Optical properties of the vibrations in charged $C_{60}$ molecules

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Abstract

The transition strengths for the four infrared-active vibrations of charged $C_{60}$ molecules are evaluated in self-consistent density functional theory using the local density approximation. The oscillator strengths for the second and fourth modes are strongly enhanced relative to the neutral $C_{60}$ molecule, in good agreement with the experimental observation of “giant resonances” for those two modes. Previous theory, based on a “charged phonon” model, predicted a quadratic dependence of the oscillator strength on doping, but this is not borne out in our calculations.
I. INTRODUCTION

Recent experimental measurements [1–3] of infrared absorption in $A_xC_{60}$ ($A = K, Rb$), ($x = 0, 1, 3, 4, 6$) have demonstrated the strong dependence on doping of the oscillator strengths for several of the $T_{1u}$ infrared-active modes of the $C_{60}$ molecule. The second and fourth modes are enhanced by roughly 100, while the first and third show little or no change in oscillator strength in going from undoped $C_{60}$ to $C_{60}^-$. The “charged phonon” model introduced by Rice and Choi [4] obtains this increase in oscillator strength from the stronger coupling of the vibrational mode to an electronic transition. In particular the transition of the dopant electrons between the $t_{1u}$ and the higher-lying $t_{1g}$ molecular orbitals could enhance the dipole associated with the vibrational modes. The result is, in addition to a softening of the phonon modes proportional to the number of dopant electrons $x$, an enhancement of the oscillator strengths proportional to $x^2$. Friedman examined the effect of doping in a tight-binding model [5,6]. One parameter set did obtain the observed enhancement in the fourth mode, but the second mode could not be explained. Furthermore, experimental evidence for the $x^2$ doping dependence appears inconclusive.

In a previous paper [7] we examined the oscillator strengths for the transitions in undoped $C_{60}$, and found that the calculations using a frozen-phonon approach in the local density approximation gave good agreement with experiment on the magnitude of the oscillator strengths, particularly when compared with a tight-binding approach. In the present paper we apply the same self-consistent density functional technique to charged $C_{60}$ molecules, evaluating the dipole moment induced on the system by the same vibrational distortion used for the undoped system.
II. THEORY

As described, we make an adiabatic approximation to calculate the oscillator strength associated with the vibrations. We will calculate by distorting the C$_{60}$ structure according to the atomic displacements in the vibrational modes, and then evaluating the dipole moment of the structure. Defining the displacement of an atom $i$ in the mode $\alpha$ by the vector $\vec{d}_i^{\alpha}$, the oscillator strength is given by the formula

$$f_\alpha = \frac{m_e(D_\alpha)^2}{M_C \sum_i \vec{d}_i^{\alpha} \cdot \vec{d}_i^{\alpha}}$$

where $D_\alpha$ is the dipole moment in the distorted structure and $m_e, M_C$ are the electron and carbon masses, respectively. The displacement vectors are the same as we used for undoped C$_{60}$ [7], calculated from the phenomenological model of C$_{60}$ vibrations in ref. [8]. Equation [1] is of course the standard way to obtain absorption strengths, although it is usually presented in terms of infinitesimal displacements (i.e. the dipole derivatives), rather than the finite displacements we use.

The electrons of the system are described by the Kohn-Sham density functional approach [9], in which an effective one-electron problem is introduced that depends on a self-consistent charge density through an approximate “exchange-correlation” functional, which takes into account the electron-electron interactions. We use the local-density approximation (LDA) [10] for this exchange-correlation functional, which has proven remarkably successful in describing the charge distributions and energies of a wide variety of solid and molecular materials. Our calculation of the electron charge density for these fixed ionic positions uses a version of the Car-Parrinello electronic structure technique [11,12] implemented in a code provided by Wiggs [13], recently modified to facilitate rapid convergence to the ground state [14]. The same pseudopotential [15] and plane-wave basis set (with 35 Ry cutoff) was used here as in our earlier work. The discretization of the plane wave basis set is equivalent to treating the problem in a cubic box with periodic boundary conditions. The equivalent box length in our calculations was 23 atomic units, or 12.2 Å. Wave functions for the charged
C$_{60}$ molecules were calculated self-consistently for the excess charge and distorted molecule conditions, with double occupancy assumed for all the lowest-energy orbitals, except that the highest occupied level contained only one electron for the odd-charge molecules. Note that the periodic boundary conditions imply that the Hamiltonian effectively has a uniform positive background charge, instead of the discrete positive ion charges that would be present in the real M$_x$C$_{60}$ material.

