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Optical properties of C_{60} vibrations

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The tight-binding and local-density approximation (LDA) models of the electronic structure for C_{60} are applied to calculate the transition strength of the four infrared-active vibrations. The tight-binding results are of the correct order of magntiude, but not accurate enough to have predictive power. The LDA results give a much better description of the relative and absolute strengths of the four modes.

I. INTRODUCTION

The electron-vibration coupling in C_{60} is of considerable interest because of the simplicity of this system and the implications for superconductivity. The infrared-active vibrational modes acquire oscillator strength because of the coupling, raising the question of how well current models can reproduce the observed strengths. There have been two previous calculations reported of the optical properties of these vibrations, using the modified neglect of differential (MNDO) approximation,[1] and using the local-density approximation (LDA).[2] In this paper, we consider the local-density approximation and the tight-binding approximation, comparing the absolute magnitudes of the oscillator strengths with data.[3]

In C_{60} there are four vibrations with T_{1u} symmetry, which is the only optically allowed symmetry. The experimental energies of these vibrations are given in Table I, compared to the LDA prediction that we will describe shortly. Our main interest is the oscillator strengths for the transitions, which are given in Table II. We use the definition of oscillator strength f as the integral over the photon cross section

$$f=\frac{mc}{2\pi^2 e^2\hbar}\int\sigma\,dE=0.91\int\sigma(\text{Å}^2)dE(\text{eV})\ . \qquad (1)$$

The oscillator strength for the entire spectrum has a value equal to the number of electrons in the system. We obtained the experimental f for the vibrational resonances from the data reported in Ref. 3. They quote an extinction coefficient in λ in a film of C_{60} at the resonance peak, and also give the width of the resonance γ. To deduce the oscillator strength for an isolated C_{60} molecule from this data, one also needs the index of refraction n of the film and the volume per molecule in the solid, V. Assuming that line shape is Lorentzian, the oscillator strength may then be obtained from the formula

$$f=\frac{mcV\lambda\gamma}{4\pi e^2\hbar}\frac{9n}{(2+n^2)^2}\ . \qquad (2)$$

The last factor gives the effect of the medium on the absorption cross section.[4] We used $n=1.9$ (Ref. 5) and $V=716$ Å^3 to obtain the numbers quoted in Table II.

II. THEORY

We determine the dipole transition matrix elements of the vibrations by distorting the C_{60} structure according to the atomic displacements in the normal vibrational modes, and then evaluating the dipole moment of the structure. Let us assume some amplitude of motion in the normal mode α, with the displacement of an atom i given by the vector $\mathbf{d}_i^\alpha$. Calling the dipole moment of the distorted structure $\mathbf{D}_\alpha$, the theoretical oscillator strength is given by the formula

TABLE I. Energies in eV of C_{60} infrared-active vibrations.

Vibrational mode	Experiment	LDA
$T_{1u}(1)$	0.065	0.064
$T_{1u}(2)$	0.071	0.069
$T_{1u}(3)$	0.147	0.149
$T_{1u}(4)$	0.177	0.197

TABLE II. Oscillator strength f of C_{60} vibrations.

Experimental (Ref. 3)	Tight binding	MNDO (Ref. 1)	LDA	LDA (Ref. 2)
1.2×10^{-5}	6.4×10^{-5}	10.0×10^{-5}	1.7×10^{-5}	$1.00c$
0.4	0.3	3.3	1.1	$0.63c$
0.3	1.1	18.9	1.0	$0.36c$
0.4	17.0	45	0.7	$0.57c$

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$$f_\alpha = \frac{m_e |D_\alpha|^2}{M_C \sum_i |d_i^\alpha|^2} , \tag{3}$$

where m_e and M_C are the electron and carbon masses, respectively. In our calculations, the normal modes were obtained from the phenomenological model of C_{60} vibrations in Ref. 6. This model describes the low-lying spectra of the vibrations fairly well, and we believe it is reliable for the normal-mode coordinates. Note that the theoretical oscillator strength from Eq. (3) does not require knowledge of the frequency.

We next describe the models for the electronic structure, which will provide the induced dipole moment.

A. Tight-binding model

In the tight-binding model, the electron wave function is represented as a linear combination of the *s* and *p* valence orbitals of the atoms. The five parameters in the Hamiltonian are the *s*-*p* splitting and the four distinct matrix elements taking an electron from an orbital on one atom to an orbital on another atom. The hopping matrix elements depend on the separation of the carbon atoms, giving an additional parametric degree of freedom. There are a number of parameter sets in the literature;[7-9] numerically they are rather close and they all assume the same dependence on distance, $v(r) \sim 1/r^2$. There are also more simplified treatments, for example, the Hückel approximation which considers only the π-type orbital in graphitelike structures.[10]

We shall use the parameter set of Ref. 7, which was used to calculate vibrational perturbations relevant to superconductivity and vibrational couplings in the optical spectrum of C_{60}. The electron wave functions for the distorted cluster may be obtained either by perturbation theory, using $\mathbf{d}\cdot\nabla H$ as a perturbation, or more simply by diagonalizing the Hamiltonian in the distorted structure. The dipole operator is evaluated assuming atomic orbitals as in Ref. 11, and neglecting wave-function overlaps between different atoms. The required dipole matrix element between *s* and *p* orbitals on an atom is taken to be 0.5 *e* Å. The results are shown as the second column in Table II. We see that the order of magnitude of the experimental results is reproduced, but that there is complete disagreement as to the relative strengths of the different vibrations.

