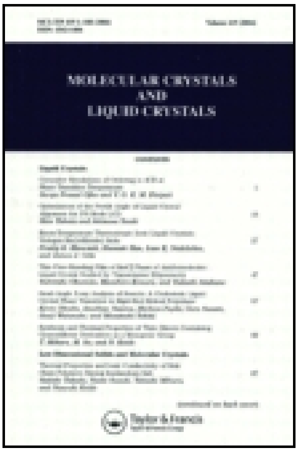

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Some Remarks on Infrared Absorption of C_{60}

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SOME REMARKS ON INFRARED ABSORPTION OF C_{60}

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Abstract I consider infrared absorption of C_{60} using a Su-Schrieffer-Heeger model supplemented by a force field model to treat molecular vibrations. Intensities are computed assuming the principal cause of absorption is the charged phonon effect. The calculated frequencies, as well as the high energy vibrational mode intensities are in reasonable agreement with experiment. For photo-excited C_{60} a number of new infrared peaks are indicated which are in principle accessible to experiment. These calculations show that infrared absorption measurements with sufficient time resolution will provide an important probe of polarons in photo-excited C_{60} as well as providing a stringent test of models of molecular vibrations for fullerenes.

Measurements of infrared absorption of C_{60} and doped C_{60} have indicated a number of interesting features[1,2]. Recall that due to the symmetry of the C_{60} molecule only four modes are infrared active, these four modes having symmetry T_{1u}. In the solid state, upon doping by alkali metal ions, the highest mode $T_{1u}(4)$ is shifted to a lower frequency and its intensity is greatly enhanced (i.e. ~ 100 times in A_6C_{60}). This softening and enhancement has been attributed by Rice and Choi[3] to the charged phonon effect, that is, the vibrational modes borrow intensity from electronic transitions. In this paper, I will investigate the charged phonon effect from a somewhat more microscopic point of view than the theory of Rice and Choi. In addition, I will investigate the effect of photo-excitation on the infrared modes of C_{60}. A number of calculations[4,5] and experiments[6,7] have indicated that upon photo-excitation an exciton polaron forms. From our experience with conducting polymers we expect the formation of polarons to have a dramatic effect on infrared absorption[8].

The model we consider for C_{60} is a tight binding model for the pi electrons with the molecular vibrations being treated by a force field model. The pi electrons and the molecular vibrations are coupled by a Su-Schrieffer-Heeger (SSH)[8,9] type term, namely the amplitude for an electron hopping from site to site depends on the distance between carbon atoms. More precisely, the Hamiltonian I treat is

$$H = \sum_{s\,<ij>} (-t + \alpha\,(X_{ij}-a))(c^{+}_{is}\,c_{js} + c^{+}_{js}\,c_{is}) + eE \cdot \sum_{s\,<i>} r_i\, c^{+}_{is}\, c_{is}$$

$$1/2 \sum_{<i>} M(\,dr_i\,/dt\,)^2 \quad + \quad V([r_i]) \qquad (1)$$

Here r_i is the position vector of the ith carbon atom and $E=E_0(e^{i\omega t} + e^{-i\omega t})$ is the electric field. The constants M, t, a, and α are the mass of the carbon nuclei, the hopping amplitude for electrons, the bare carbon-carbon bond length and the electron-phonon coupling constant. X_{ij} is the distance between sites i, j (nearest neighbor hopping) and $V([r_i])$ is potential energy term for the molecular vibrations. I shall use two different forms for $V([r_i])$, one model due to You et al.[9], the second proposed by Snoke and Cardona[10] (We will discuss the detailed form of these potentials below). I have neglected any explicit electron-electron interaction. For vibrational properties, I expect this to be at least a qualitatively correct approximation[5].

The calculation proceeds in several steps. Firstly, one solves the Hamiltonian (1) (with E=0) in the adiabatic approximation for the ground state treating the carbon nuclei classically. This calculation yields the equilibrium positions for the carbon nuclei (i.e. two bond lengths for a C_{60} molecule). We then linearise about this ground state, solving for molecular vibration eigenvectors and vibrational frequencies. Using these eigenvectors and frequencies we calculate the infrared absorption intensity following the calculation of Ito and Ono[11] for infrared absorption of polyacetylene (for a more detailed discussion see reference [12]).

As a first application of these ideas, let us consider the calculation of the infrared absorption for C_{60}. In all the calculations reported here we work in the zero band width limit (isolated C_{60} molecule). It makes sense to apply these calculations to the C_{60} solid since solid C_{60} is a molecular crystal. In particular, the infrared absorption (>500 1/cm) is very similar for the solid and C_{60} in solution.

