonon $E_{\nu\mathbf{q}}$, where $H_{j\gamma,l\mu}$ is the matrix element of the Hamiltonian between the functions on the atoms labeled by $j\gamma$ and $l\mu$. We introduce

$$\Delta H_{j\gamma,l\mu,k} = \frac{\partial}{\partial R_{j\gamma,k}}H_{j\gamma,l\mu} \tag{12}$$

If we keep the radial p-orbital fixed as the atoms are moved, it follows that $\partial H_{j\gamma,l\mu}/\partial R_{l\mu,k} = -\Delta H_{j\gamma,l\mu,k}$. We can then calculate the coupling constants as

$$g_{n\mathbf{k},m(\mathbf{k+q})}(\nu) = \sum_\mu\sum_{jl} c_j^*(n\mathbf{k})c_l[m(\mathbf{k}+\mathbf{q})]$$
$$\times\sum_k \Delta H_{j0,l\mu,k}[e_{\nu 1}(j,k)e^{i\mathbf{k}\cdot\mathbf{R}_\mu} - e_{\nu 1}(l,k)e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}_\mu}] \tag{13}$$

Here $\mu$ includes a sum over both an on-site term ($\mathbf{R}_\mu = 0$) and the nearest neighbors, while more distant neighbors give a negligible contribution. We are now in the position of performing the calculations in Eq. (5). The $\delta$-functions are replaced by Gaussians

$$\delta(\epsilon) \rightarrow \frac{1}{\Delta\sqrt{\pi}}e^{-\epsilon^2/\Delta^2} \tag{14}$$

where we have used $\Delta = 0.0125$ eV. We have used 1000 $\mathbf{k}$-points per Brillouin zone. The phonon eigenvectors obtained from the *ab initio* calculation were used.

## V. RESULTS FOR THE ELECTRON-PHONON INTERACTION FOR INTRA-MOLECULAR PHONONS

The results for the electron-phonon interaction are shown in Table III for the different modes of $H_g$ symmetry. All results have been multiplied by a factor 5 to take into account the degeneracy of the $H_g$ mode. We first show TB results (Bz) performing the full Brillouin zone summations. These results are compared with results (Free mol) where the couplings between the molecules have been broken. The two columns show generally good agreement, with the deviations being typically only a few per cent for modes with a strong coupling. The relative errors for the two lowest modes are larger, but still rather small in absolute values. These results therefore suggest that it should not be necessary to perform the Brillouin zone integration in the LMTO calculation, and that the assumption $t_{inter}/t_{intra} << 1$ is indeed a good approximation.

It is interesting to ask if it is possible to consider some representative point in the Brillouin zone for the solid, and from the splitting at this point determine the value of $\lambda$. Such a procedure may include effects of having a solid instead of a free molecule, in particular that the inter molecular hopping matrix elements are changed when a phonon is introduced, but also that the inter molecular hopping mixes in other orbitals than the $t_{1u}$ orbital. It is then natural to consider the $\Gamma$-point, for which the $t_{1u}$ level is not split in the absence of phonons. For the free molecule the coupling can either be expressed in terms of the splitting or the second moment of the $t_{1u}$ levels for a $\theta$-mode. In the solid the splittings at the $\Gamma$-point are not of the simple type -$\delta\epsilon$, -$\delta\epsilon$, $2\delta\epsilon$, obtained for a molecule, and the two approaches give different results, as can be seen from the two columns "Split" and "Secm". "Secm" gives more accurate results than "Split" as a comparison with "Bz" shows, and for all the higher modes "Secm" is almost as accurate as "Free mol". For the two lowest modes, however, "Secm" misrepresents the relative strength of the coupling in this TB model, although the total coupling is fairly accurately reproduced. The reason is that the solid state corrections may enter with different signs in different parts of the Brillouin zone, and the $\Gamma$-point then presumably misrepresents these effects. We notice that "Secm" is worse for the modes with a large radial character, where the changes of the inter molecular matrix elements are more important. The rather accurate results in the column "Free molecule" indicate that even in these cases, however, the solid state effects average out to a large extent and that the intra molecular effects, described by the calculation for the free molecule, tend to dominate the results.

Next, we compare with the results from the LMTO calculation. There are substantial differences in the magnitudes between the TB and LMTO results, although the trends are similar. The size of the deviations may be somewhat surprising in view of the excellent agreement for the band structure.[23] In the present case we are, however, interested in *changes* due to displacements of atoms, which puts stronger requirements on the parameterization. We have also considered the parameterization of Tomanek and Schluter,[32] which includes 4 basis states (2s and 2p) per atom instead of the approach here, which only includes one ("radial" 2p) function per atom. This parameterization gives an appreciable improvement, but is still not in very satisfactory agreement with the LMTO-calculation. This was also found by Schluter et al,[2] who noticed that a change of the distance-dependence in the original parameterization gave a better representation of the LDA results for the electron-phonon interaction.

For the LMTO calculations, we show results for a free molecule, using the ASA and the full-potential (FP) methods as described in Sec. II. We can see that the two calculations are in quite satisfactory agreement. We also compare with the results obtained from a bulk calculation, using the eigenvalues at the $\Gamma$-point ("Split" and "Secm"). These calculations are in good agreement with the calculations for a free molecule for the uppermost modes, while for the lower modes the agreement is not quite so good. This agrees with the experience from the TB-calculations.

The total $\lambda$ is obtained by adding the different contribution in Table III and for the FP molecular calculation it is given by $\lambda = 0.068N(0)$, where $N(0)$ is the density of states per eV, spin and $C_{60}$. This can be compared with the results $0.056N(0)$ by Varma et al,[1] $0.052N(0)$ and $0.040N(0)$ by Schluter et al,[2] based on their LDA and tight-binding calculations, respectively, together with a bond charge model for the phonons and $0.037N(0)$ by Mazin et al.[3] We have also calculated the Hopfield factor,[33] which separates out the electronic contribution from the phonon contribution. We find the results $\eta$=4.8$N(0)$ eV/Å, where $N(0)$ as usual is expressed in states per eV, spin and $C_{60}$. From the calculations of Varma et al,[1] Schluter et al[2] and Mazin et al[3] we deduce the results $4.6N(0)$, $3.0N(0)$ and $1.5N(0)$, respectively, where we have again used the Schluter et al LDA calculation, and assumed that their $\lambda$ was calculated using the calculated phonon frequencies. Although we might have expected that the Hopfield factors would differ less between the different theories, since the use of different phonon models should play no role any more, we actually find a larger difference. This suggest an appreciable uncertainty in the calculated electron-phonon interaction.