The MNDO approximation used in Ref. 1 is quite similar in spirit to the tight-binding approximation. Both assume a wave function of the form of a linear combination of atomic orbitals, which the wave function represented as a vector of these atomic-orbital amplitudes. However, quite different aspects of the single-particle Hamiltonian are emphasized in constructing the wave function. In the tight-binding approximation, the Coulomb interactions are ignored, and all of the electron-vibration coupling is produced by the hopping matrix elements. In contrast, in the MNDO, the structure-dependent aspects of the dynamics arise from the Coulomb interactions among the electrons and ions; the hopping matrix elements are taken as constants. The predictions of the MNDO are shown in the third column of Table II. It may be seen that the agreement is no better for this model than for the tight-binding model. Both produce much too large strengths in the lowest and highest modes. This indicates that the different terms in the Hamiltonian have mutually canceling effects on electron-vibration coupling, and it is not justified to neglect one class of terms.

To understand somewhat better where the dipole moment comes from in the tight-binding approximation, we have examined the contributions of individual orbitals to the dipole moment of the $T_{1u}(2)$ mode. This mode has a rather simple structure; the carbon atoms are pushed together on one side of the icosahedron and are pulled apart on the opposite side. For this mode, the lowest σ- and π-electron orbitals behave in a rather simple way: the electron density is increased where the atoms are closer together, because the hopping matrix element is larger in that region. However, the higher orbitals are polarized differently, nearly canceling this effect. Thus the net dipole moment comes about after a delicate cancellation, and does not have a simple interpretation.

B. LDA theory

The Kohn-Sham[12] self-consistent single-particle theory goes beyond Hartree-Fock theory in that effects of electron correlation are incorporated into an effective single-particle Hamiltonian. Approximating the exchange and correlation energies by that of the free-electron gas[13] leads to the local-density approximation (LDA). In our calculations, based on the Car-Parrinello electronic structure technique[14,15] using a code provided by Wiggs,[16] we make the further approximations that the core electrons can be adequately represented by a relatively soft norm-conserving nonlocal pseudopotential[17] cast in separable form,[18] that we can calculate the properties of an isolated C_{60} molecule in a box with periodic boundary conditions, and that the wave functions are well described by a plane-wave basis set with kinetic energy up to 35 Ry. The pseudopotential we use produced total energies converged to 0.5 eV/atom and relative energies converged to better than 0.1 eV/atom for this energy cutoff, and has been used successfully in earlier studies of charge transfer and energetics for graphite intercalates.[19] Similar LDA calculations have been previously reported for various aspects of C_{60} structure and properties.[20-25]

For the calculation of dipole moments, it is essential that the periodic box size be large enough that neighboring C_{60} molecules do not interfere. We found that the moments had converged to within a few percent for a cubic box of 12.2 Å on a side, giving a vacuum gap of 5.6 Å between molecules. The associated basis set contained 21 250 plane waves and produced a Fourier-transform mesh in real space (on which the charge density was calculated) of 64^3 points. A test calculation of the dipole moment for the lowest T_{1u} mode with a 40-Ry cutoff changed the dipole moment by only 1% from the result at 35 Ry.

This technique was then applied to calculate the charge density and dipole moment for each of the frozen T_{1u}

modes of C_{60} using a displacement of amplitude $\sqrt{\sum_i d_i^\alpha d_i^\alpha}=1$ Å. The moments for a displaced C_{60} molecule and one of the G modes were calculated using exactly the same techniques, and were found to be below 0.02 e Å, or 1–2 % of the moments calculated for the T_{1u} modes. Since these should have been zero, this provides a measure of the accuracy of the technique. The lowest T_{1u} mode was also evaluated with amplitude 0.25 Å as a check of the linearity. The energies of the frozen vibrational modes were also evaluated and converted to harmonic vibrational frequencies, shown as the last column in Table I. These vibrational frequencies have previously been calculated in the LDA,[22,21] reproducing experimental values to 5–15 %. Our results are also quite good, showing remarkable agreement for the lowest three frequencies.

The oscillator strengths predicted by the LDA are shown in Table II; we see that the theory gives a rather good description of the relative strengths of the four modes. The absolute value seems to be roughly a factor of 2 too large. However, experimental uncertainties are in the 30% range,[26] so the quantitative disagreement may not be serious. (See note added in proof below.)

The LDA calculations reported in Ref. 2 are based on the same physical approximations as our LDA calculations, differing only in details of pseudopotentials and numerical implementation of the Kohn-Sham equation, and we expect the results should be very similar to ours. Unfortunately, these authors did not present their absolute transition strengths. We quote their results in Table II, indicating the unspecified normalization by the factor c. It may be seen that the relative magnitudes agree reasonably well with our results and with the experimental data.

III. CONCLUSION

The success of the LDA and the relatively poor showing of simplified models such as the tight-binding model have implications for the treatment of the electron-vibration coupling in other contexts. In particular, in the theory of the superconductivity of C_{60}, one needs to understand the couplings that connect electrons in the t_{1u} lowest unoccupied molecular orbital (LUMO). Calculations have been reported with the tight-binding model,[27] another semiempirical model based on atomic orbitals,[28] as well as more complete LDA calculations.[25] We have not examined atomic-orbital models other than the tight-binding model, but our results suggest that only the LDA is sufficiently reliable to be of interest.

Unfortunately, the LDA requires the largest computer resources available and so is not very convenient to use. Clearly, it would be desirable to understand the character of the approximations better, to construct models that have the physics of the LDA without the necessity for such a large basis of states. One obvious path to pursue is to include some of the Coulomb physics in the tight-binding model. In particular, the on-site Coulomb repulsion would be easy to add.

Note added in proof. We just became aware that absolute oscillator strengths are also available from the measurements of Martin, Koller and Mihaly.[29] Their absolute strengths are about a factor of 4 larger than the measurements of Ref. 3 and a factor of 2 larger than our LDA calculation. The relative strengths agree well with the LDA calculation.

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