This technique was then applied to calculate the charge density and dipole moment for each of the frozen T$_{1u}$ modes for the C$_{60}$ ions, using a displacement of net amplitude of 1Å, which in our earlier work was shown to be still within the regime where the moment varies linearly with the displacements. We estimate the random errors (due to insufficient convergence or box size) in the resulting dipole moments to be roughly 0.1 eÅ, or between 6% for the largest moments and 100% for the smallest (i.e. the smallest $f$-strengths we calculate are not significantly different from zero).

Before proceeding to the oscillator strengths, we note that the vibrational frequencies are readily obtained from the energy differences due to these displacements, and we have tabulated the results for neutral and charge -6 C$_{60}$ in Table I. The pronounced mode softening apparent in the experiments for the first and fourth modes is absent in our calculated results - in fact we find the first mode increases in frequency. This is most likely a consequence of our assumption of identical vibrational displacements in the neutral and charged systems.

The results for the oscillator strengths are much more conclusive. As can be seen from Figure 1, none of the oscillator strengths we obtain increases quadratically with $x$. In agreement with experiment, the second and fourth modes are strongly enhanced in strength. Our calculations find the first and third to actually diminish in oscillator strength with doping. The experiments do not clearly demonstrate this, although the fact that these peaks are not observed in some of the experiments at intermediate doping is evidence that they may have decreased in amplitude.

Figure 2 shows the relation between our calculations for the neutral and charged C$_{60}$ molecules and the available experiments on the undoped and doped systems. We have con-
verted the experimental measurements to units corresponding to our theoretical isolated $C_{60}$ $f$-strengths as outlined in the appendix. Theory and experiment are generally in agreement to within a factor of 2, which is remarkable because the strengths vary over 2 orders of magnitude, and different experiments themselves have discrepancies of roughly the same size. However, there are a few modes which were observed experimentally to have appreciable strength even though the theoretical strengths were much smaller - in particular the first mode for $C_{60}^{3-}$ and the first and third modes for $C_{60}^{6-}$. This could be due to a breakdown in the theoretical approximations, or possibly due to contamination of the experimental samples by some fraction of neutral or charge -1 $C_{60}$. The most significant disagreement appears to be for the fourth mode of the charge -6 species, where the theoretical strength is between 3 and 5 times smaller than the experimental numbers. The most likely explanation of this is the breakdown of our theoretical assumption that the atomic motions in the vibrational modes are independent of charge state. However there may be other approximations (such as ignoring the actual positions of the compensating charges, or the conversion from solid to molecular strengths) that are invalid for this particular data point.

III. CONCLUSION

Our calculations based on the Kohn-Sham density functional theory thus appear to be in excellent agreement with the available experiments. In particular, this self-consistent approach correctly predicts the strong enhancement of the second and fourth modes in the doped systems. The quantitative agreement is generally within a factor of two, which is also roughly the extent to which different experiments agree. However, all but one of the modes for the $C_{60}^{6-}$ ion are significantly weaker in the theoretical calculations than in the experiments, possibly indicating that for such a highly charged ion the approximations we have made are no longer suitable. The experimental observation of the weak first and third modes could also be ascribed to sample inhomogeneities and resulting contamination from other charge states, however.
We note here that the net dipole moment for a particular oscillation mode results from a very delicate cancellation of contributions from almost all of the electronic states in the system - most of the states have contributions to the total dipole that are roughly of the same magnitude (one electron-Å) as the final dipole moment. Thus the charged-phonon model of Rice and Choi [4] appears to be oversimplified. As shown in our Figure 1, the quadratic doping dependence of the strengths predicted by that model is not observed for any of the modes in the theoretical calculations. Unfortunately, our calculations do not suggest any simple explanation of the doping dependence - it appears that the only way to obtain meaningful theoretical numbers is through such a self-consistent calculation of the response of the electrons to the vibrations.