We next consider the partial contributions, $\lambda_\nu$, from different modes to $\lambda$. We first notice that the *distribution* of coupling strength between the different modes, depends sensitively on the phonon eigenvectors, while the total coupling is less sensitive. This is illustrated by the following considerations. Let the shift of the $t_{1u}$ level $\alpha$ at the $\Gamma$-point be $\Delta\epsilon_{\nu\alpha}$ for the distortion $\gamma e_{\nu\tau}$. The corresponding contribution to $\lambda_\nu$ is then proportional to $(\Delta\epsilon_{\nu\alpha}/\omega_\nu)^2$ according to Eqs. (7,10). Let us now assume that the exact modes $e_{\nu\tau}^{\rm exact}$ can be written as the linear combinations

$$e_{\nu\tau}^{\rm exact} = \sum_{\nu'=1}^{8} c_{\nu\nu'}^{\rm exact} e_{\nu'\tau} \tag{15}$$

of the calculated ones $e_{\nu\tau}$. The new shifts $\Delta\epsilon_{\nu\alpha}^{\rm exact}$ can then be written as

$$\Delta\epsilon_{\nu\alpha}^{\rm exact} = \sum_{\nu'=1}^{8} c_{\nu\nu'}^{\rm exact} \Delta\epsilon_{\nu\alpha'} \tag{16}$$

It then immediately follows that $\sum_{\nu\alpha}(\Delta\epsilon_{\nu\alpha}^{\rm exact})^2 = \sum_{\nu\alpha}(\Delta\epsilon_{\nu\alpha})^2$. Thus the mixing of modes only redistributes the total quadratic shifts between the modes without changing its magnitude. To obtain $\lambda$ we have to divide by the $\omega_\nu^2$. Moving shifts towards higher modes then means a reduction of $\lambda$, but this effect is moderate. On the other hand the redistribution of weight can be very large. Let us assume, for instance, that the two highest eigenvectors should have had a 5 % mixing

$$e_{7\tau}^{\rm exact} = \sqrt{0.95}e_{7\tau} - \sqrt{0.05}e_{8\tau} \tag{17}$$

$$e_{8\tau}^{\rm exact} = \sqrt{0.05}e_{7\tau} + \sqrt{0.95}e_{8\tau} \tag{18}$$

Then we would obtain the values 0.010 and 0.030 eV for $\lambda_7/N(0)$ and $\lambda_8/N(0)$, respectively, instead of the present results 0.020 and 0.022 eV using the FP Mol results. We can see that this would lead to a very strong redistribution of the couplings, but have practically no effect on the total value of $\lambda$.

In Table IV we show results of different groups for the partial coupling constants $\lambda_\nu/N(0)$, compared with our FP Mol results. We can see that our calculation is similar to the one of Varma et al[1], which also emphasized the coupling to the two highest modes, although their distribution of weight between these two modes is quite different and they also had less coupling to the low-lying modes. Although Mazin et al[3] did not calculate the coupling to the individual modes, they emphasized the coupling to tangential modes. This appears to be consistent with our results, although the relatively small tangential character of the low-lying modes could be sufficient to also give a strong coupling to these modes.

The relative coupling strengths for the different modes can be compared with Raman data for undoped and doped $C_{60}$ compounds.[28,29] For the doped compounds, the Raman lines obtain an additional broadening due to the electron-phonon coupling, which allows a phonon to decay via the excitation of an electron-hole pair. For a periodic system, the intra molecular phonons could only decay via inter band transitions in Raman scattering due to **q**-conservation. Due to disorder and the small thickness[29] of the sample, such selection rules should not be valid for the actual experimental situation. The experimental broadenings suggest that the coupling to the high-lying modes is primarily to the 7th and 8th mode, and that the coupling to the 8th mode is the strongest. The coupling to the low-lying modes should primarily be to the second mode and, to a smaller extent, the third mode. These results seem to be in qualitative agreement with our results, although the coupling to the 8th mode probably is even stronger than in our calculation. Neutron scattering[17] also suggests a stronger coupling to the second mode than to the other low-lying modes, while the large broadening for the higher modes makes it hard to determine the relative coupling for these modes.

In the calculation of the $\lambda$ entering superconductivity, we have *not* included the contribution from the $A_g$ modes. The reason is that the $A_g$ modes cause a shift but not splitting of the $t_{1u}$ level.[2] Such a shift should be effectively screened by a transfer of charge from the molecules where the levels are shifted upwards to the molecules where the levels are shifted downwards. In a calculation for phonons with $\mathbf{q} \neq 0$, this would automatically be included, while the screening does not show up in our $\mathbf{q} = 0$ calculation. For $\mathbf{q} = 0$, the shift instead leads to a shift of the Fermi level, and since the shift should be counted relative to the Fermi level,[35] there is little contribution even for $\mathbf{q} = 0$.

## VI. RESULTS FOR THE ELECTRON-PHONON INTERACTION FOR LIBRATIONS AND ALKALI PHONONS

We next consider the electron-phonon coupling for the librations. With one molecule per unit cell, there are three modes. We have considered the three independent but equivalent rotations around the x-, y- and z-axes. The true modes are linear combinations of these rotations. According to the arguments in Sec. V it follows, however, that in the linear regime, the quadratic shifts of the $t_{1u}$ eigenvalues summed over the three modes is the same as for the rotations around the x-, y- and z-axes. To obtain the electron-phonon couplings we have to divide the quadratic shifts for each mode by the corresponding frequency squared. If, however, we can neglect the spread of the libration energies around the average energy ($\hbar\omega_l \sim$4 meV $\approx$ 32 cm$-1^{36}$), we do not need to know the distribution of quadratic shifts between the different modes. According to the sum rule, it is then sufficient to know the shifts for the rotations around the Cartesian axes.

We consider a libration at the $\Gamma$-point, and perform an *ab initio* calculation, where the molecule is rotated by $\pi/100 \sim 2^\circ$ around a Cartesian axis. Tight-binding (TB) calculations with one "radial" p-orbital per carbon atom indicate that nonlinear coupling may enhance the splitting by a factor 1.5 for such an angle, but a smaller angle would have caused too large numerical uncertainties. The *ab initio* calculation gives a splitting of 0.007 eV, or 0.2 eV per rad, with one eigenvalue lying in the middle between the two extremes. Performing the same calculation within the TB formalism gives a splitting which is three to four times larger.