I have done calculations using two models for $V([r_i])$. The first model, which will be referred to as model 1, is due to You et al., it consists of two pieces, a bond stretching term (springs connecting nearest neighbor carbons) and a bond bending term. These two terms lead to three additional phenomenological constants K_1 referring to bond stretching and K_2, K_3 referring to either 109 or 120 degree angles. I use the same parameters as You et al. namely $t=1.91$ eV, $\alpha=5.0$ eV/Å, $K_1=42$ eV/Å^2, $K_2=8.0$ eV/rad^2, $K_3=7.0$ eV/rad^2 and $a=1.5532$ Å. The strengths of this model is its relative simplicity, that the bond lengths (in the ground state of C_{60}) are accurately reproduced (1.40 Å for a h-h bond, a bond separating 2 hexagons, 1.44 Å for a h-p bond, a bond separating a pentagon and a hexagon) and that the A_g modes are accurately reproduced. The model's weakness is that the higher H_g modes are too high namely $H_g(8)$=1810 1/cm vs. 1575 (experiment) and $H_g(7)$=1540 1/cm vs. 1428(experiment).

The second model, which will be called model 2, is a modification of a force field model due to Snoke and Cardona for the vibrational modes of C_{60}. In its original form, this model contained no electron-phonon coupling (α=0) and consisted of a nearest neighbor bond stretching term (with parameter K_n), a next nearest neighbor stretching term (with parameter K_{nn}), a bond bending term between two σ-bonds ($k_{\sigma\sigma}$) and a bond bending term between a σ-bond and a pi-orbital ($k_{\sigma\pi}$). The strong point of this model is that by judiciously adjusting these parameters (and in fact adding four more parameters by making a distinction between h-p and h-h bonds) one can obtain excellent agreement (~2 %) with the experimental frequencies of vibration of C_{60}. I have modified this model by adding a fairly weak electron-phonon coupling constant and readjusting the Snoke Cardona parameters within a four parameter model. Explicitly we have chosen the parameters t=2.1 eV, a=1.505 Å, α=4.8 eV/a = 3.2 eV/Å, K_n=75.6 eV/a^2 = 33.4 eV/Å^2, K_{nn}=4.3 eV/a^2 = 1.9 eV/Å^2, $k_{\sigma\sigma}$=3.2 eV/rad^2 and $k_{\sigma\pi}$=3.4 eV/rad^2. Not surprisingly, the vibrational frequencies are fairly accurately reproduced, for example $H_g(8)$=1567 and $H_g(7)$=1464. The weakness here is that the bond length difference does not agree well with experiment, that is, within this model the h-p length=1.439 Å while the h-h length =1.415 Å. Apparently, in this model, the electron-phonon coupling constant is too weak. In any case, we view the two models we have chosen, though not being altogether realistic, as providing a representative sample of a range of electron-phonon couplings.

Our calculation for C_{60} is summarised in table I.

TABLE I Infrared Absorption of C_{60}.

	ω_{ex}	ω_1	ω_2	I_1	I_2
$T_{1u}(1)$	526	425	572	.0008	.0003
$T_{1u}(2)$	576	580	613	.004	.003
$T_{1u}(3)$	1182	1321	1259	.48	.11
$T_{1u}(4)$	1424	1492	1467	1	1

The first three columns are the frequencies of the infrared active modes in 1/cm, column 1 being experiment, columns 2 and 3 being calculated from model 1 and 2 respectively. Columns 4 (5) are the relative intensities of these modes using model 1(2). The intensities are normalized to the highest intensity mode for the respective model.

We see from these calculations that either model reasonably reproduces the mode frequencies while neither is accurate in so far as the infrared intensity is concerned. That is, experiment tells us that modes 1 and 2 have a large intensity[1,2] as compared to modes 3 and 4 while in our calculation modes 1 and 2 have a very small intensity. I can rationalize this disagreement by assuming that modes 1 and 2 contain a large direct ionic contribution which is not included in the calculation or that my calculation simply does not treat these low frequency modes very realistically. Qualitatively, at least for model 1, our calculations show modes 3 and 4 have comparable intensity. Although this feature agrees with experiment clearly we cannot claim any quantitative success. I expect an SSH type model to be better for the high frequency tangential modes and our experience here agrees with this intuition.

We now turn to A_6C_{60}. My calculation is summarized in table II.

TABLE II Infrared Absorption of A_6C_{60}.

	ω_{ex}	ω_1	ω_2	I_1	I_2
$T_{1u}(1)$	467	420	567	.64	.23
$T_{1u}(2)$	565	574	612	2.3	.66
$T_{1u}(3)$	1182	1223	1264	140	.50
$T_{1u}(4)$	1342	1376	1372	29	106

This table is arranged in the same way as table I with intensities normalized to the highest intensity mode for the respective model applied to C_{60}. The experimental data is taken from reference [1].