IV. ACKNOWLEDGMENT

We thank J. Wiggs for providing us the LDA program used for these calculations. This work was supported partly by the Department of Energy under Grant FG06-90ER-40561 and partly by the National Science Foundation under award number CHE-9217294 (CARM).

APPENDIX: THE EXPERIMENTAL OSCILLATOR STRENGTHS

In the published experimental work, the absolute strengths of the absorption peaks are generally expressed in terms of an effective plasma frequency $\omega_p$ for each mode, i.e. a contribution

$$4\pi \chi_j(\omega) = \omega_p^2 / (\omega_j^2 - \omega^2 - i \omega \gamma_j)$$  \hspace{1cm} (A1)$$

associated with mode $j$ to the dielectric function of the solid material, where $\omega_j$ is the observed frequency of the resonance. Theoretically, the dielectric response $\varepsilon(\omega)$ of the solid derives from the polarizability $\gamma_{mol}(\omega)$ of the single molecule through the Clausis-Mossotti relation:
\[ \epsilon(\omega) = 1 + 4\pi \frac{N\gamma_{mol}(\omega)}{1 - \frac{4}{3}N\gamma_{mol}(\omega)} \]  

(A2)

where \( N \) is the density of molecules in the solid. The fundamental \( f \)-strengths we calculate are associated with the single-molecule polarizability (ignoring damping) due to all electromagnetic resonance modes in the molecule:

\[ \gamma_{mol}(\omega) = \frac{e^2}{m} \sum_j f_j \left( \frac{\omega_j^2}{\omega_{j0}^2} - 1 \right) \]  

(A3)

The denominator in equation (A2) shifts the resonant frequency from \( \omega_{j0} \) to \( \omega_j \), and also changes the overall strength by a factor depending on the other modes. These other modes can be absorbed into a real net background contribution to the dielectric function that manifests itself simply as a value of the refractive index \( n \) different from 1 (recall \( \epsilon = (n + ik)^2 \)). The resulting relation between the effective plasma frequency \( \omega_p \) for a mode and the associated molecular \( f \)-strength \( f_j \) is:

\[ f_j = \frac{9}{(n^2 + 2)^2} \frac{m}{4\pi Ne^2} \omega_p^2. \]  

(A4)

We have used equation (A4) directly to convert the results of reference [3]. The experimental results of reference [2] require multiplication of the tabulated \( S \) by the vibrational frequency \( \omega_{j0}^2 \) to obtain \( \omega_p^2 \), and then \( f_j \). Reference [16] was treated in our previous paper [7]. Reference [1] only provided relative strengths between the charge -6 and neutral species: we assumed the numbers for the neutral species were identical to that of reference [2], and plotted the resulting \( f \)-strengths for the charged molecule.
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TABLE I. Energies of the vibrations, in eV.

| Label     | C_{60} |       | C_{60}^{6^-} |       |
|-----------|--------|-------|--------------|-------|
|           | Experiment | LDA  | Experiment | LDA  |
| T_{1u}(1) | 0.065  | 0.065 | 0.058       | 0.069 |
| T_{1u}(2) | 0.071  | 0.070 | 0.070       | 0.070 |
| T_{1u}(3) | 0.147  | 0.149 | 0.147       | 0.146 |
| T_{1u}(4) | 0.177  | 0.197 | 0.166       | 0.195 |
FIGURES

FIG. 1. $f$-strengths per $C_{60}$ from our LDA calculations for the neutral and charged molecules with up to 6 extra electrons, for the four $T_{1u}$ vibrational modes. The curves are labeled by the associated vibrational mode.

FIG. 2. Comparison of our calculated strengths with published experimental measurements for each of the vibrational modes for (a) neutral $C_{60}$, and charges of (b) -1, (c) -3, (d) -4, and (e) -6. The experimental numbers come from references [16] (circles), [1] (bursts), [2] (diamonds), and [3] (squares).
(d) $C_{60}^{-4}$

- $f$-strengths per $C_{60}$

- Vibrational mode

- $10^{-7}$ to $10^{-3}$