We now estimate the electron-phonon coupling in the same approximation as used above for the intra molecular phonons, i.e., we neglect all dispersional effects on the librations and we only use the results for the $t_{1u}$ level at the $\Gamma$-point. The $C_{60}$ molecule is treated as a spherical shell, which has the moment of inertia around an arbitrary axis, $I_{ii} = 40MR^2$, where $M$ is the mass of a carbon atom and $R$ is the radius of a $C_{60}$ molecule. Treating the librations as simple oscillations around a given axis, we derive the total contribution from the three modes

$$\lambda_l = \frac{1}{3}\frac{\hbar^2}{I_{ii}}N(0)\sum_\alpha(\frac{\delta\epsilon_\alpha}{\hbar\omega_l})^2 \tag{19}$$

where $\delta\epsilon_\alpha$ are the shifts of the $t_{1u}$ levels. We then obtain $\lambda_l = 0.0003N(0)$ per eV, spin and molecule for the librational contribution to $\lambda$.

We note, however, that there is no reason to expect the results for the $\Gamma$ point to be an accurate representation for the whole Brillouin zone. For the intra molecular phonons this result followed since the displacements of the atoms primarily result in a change of the intra molecular hopping matrix elements, and therefore the calculation of the electron-phonon coupling is primarily a molecular problem. Here the molecules are rotated rigidly, with no change of the intra molecular hopping matrix elements, and the whole effect results from the inter molecular hopping.

We have therefore performed tight-binding calculations, using one "radial" p-orbital per atom, as above. The libration dispersion was neglected and the libration eigenvectors were assumed to be **q**-independent. As before we can then perform the Brillouin zone sums. We find that the coupling is about a factor of four larger than what is obtained from the second moment of the splittings at the $\Gamma$-point. If the same factor would apply also to the *ab initio* calculation, this would imply that $\lambda_l = 0.0012N(0)$ per eV, spin and molecule. With values of $N(0)$ of the order 10 states per eV, spin and molecule, this gives a value of $\lambda_l$ of the order 0.01, i.e., very small. In the TB calculation, the splitting at the $\Gamma$-point is about a factor three to four larger than in the *ab initio* calculation, giving $\lambda_l \sim 0.1$ in the TB-calculation, which is still rather small. Probably, however, the *ab initio* calculation is more reliable. We notice that based on neutron scattering measurements,[36] it has been argued that $\lambda_l < 0.08$, which is consistent with our results.

Finally, we recall that for a rotation of $2^\circ$, which is of a magnitude relevant for a system well below the temperature where the molecules start to rotate freely, the nonlinear splitting is 1.5 times the linear splitting in the tight-binding calculation. Given that the coupling is proportional to the splitting squared, this suggests an appreciable nonlinear coupling.

The alkali optical phonons have been proposed as a source of the attractive interaction in doped $C_{60}$ compounds.[18] Later experimental results have shown that $T_c$, for a fixed lattice parameter, shows no detectable dependence on the mass of the alkali atom,[34] suggesting a small contribution of the alkali modes to $T_c$. For a symmetric mode, where some or all alkali atoms around a certain $C_{60}$ molecule move towards this molecule, this result has been rationalized in terms of the effective metallic screening in doped $C_{60}$.[4] Thus, if an electron is removed from a $C_{60}$ molecule, charge from the surrounding molecules move in to screen the created hole. Within the random phase approximation (RPA), it has been estimated that this reduces the coupling to symmetric alkali modes by almost two orders of magnitude.[4] Without this screening the coupling should have been strong,[18] and even with screening it may not be completely negligible. We note furthermore, that this efficient screening refers to low energy phenomena. It remains an interesting question if symmetric alkali modes play a role in, for instance, the photoemission spectrum away from the threshold, where the screening may be inefficient.

The arguments above referred to a symmetric mode where alkali atoms move in such a way that the angular averaged potential on a $C_{60}$ molecule is changed and the metallic screening is efficient. For a mode for which the angular averaged potential on a $C_{60}$ molecule is unchanged, the metallic screening should be much less efficient. The question is if such a mode may couple more strongly.

In the unit cell there are two alkali atoms at the positions (±1/4,±1/4,±1/4) (in addition to the atom at (1/2,0,0)). We now consider the mode where these two atoms move towards the $C_{60}$ molecule. A given $C_{60}$ molecule has in addition 6 equivalent nearest neighbor alkali atoms belonging to different unit cells. These atoms move in such a way that for a $\mathbf{q}=0$ phonon the change in the angular averaged potential is zero. As a preliminary calculation, we have considered the tight-binding model used above with one "radial" p-orbital per C atom together with point charges representing the alkali atoms. We only consider the potential from the nearest neighbor alkali atoms, allow for no screening and consider a $\mathbf{q}=0$ phonon. Assuming that all $\mathbf{q}$ give the same contribution and putting the alkali phonon energy to $\sim$0.013 eV,[17] we estimate that $\lambda = 0.004N(0)$ per eV, spin and $C_{60}$, i.e., a small contribution, although not quite negligible if we take into account that there are several modes of this type. We have then performed a full LMTO calculation for the same mode. There is then an additional substantial reduction of the coupling, so that the contribution to $\lambda$ is essentially zero, also for this mode.