Let us compare the results of the models to experiment. Firstly, neither model works well for the low frequency modes ($T_{1u}(1)$ and $T_{1u}(2)$. I believe to accurately model these modes a more microscopic and complicated model is needed. I have had much better luck with the high frequency modes. Experimentally, the $T_{1u}(3)$ varies very little in frequency while the $T_{1u}(4)$ mode is substantially softened. Model 2 captures both these features nicely, the $T_{1u}(4)$ mode softens 95 1/cm and the $T_{1u}(3)$ mode shifts only 5 1/cm (it actually hardens). Furthermore, model 2 seems to capture well the increase in the intensity of the highest two modes. That is, in model 2 the sum of the intensity of $T_{1u}(3)$ and $T_{1u}(4)$ is enhanced a factor of 96 versus an experimental enhancement[1] of ~90. We also notice that the $T_{1u}(4)$ mode is intensified much more than the $T_{1u}(3)$ mode, again in agreement with measurements. Model 1 does not fare so well in comparison to experiment. Within this model, the $T_{1u}(4)$ is substantially softened, however $T_{1u}(3)$ is also greatly reduced in frequency. The combined intensity enhancement ($T_{1u}(3)+T_{1u}(4)$) is in reasonable agreement with experiment (~110 times), however within this model it is the $T_{1u}(3)$ mode which is greatly intensified. In summary, model 2, based on the Snoke Cardona potential energy, seems to capture well the behavior of the high frequency infrared modes.

We now consider photo-induced infrared absorption. Our physical picture of photo-excitation is as follows: by a complicated dynamical process an electron in the h_u orbital is excited to the t_{1u} orbital (note the direct process is forbidden by parity). The calculation therefore consists of first solving for the minimum energy state when one electron is in the t_{1u} orbital and there is one hole in the h_u orbital. Consistent with previous calculations[4,5], we find using either model that the molecule distorts, on a ring circling the C_{60} molecule the bond length difference is virtually destroyed and two single particle energy states are pulled into the gap (i.e. an exciton polaron forms). My calculation for the photo-induced infrared absorption is summarized in table III. We only show the results for model 2 since from our previous experience model 2 seems more reliable.

TABLE III Photo-induced infrared absorption.

frequency 1/cm	1396	1441	1471	1490
intensity a.u.	.17	.97	.07	1

In this table I have indicated all absorptions having strength >1/20 the maximum absorption (i.e. the absorption at 1490 1/cm). The maximum absorption here has a strength approximately three times the calculated maximum intensity of C_{60} so it should be quite intense. If we consider frequencies >1400 1/cm, for C_{60} there is one absorption peak while for photo-excited C_{60} there are two intense peaks and two weak peaks with the peaks being well separated in frequency. It therefore seems photo-excited C_{60} (when a polaron is present) should be readily observable by infrared absorption.

How does this prediction compare to experiment? To the best of my knowledge there has been only one photo-induced absorption experiment reported in the literature. The results of this experiments is in total disagreement with my calculation, that is Kim, Li and Diederich[13] detected no new infrared peaks. However, this experiment is limited to time scales which are long compared to characteristic time scales of polaron formation and luminescence. Of course, it would be interesting to do experiments that probe shorter time scales.

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REFERENCES

1. K. J. Fu et al.,Phys. Rev. B 46, 1937 (1992).
2. M. C. Martin, D. Koller, and L. Mihaly, Phys. Rev B 47, 14607 (1993).
3. M. J. Rice and H. Y. Choi, Phys. Rev. B 45, 1073 (1992).
4. B. Friedman and K. Harigaya, Phys. Rev. B 47, 3975 (1993).
5. J. Fagerström and S. Stafström, Phys. Rev. B 48, 11367 (1993).
6. P. A. Lane et al.,Phys. Rev. Lett. 68, 887(1992).
7. M. Matus, H. Kuzmany, and E. Sohmen, Phys. Rev. Lett. 68, 2822 (1992).
8. A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W . P. Su, Rev. Mod. Phys. 60, 781 (1988).
9. W. M. You, C. L. Wang, F. C. Zhang, and Z. B. Su, Phys. Rev B 47, 4765 (1993).
10. D. W. Snoke and M. Cardona, Sol. State Comm. 87, 121 (1993).
11. H. Ito and Y. Ono, J. of Phys. Soc. Japan 54, 1194 (1985).
12. B. Friedman, Phys. Rev. B 48, 17551 (1993).
13. Y. H. Kim, F. Li, and F. Diederich, Phys. Rev. B 45, 10169 (1992).