## VII. ELECTRON-PHONON INTERACTION IN PHOTOEMISSION

In photoemission, the coupling to the phonons leads to a series of satellites at -$\omega_\nu$, -2$\omega_\nu$ and so on. The coupling $g_{\alpha\alpha'}(\nu)$ is a relevant quantity for calculating these satellites. The coupling enters, however, with a different weighting than in superconductivity. This can be seen if we consider the $\theta$-mode, where the $g$-matrix is diagonal. For non diagonal matrices, as is the case for three of the five partners of the $H_g$ modes, the situation is more complicated. This intrinsic complication of the Jahn-Teller problem will not be discussed further here. We consider the Hamiltonian for the coupling to one of the $t_{1u}$ levels, $\alpha$, in a free molecule

$$H = \epsilon_0 c^\dagger c + \omega_\nu b^\dagger b + g_{\alpha\alpha}(\nu)(b^\dagger + b)cc^\dagger \qquad (20)$$

where $\epsilon_0$ is the energy of the electronic (spinless) level, $\alpha$, and $c$ and $b$ describe the annihilation of an electron and a phonon, respectively. The last term describes the electron-phonon interaction. States with one electron and a fixed number (e.g., zero) of phonons are eigenstates of $H$, while states with no electron and a fixed number of phonons are not eigenstates of $H$. The Hamiltonian therefore describes how phonons can be excited when an electron is removed. The photoemission spectrum of the model can be written as a Poisson distribution of satellites[40]

$$f_{\alpha\nu}(\epsilon) = e^{-a_\alpha(\nu)} \sum_{n=0}^{\infty} \frac{1}{n!}[a_\alpha(\nu)]^n \delta(\epsilon - \epsilon_0 - \epsilon_r + n\omega_\nu) \qquad (21)$$

where coupling $a_\alpha(\nu) = (g_{\alpha\alpha}(\nu)/\omega_\nu)^2$ and the relaxation energy $\epsilon_r = g^2_{\alpha\alpha}/\omega_\nu$ have been introduced. The relevant quantity is then $a_\alpha(\nu)$ averaged over the $t_{1u}$ levels $\alpha$. For the $\theta$-mode we obtain

$$a(\nu) = \frac{1}{3}\frac{\mathrm{Tr}\ g(\nu)g(\nu)}{\omega_\nu^2} = \frac{3}{2}\frac{\lambda\nu}{N(0)\omega_\nu} \qquad (22)$$

Thus, while in superconductivity, the coupling to phonons depends on the density of states, this is not the case within this model of photoemission, as is also immediately clear from the assumptions. Furthermore, the low-energy phonons play a more important role in photoemission than in superconductivity, due to the factor $1/\omega_\nu$ in Eq. (22).

It is interesting to ask if the couplings $g$ entering in superconductivity and in photoemission may be different. In photoemission an electron is removed from a $C_{60}$ molecule, changing the net charge of the molecule, while in the calculation of the $\lambda$ for superconductivity, we assume that the net charge of the molecule is unchanged. This difference may be particularly large for the symmetric $A_g$ modes. For instance, one could imagine that the charging of the molecule could change its radius, which would imply a coupling to the $A_g(1)$ mode.

We have studied this in more detail for the $A_g$ modes, by calculating the equilibrium bond lengths for a free neutral $C_{60}$ molecule and for a negatively charged molecule. For the Hamiltonian in (20) no phonon is excited in the ground-state in the presence of one electron. If this electron is removed, the new ground-state is obtained by introducing $\widetilde{b} = b + g_{\alpha\alpha}(\nu)/\omega_\nu$ which diagonalizes the Hamiltonian in the absence of an electron. The corresponding distortion of the molecule can be obtained from

$$\delta R_{ik} = \sum_\nu \sqrt{\frac{1}{2M\omega_\nu}} (e_\nu(i,k) b_\nu^\dagger + e_\nu^*(i,k) b_\nu) \qquad (23)$$

where $\delta R_{ik}$ is the change of the $k$th Cartesian coordinate for the $i$th atom in a $C_{60}$ molecule, and $e_\nu(i,k)$ is the eigenvector corresponding to the mode $\nu$. Since $\widetilde{b}|\widetilde{0}>= 0$ for the ground-state $|\widetilde{0}>$ in the absence of an electron, we have that

$$<\widetilde{0}|b + b^\dagger|\widetilde{0}>= -\frac{2g_{\alpha\alpha}(\nu)}{\omega_\nu} \qquad (24)$$

The distortions are then given by

$$\delta R_{ik} = -\sum_\nu \sqrt{\frac{1}{2M\omega_\nu}} \frac{2g_{\alpha\alpha}(\nu)}{\omega_\nu} e_\nu(i,k) \qquad (25)$$

where we have used that fact that $e_\nu(i,k)$ can be chosen real. From the calculated values of the distortion when an electron is removed, we can then calculate the coupling constants to the two $A_g$ modes.

The results for the bond lengths for a neutral and a negatively charged $C_{60}$ molecule are shown in Table V. Similar results have also been obtained by Pederson.[37] We can see how the length of the double bond grows while the single bond becomes slightly shorter as an electron is added to the molecule. This effect has been discussed extensively by Stollhoff.[38]

The results for $a(\nu)$, calculated both from Eq. (25), taking into account that the molecule is charged in the photoemission process ($a^{PES}$), and from the shift of the $t_{1u}$ levels when the molecule is distorted, neglecting the charging of the molecule ($a^{su}$) (Eqs. ( 10,22)), are shown in Table VI. As a comparison, we also show $a^{su}$ converted to a $\lambda$ appropriate for superconductivity, although we recall that the $A_g$ modes *are* not included in the calculation of the total $\lambda$, as discussed in Sec. V, due to screening effects. For the $A_g(2)$ mode the two values $a^{PES}$ and $a^{su}$ are very similar, while for the $A_g(1)$ mode there is a large difference. The reason for this difference is not clear. We can see that the values of $a$ are relatively small for both $A_g$ modes, and the effects considered here are not very important.

## VIII. ELECTRON-PLASMON COUPLING

The width of the $t_{1u}$ band is about 1/2 eV according to band theory.[23] For $K_3C_{60}$ and $Rb_3C_{60}$ the $t_{1u}$ band is half-full, and one therefore expects to see a width of the occupied $t_{1u}$ band of about 1/4 eV in photoemission. The actually observed width is, however, at least a factor four larger.[39] In a short communication,[6] we showed that the coupling of the electrons to phonons and plasmons can explain this anomalously large width in terms of phonon and plasmon satellites. Below we give details about the calculation of the electron-plasmon coupling used in this earlier work.[6]

We follow Lundqvist,[41] who studied the GW approximation for the self-energy,[42] i.e., included the lowest order diagram in the screened interaction. This self-energy can also be obtained from a model Hamiltonian similar to Eq. (20), but with $\mathbf{k}$-dependent electron states and $\mathbf{q}$-dependent bosons (plasmons), by treating the electron-boson coupling to second order. By requiring that the two self-energies are equal, Lundqvist obtained an expression for the electron-plasmon coupling. We have slightly generalized this approach to a periodic solid, and expressed the coupling in terms of matrix elements of the screened interaction $W(\mathbf{r}, \mathbf{r}', \omega)$ between Bloch states $\psi_{\mathbf{k}m}(\mathbf{r})$ corresponding to the $t_{1u}$ orbitals. Thus close to the plasmon energy $\hbar\omega_p(\mathbf{q})$ we write the screened interaction as

$$\mathrm{Im} <\psi_{\mathbf{k+q}}|W(\omega)|\psi_\mathbf{k}>= \frac{A(\mathbf{q})}{|\mathbf{q}|^2}\delta(\omega - \omega_p(\mathbf{q})), \qquad (26)$$

which is $\mathbf{k}$-independent in the TB approximation used below. We also neglect the dispersion of the plasmon and integrate the coupling strength over the Brillouin zone assuming a spherical Brillouin zone with the radius $q_0$. We then find the coupling

$$\left(\frac{g}{\hbar\omega_p}\right)^2 = \frac{a^3}{(\hbar\omega_p)^2} \int_0^{q_0} \frac{dq}{(2\pi)^3} \hbar A(q), \qquad (27)$$

where $a$ is the fcc lattice parameter. In $K_3C_{60}$ and $Rb_3C_{60}$, this plasmon is well-defined through the whole Brillouin zone, and we do therefore not introduce any cut off $q_c < q_0$.

$A_3C_{60}$, with A=K or Rb, has a plasmon with the energy 0.5 eV, which essentially corresponds to oscillations of the three electrons in the $t_{1u}$ band.[43] This can, for instance, be seen in the following way. The electron density $n$ corresponding to the three $t_{1u}$ electrons in $Rb_3C_{60}$ leads to a plasmon energy $\hbar\omega_p^0 = \hbar\sqrt{4\pi ne^2/m} = 2.4$ eV, where $m$ is the free electron mass. From the total calculated band width, we estimate the effective mass $m^*/m$=4 for $Rb_3C_{60}$. Using the dielectric constant $\epsilon_0 \sim 4.4$[44] for undoped $C_{60}$, we estimate $\hbar\omega_p = \hbar\omega_p^0/\sqrt{\epsilon_0 m^*/m} = 0.6$ eV, in rather good agreement with experiment,[43] and confirming that this plasmon essentially corresponds to charge oscillations of $t_{1u}$ electrons screened by the dielectric function due to the inter band electronic transitions. We now want to calculate the coupling to this plasmon.

First we consider a simple electron gas like model, where, however, we have included the effects of the static dielectric function $\epsilon_0$ of undoped $C_{60}$ and the effective mass $m^*/m$ of the $t_{1u}$ electrons. We therefore consider the model

$$\epsilon(\omega) = \epsilon_0 - \frac{(\omega_p^0)^2}{(m^*/m)\omega^2}, \tag{28}$$

where we have assumed that $\epsilon_0$ is $\omega$-independent, since most of the inter band transitions correspond to a much larger energy scale than considered here. This model has the plasmon frequency $\omega_p = \omega_p^0/\sqrt{\epsilon_0 m^*/m}$ as above. We then obtain

$$\frac{1}{\pi}\mathrm{Im}\frac{1}{\epsilon(\omega)} = \frac{1}{2}\frac{\omega_p}{\epsilon_0}\delta(\omega - \omega_p), \tag{29}$$

which is the same expression as for the normal electron gas, except for the factor $1/\epsilon_0$. Thus the effects of the effective mass $m^*/m$ have been included implicitly in the reduced value of $\omega_p$. Inserting this result in Eq. (27), we obtain

$$\left(\frac{g}{\omega_p}\right)^2 = \frac{1}{\epsilon_0}\frac{e^2 q_0}{\pi\hbar\omega_p} = \sqrt{\frac{m^*/m}{\epsilon_0}}\frac{e^2 q_0}{\pi\hbar\omega_p^0}. \tag{30}$$

Using parameters appropriate for $Rb_3C_{60}$, we obtain $(g/\omega_p)^2 = 0.95$. We can see that for a given value of $\omega_p$, the coupling is multiplied by a factor $1/\epsilon_0$ compared with the electron gas result, or that for a given value of the density $(\omega_p^0)$ it is multiplied by $\sqrt{(m^*/m)/\epsilon_0}$. Since the density of the $t_{1u}$ electrons in $Rb_3C_{60}$ corresponds to $r_s = 7.4$ and $\sqrt{(m^*/m)/\epsilon_0} \sim 1$, we expect a coupling of roughly the same strength as for an electron gas with $r_s \sim 7$. From electron gas calculations,[41] we know that the weight of the main peak and the plasmon satellite(s) are comparable for $r_s = 7$, and we expect a coupling strength of the order one. This calculation neglects all local field effects.

We next consider a more realistic model of $Rb_3C_{60}$ with one $2s$ and three $2p$ basis states per C atom,[4] together with the parameterization of Tomanek and Schluter.[32] For the Coulomb integrals between the atomic orbitals, we only include the monopole integrals, corresponding to the interaction between the product of two equal atomic orbitals (same quantum numbers and centered on the same atom) with the product of two other equal atomic orbitals. This means that we allow the polarization of the molecules due to charge transfer between the C atoms, but not polarization of the individual C atoms.[4] This model leads to the polarizability $\alpha = 50$ Å$^3$ for a free, neutral $C_{60}$ molecule, compared with the result 80-90 Å$^3$, derived from the experimental dielectric constant for undoped $C_{60}$[44] together with the Claussius-Mosotti relation or from an accurate LDA calculations.[45] Since the plasmon frequency $\hbar\omega_p$ depends on the dielectric function, we have readjusted our model to produce the experimental dielectric function for undoped $C_{60}$ by expanding the radius of the molecule by 23 %. We have also reduced the $t_{1u}$ to $t_{1g}$ splitting from 1.4 eV to the more realistic 1.1 eV. We then calculate the dielectric function and the screened interaction for $Rb_3C_{60}$, and look for the plasmon pole corresponding to the $t_{1u}$ plasmon. We obtain the plasmon energy 0.68 eV. To obtain the experimental energy 0.5 eV, we have reduced the calculated[23] band width for $Rb_3C_{60}$ by a factor 0.6. The strength of the pole in the screened interaction is then extracted and integrated over $q$ according to Eq. (27). This leads to the result

$$\left(\frac{g}{\omega_p}\right)^2 \approx 1.0. \tag{31}$$

This result, obtained from a more realistic calculation, including, e.g., local field effects, is very close to what was obtained in the electron gas like calculation above. This coupling strength is appreciable, and leads to plasmon satellites, which, together with phonon satellites, can explain the large $t_{1u}$ band width observed experimentally.[6]

Translated into a superconductivity coupling, $(g/\omega_p)^2 \sim 1$ leads to $\lambda_p \sim 3$. This might suggest a very strong contribution from plasmons to the superconductivity. However, the plasmons have already been taken into account in the screening of the Coulomb interaction via the dielectric function. Thus the plasmons are essential for the *relatively* small value of the Coulomb pseudopotential $\mu^*$.[4] To simply add $\lambda_p$ to the electron-phonon $\lambda$ would therefore be double-counting and definitely wrong. Nevertheless, the large value of $\lambda_p$ suggests that it might be important to treat the plasmons beyond the approximations used in the calculations of $\mu^*$,[4] where the random phase approximation was used and only the statically screened interaction was considered.

## IX. SUPERCONDUCTIVITY AND RESISTIVITY

As a test of the calculated electron-phonon coupling constants $\lambda_\nu/N(0)$, we have calculated the superconductivity transition temperature $T_c$ using these values of $\lambda_\nu/N(0)$ and the value of $\mu^* = 0.4$ estimated earlier.[4] The values of the density of states per spin at the Fermi energy $N(0)$ was obtained from previous band structure calculations.[23] Thus we used the value $N(0) = 10$ states per spin, eV and $C_{60}$ molecule for $Rb_3C_{60}$, which gives a total $\lambda = 0.68$. We have solved the Eliashberg equation, using a generalization[46] of a program[47] which treats an isotropic, strong-coupling system. The generalization allows for a band with a Lorentzian shape and a finite width, which is important in the present case, where the $t_{1u}$ band width is only of the order 1/2 eV. Below we have assumed the full width at half maximum to be 0.4 eV.

To obtain the experimentally observed value of $T_c = 28$ K,[48] we then had to increase the values of $\lambda_\nu$ by an empirical factor 1.3. Alternatively, $T_c = 28$ can be obtained by using the calculated values of $\lambda_\nu$ and reducing $\mu^*$ from

0.4 to 0.23. We have also calculated the isotope effect which was found to be $\alpha$ =0.41 for the calculated values of $\lambda_\nu$ multiplied by 1.3 and $\mu^* = 0.4$. This is in satisfactory agreement with experiments considering a complete replacement of $^{12}$C by $^{13}$C, which find $\alpha \sim 0.30 \pm 0.05$.[49] Using the calculated values of $\lambda_\nu$ and $\mu^* = 0.23$, we found $\alpha = 0.45$.

A large uncertainty in our calculated value of $\lambda$ is due to the uncertainty in the density of states per spin, $N(0)$. Above we have used the value 10 states per eV, spin and molecule for $Rb_3C_{60}$, which was obtained from an ASA calculation,[22] for the uni-directional structure (one molecule per unit cell). For $K_3C_{60}$ there are several calculations available. Thus an ASA calculation,[22] corresponding to the calculation for $Rb_3C_{60}$ above, gave $N(0) = 8.6$ for the uni-directional structure. Full potential, linear combination of Gaussian orbital calculations gave $N(0) = 6.6$[50] for the uni-directional structure. Full potential LMTO calculations give $N(0) = 5.6$ and $N(0) = 8.8$ for the uni- and bi-directional (two molecules per unit cell rotated $90^o$ relative to each others) structures, respectively, where we expect the bi-directional structure to be the more relevant one.[21] The value of $N(0)$ has also been deduced by comparing band structure calculations with the damping rate in NMR experiments.[51] Good agreement with experiment was obtained by using the *bare* values $N(0) = 7.2$ and 8.1 for $K_3C_{60}$ and $Rb_3C_{60}$, respectively, and the enhanced values 9.0 and 10.5 for these compounds. Here the enhanced values contain enhancement of the susceptibility due to many-body effects, while in the unenhanced values this effect has been subtracted out using the LDA Stoner enhancement. This suggests a factor of 1.5 between the lowest and highest estimate of $N(0)$, where we have here used a value closer to the upper end. Finally, we note that we have here focused on the density of states at the Fermi energy, while the phonons would average the density of states over an appreciable fraction of the band width.

We note that all these calculations are based on the Migdal theorem.[52] In the present case the maximum phonon energy ($\sim$ 0.2 eV) is, however, comparable to the band width ($\sim$ 0.5 eV), and there is no justification for the Migdal theorem. Pietronero and Strässler[53] have studied corrections to the Migdal theorem and concluded that these corrections would increase the $T_c$, which is consistent with our findings that the calculated values of $\lambda$ and $\mu^*$ give too small a $T_c$.

As a further test we have calculated the temperature-dependent resistivity $\rho(T)$, due to scattering from phonons. We have used Ziman's formula[54]

$$\rho(T) = \frac{4\pi m}{ne^2 k_B T} \times \int_0^{\omega_{max}} d\omega \frac{\hbar\omega\alpha_{tr}^2 F(\omega)}{[exp(\hbar\omega/k_BT) - 1][1 - exp(-\hbar\omega/k_BT)]} \quad (32)$$

where we assume that the transport coupling function $\alpha_{tr}^2 F(\omega)$ can be replaced by the electron phonon coupling appropriate for superconductivity

$$\alpha^2 F(\omega) = \frac{1}{2}\sum_\nu \omega_\nu \lambda_\nu \delta(\omega - \omega_\nu). \quad (33)$$

This approach involves a number of approximations, but is still expected to describe the main features of the phonon induced resistivity. We have included all the intra-molecular phonons calculated above, with the calculated coupling constants $\lambda_\nu$. In addition, we have included the coupling to libration modes with the energy $\hbar\omega_l = 4$ meV (32 cm$^{-1}$) and the coupling $\lambda_l$ and to translational modes with the energy $\hbar\omega_t = 14$ meV (113 cm$-$1)[17] and the coupling $\lambda_t$, where the translational modes may refer to inter molecular vibrations of the $C_{60}$ molecules or to alkali optical phonons. We further assume that there is a temperature independent mechanism, giving rise to the $T = 0$ resistivity, but neglect all other mechanisms, such as electron-electron scattering, or $T$-dependent resistivity due to a $T$-dependent variation of the orientational order.[21] Similar calculations have been performed by V.H. Crespi et al.[55]

In Fig. 1 the calculated $\rho(T)$ is compared with the experimental results of Xiang et al[55] for $K_3C_{60}$. We observe that fairly different experimental results have been obtained by a different group[56] for $Rb_3C_{60}$, introducing an element of uncertainty about the experimental results. We have first used the calculated value of $\lambda_l/N(0) = 0.0012$ eV and treated $\lambda_t/N(0) = 0.004$ eV as an adjustable parameter. We obtain a satisfactory description of experiment (full curve), although the resistivity is too large at small $T$ ($\sim$ 50 K). A substantially better description of the resistivity would be obtained if we assumed the translational mode to be at 150-200 cm$^{-1}$. This assumption is, however, difficult to justify from the neutron data. With the present choice of $\omega_t = 113$ cm$^{-1}$, the translational modes give an appreciable contribution in the range $T \sim 50$ K, where the theoretical resistivity is too large.

The coupling to the intra molecular modes is essential. If this coupling is neglected, the resistivity deviates strongly from the measured one, for any combination of $\lambda_l$ and $\lambda_t$. The lower dashed curve shows a calculation for the calculated coupling to the librations but with the coupling to the translational modes set equal to zero. In this case the resistivity is too small in the range $T = 100-200$ K. Using our intra molecular couplings, it is therefore essential to have some (weak) coupling to the translational modes. We note that such a weak coupling is consistent with the conclusions above about the coupling to symmetric alkali optical modes. The value of $\lambda_t$ needed to describe the resistivity, does, however, depend on the distribution of the couplings to the intra molecular modes. We are therefore not able to draw any definite conclusions about the strength of this coupling, but it cannot be very large.

A slightly better description of experiment could be obtained by reducing the coupling $\lambda_l$ to the librations. Due to the uncertainties in terms of the contribution from the translational modes, we are, however, not able to tell if the calculated $\lambda_l$ is too large. We note, however, that if the translational modes would not contribute in the region $T \sim 50$ K, the librations would describe this region very well, as illustrated by the lower dashed curve. As a further test, we have increased the coupling to the librations to $\lambda_l/N(0) = 0.0036$ eV, i.e., three times the value estimated from the *ab initio* calculations (upper dashed line). At the same time $\lambda_t/N(0)$ was reduced to 0.001 to avoid that $\rho(T)$ is overestimated in the range $T = 100-200$ K. We can see that this leads to an overestimate of the resistivity for $T \sim 50$ K. This remains true, even if we set the coupling to the translational modes equal to zero, and the overestimate can therefore in this case not be due to the uncertainty in the coupling to the translational modes. Thus we conclude that the coupling to the librations cannot be much larger than the calculated one (except for the overall normalization constant discussed below), but it could be even smaller.

To calculate the absolute value of the total resistivity we set $4\pi ne^2/m = \omega_p^2$. We have calculated $\omega_p = 1.36$ eV for $K_3C_{60}$ by averaging the square of the electron velocity over the Fermi surface. Using this value, we find that the total resistivity due to the phonons at $T = 260$ K is 0.069 m$\Omega$cm. The data presented in the in the paper of Crespi et al,[55] correspond to an increase in $\rho(T)$ from small temperatures to $T = 260$ K of 0.16 m$\Omega$cm.[57] To reproduce this value we would need to multiply our values of $\lambda_\nu$ by a factor 2.3. If we more consistently use $\omega_p = 1.2$ eV, as assumed by Crespi et al[55] when deducing $\rho(T)$, we find that we need an enhancement by a factor of 1.8. From the fluctuations just above $T_c$, Xiang et al[58] have deduced that $\rho$ is 0.12 m$\Omega$cm at small $T$. Using this value to establish the absolute values in the measurements of $\rho(T)/\rho(T=260)$ together with $\omega_p = 1.2$ eV, we need an enhancement factor 1.2 for our calculated values of $\lambda_\nu$ to reproduce the increase in $\rho$ from small temperatures to $T = 260$ K. *If* the phonons give the main contribution to the resistivity and the estimates of the resistivity are essentially correct, these results suggest that our calculated value of $\lambda$ may be too small by a factor 1-2.

## X. CONCLUDING REMARKS

We have presented *ab initio* calculations for the frequencies of the intra molecular phonons and for the electron-phonon coupling for the intra molecular phonons, the librations and some alkali optical phonons. The calculated phonon frequencies typically agree with experiment to within 5 %. It is harder to test the accuracy of the calculated electron-phonon interaction. Raman scattering provides some support for the distribution of coupling between the different low-lying intra molecular phonons (strong coupling to $H_g(2)$) and between the different high-lying modes (strong coupling to $H_g(8)$ and $H_g(7)$). If our previous estimate of $\mu^*$ ($\sim 0.4$) is correct, a somewhat stronger (30 %) coupling than the calculated one is needed to describe the superconductivity transition temperature, implying values of $\lambda$ and $\mu^*$ which are also consistent with the isotope effect. These estimates are, however, based on the Migdal theorem. A somewhat stronger coupling was also deduced from the photoemission spectrum from the $t_{1u}$ level in doped $C_{60}$ compounds[6] and from the absolute value of the resistivity at $T = 260$ K, assuming that the resistivity is mainly due to phonons. All three estimates contain, however, substantial uncertainties. From the temperature dependent resistivity we have deduced that the coupling to the librations is small, as was also obtained in the calculation. It was also concluded that the coupling to translational modes, although nonnegligible, cannot be large, which is consistent with our estimates.


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* Present Address: Ames Laboratory, Iowa State University, Ames, Iowa 50011



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TABLE I. Phonon frequencies in $cm^{-1}$ for the $H_g$ and $A_g$ modes. the present calculations are compared with two previous *ab initio* calculations as well as experimental results for $K_3C_{60}$ (Ref. 28) for $Rb_3C_{60}$ (Ref. 29) and (in paranthesis) results for undoped $C_{60}$ (Ref. 30). The fraction of radial character of the modes(Rad char) is also shown.

| Mode | Energy | | | | Rad char |
|---|---|---|---|---|---|
| | Present | Exp[a] | Adams [b] | Koh.[b] | Present |
| $H_g(8)$ | 1462 | 1547(1575) | 1484 | 1726 | 0.02 |
| $H_g(7)$ | 1387 | 1408(1428) | 1315 | 1624 | 0.02 |
| $H_g(6)$ | 1290 | (1250) | 1140 | 1453 | 0.11 |
| $H_g(5)$ | 1091 | (1099) | 1036 | 1209 | 0.11 |
| $H_g(4)$ | 785 | 744(774) | 731 | 845 | 0.27 |
| $H_g(3)$ | 753 | 723,700(710) | 710 | 681 | 0.84 |
| $H_g(2)$ | 454 | 431,408(437) | 410 | 413 | 0.81 |
| $H_g(1)$ | 281 | 271,265(273) | 246 | 249 | 0.82 |
| $A_g(2)$ | 1463 | 1453,1441(1470) | 1365 | 1680 | |
| $A_g(1)$ | 458 | 497,487(496) | 455 | 537 | |

[a]Ref. 28–30
[d]Ref. 10
[e]Ref. 11

TABLE II. Coefficients $c_{\nu\nu'}$ expressing the *ab initio* phonon modes in the modes in the model of Wu et al[9] using the parameters of Week and Harter[9], according to Eq. (2). Each row corresponds to an eigenvector.

| $\nu$ | $\nu'$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 1 | .948 | -.269 | -.104 | -.111 | .000 | -.009 | .069 | .020 |
| 2 | -.298 | -.884 | -.137 | -.242 | .173 | -.146 | .032 | .030 |
| 3 | -.043 | .177 | -.929 | .168 | .149 | -.168 | .092 | .130 |
| 4 | -.009 | .335 | .021 | -.848 | .342 | -.181 | .040 | .131 |
| 5 | .088 | .035 | .240 | .389 | .775 | -.393 | -.090 | -.139 |
| 6 | .014 | -.028 | -.179 | -.086 | .345 | .694 | -.555 | -.227 |
| 7 | .036 | .014 | -.086 | -.097 | -.334 | -.531 | -.707 | -.298 |
| 8 | .026 | -.036 | .102 | .116 | .019 | -.005 | -.411 | .897 |

TABLE III. The partial electron-phonon coupling constants $\lambda_\nu/N(0)$ [in eV] in the tight-binding scheme (TB) and in the LMTO calculation. In the TB calculation we compare results obtained by performing the Brillouin zone integrations (Bz) with the results obtained when the couplings to the neighboring molecules have been cut (Mol) and when the coupling is determined from the splitting at the $\Gamma$-point (Split) or the second moment at the $\Gamma$-point (Secm). In the LMTO calculations, the results for the free molecule were obtained both in a full potential (FP) and an ASA calculation. The calculated energies (in $cm^{-1}$) of the modes is also given.

| Mode | Energy | $\lambda_\nu$ (TB)/$N(0)$ | | | | $\lambda_\nu$ (LMTO)/$N(0)$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Bz | Mol | Split | Secm | Mol | | Split | Secm |
| | | | | | | FP | ASA | | |
| $H_g(8)$ | 1462 | .0071 | .0069 | .0075 | .0071 | 0.022 | 0.024 | .025 | .024 |
| $H_g(7)$ | 1387 | .0038 | .0037 | .0047 | .0040 | 0.020 | 0.017 | .021 | .018 |
| $H_g(6)$ | 1290 | .0016 | .0017 | .0020 | .0019 | 0.008 | 0.009 | .004 | .004 |
| $H_g(5)$ | 1091 | .0001 | .0001 | .0003 | .0002 | 0.003 | 0.002 | .002 | .001 |
| $H_g(4)$ | 785 | .0001 | .0001 | .0001 | .0001 | 0.003 | 0.002 | .000 | .000 |
| $H_g(3)$ | 753 | .0014 | .0014 | .0023 | .0019 | 0.003 | 0.001 | .003 | .002 |
| $H_g(2)$ | 454 | .0002 | .0001 | .0040 | .0030 | 0.006 | 0.007 | .006 | .004 |
| $H_g(1)$ | 281 | .0035 | .0025 | .0002 | .0002 | 0.003 | 0.004 | .000 | .000 |

TABLE IV. The partial electron-phonon coupling constants $\lambda_\nu/N(0)$ [in eV] according to the present calculations (Present), the calculations of Varma et al[1] and LDA calculations by Schluter et al[2] using a bond charge model for the phonons. We also show the calculated energies (in cm−1) of the modes.

| Mode | Energy | $\lambda_\nu/N(0)$ | | |
|---|---|---|---|---|
| | | Present | Varma | Schluter |
| $H_g(8)$ | 1462 | .022 | .011 | .009 |
| $H_g(7)$ | 1387 | .020 | .034 | .013 |
| $H_g(6)$ | 1290 | .008 | .000 | .003 |
| $H_g(5)$ | 1091 | .003 | .006 | .001 |
| $H_g(4)$ | 785 | .003 | .000 | .007 |
| $H_g(3)$ | 753 | .003 | .001 | .004 |
| $H_g(2)$ | 454 | .006 | .001 | .007 |
| $H_g(1)$ | 281 | .003 | 003 | .008 |

TABLE V. The single ($b_p$) and double ($b_h$) bond lengths in Å for a neutral and negatively charged $C_{60}$ molecule.

| Charge | $b_p$ | $b_h$ |
|---|---|---|
| Neutral | 1.448 | 1.378 |
| Negative | 1.447 | 1.382 |

TABLE VI. The electron-phonon coupling $a_\nu$ to the A$g$ modes as calculated in Sec. V using the shift of the $t_{1u}$ levels and assuming no change in the charge of the cluster ($a_\nu^{sc}$) and in Sec. VII assuming charging ($a_\nu^{PES}$)). Also shown is the quantity $\lambda/N(0)$, calculated from the shifts of the $t_{1u}$ levels of the neutral system.

| Mode | $a_\nu^{PES}$ | $a_\nu^{sc}$ | $\lambda/N(0)$ |
|---|---|---|---|
| A$_g$(2) | 0.09 | 0.08 | 0.009 |
| A$_g$(1) | 0.01 | 0.08 | 0.003 |

Fig. 1. The temperature-dependent resistivity, normalized to its value at 260 K, $\rho(T)/\rho(T=260)$. The dots show the experimental results of Crepsi et al,[55] the full curve shows the theoretical result. The upper dashed curve shows results for an increased (factor three) coupling to the librations and the lower dashed curve the results without the coupling to the translational modes.