

Quantum lattice fluctuations and luminescence in C₆₀

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We consider luminescence in photoexcited neutral C₆₀ using the Su-Schrieffer-Heeger model applied to a single C₆₀ molecule. To calculate the luminescence we use a collective-coordinate method where our collective coordinate resembles the displacement of the carbon atoms of the Hg(8) phonon mode and extrapolates between the ground-state "dimerization" and the exciton polaron. There is good agreement for the existing luminescence peak spacing and fair agreement for the relative intensity. We predict the existence of further peaks not yet resolved in experiment.

In a recent experiment, Matus, Kuzmany, and Sohm¹ measured luminescence from C₆₀ films and interpreted their results in terms of an exciton polaron. The main purpose of this paper is to support the above authors' interpretation with some simple calculations and to

clarify a few points.

We interpret the luminescence in C₆₀ within the Su-Schrieffer-Heeger² (SSH) model applied to a single C₆₀ molecule.³ That is, we work with the Hamiltonian

$$H = \sum_{\langle i,j \rangle} \left\{ - \left[t - \alpha(X_{ij} - a) \right] \sum_{\sigma} [c_{i,\sigma}^{\dagger} c_{j,\sigma} + \text{H.c.}] + \frac{K}{2} (X_{ij} - a)^2 \right\} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_j m \left(\frac{d\mathbf{r}_j}{dt} \right)^2. \quad (1)$$

Here \mathbf{r}_j is the Cartesian coordinate of the j th carbon atom, a is the bare carbon-carbon bond length, and X_{ij} is the distance between the i th and j th carbon atoms. Our experience with luminescence in conducting polymers⁴ leads us to two assumptions: (i) We neglect intermolecular hopping. (ii) We set $U=0$ (explicit electron-electron interaction is neglected). When considering vibrational properties of conducting polymers this is a good zeroth-order approximation. In C₆₀ we also believe assumptions (i) and (ii) to be good approximations.

Physically we expect assumption (i) to be reasonable in C₆₀ since C₆₀ is a weakly (intermolecularly) bound Van der Waals solid. If we examine the optical absorption of C₆₀ solutions versus C₆₀ films⁵ the major features are very similar, giving strong experimental evidence that intramolecular interactions are dominant. Vibrational properties are also seen to be dominated by intramolecular interactions. As evidence of this, note that the experimental Raman frequencies of solid C₆₀ are in good agreement with single molecule calculations.⁶

The justification of assumption (ii) is similar to the standard arguments given in conducting polymers.² In both conducting polymers and C₆₀ it is likely that U is considerably larger than t .^{7,8} Nevertheless, in conducting polymers, the Hubbard term can be treated perturbatively due to the gap in the single-particle spectrum. Since the single-particle spectrum is also gapped for C₆₀ we also

expect the $U=0$ case to be a good zeroth-order approximation. We further expect electronic properties to be more greatly affected by electron-electron interaction than vibrational properties. Our main concern here will be phonon sideband peaks and consequently we set $U=0$.

A number of authors³ have treated the above Hamiltonian (1) using these approximations under the further restriction that the lattice (the 60 carbon atoms) is treated classically. For our purposes, the most important result of these studies is the formation of the exciton polaron when an electron is promoted from the H_u orbital to the T_{1u} orbital. That is, the lattice distorts in the sense that the dimerization (the difference in the two different bond lengths) is virtually destroyed on a ring circling the C₆₀ molecule. Concurrent with the lattice distortion, two electronic states are pulled into the gap. Electrons occupying these states live predominantly on the distorted part of the lattice (i.e., the ring). It is important to note that the exciton polaron does not break the inversion symmetry of the system.

Our picture of luminescence in C₆₀ is then as follows: By a complex dynamical process the photoexcited C₆₀ molecule evolves into the state where one electron occupies the lower gap energy level and one electron occupies the upper gap energy level. By spontaneous emission the system then decays into the electronic ground state and a

possibly excited lattice vibrational state. A complication here is that the exciton polaron does not break parity and the transition from the highest occupied molecular orbital to the lowest unoccupied orbital is dipole forbidden.

The above picture entails that we must treat the lattice quantum mechanically. We continue to work within the adiabatic approximation. However, it is difficult to work in the adiabatic approximation without further approximation since the lattice has 180 degrees of freedom. We therefore adopt the collective-coordinate method,⁴ reducing the problem of 180 degrees of freedom to a single judiciously chosen collective coordinate. This method has been used with reasonable success to calculate the absorbance and luminescence in nondegenerate conducting polymers.⁴

The key ingredient for the collective-coordinate method is, not surprisingly, a good choice for the collective coordinate. In conducting polymers, a good collective coordinate has been found to be a one-parameter family of lattice configurations that extrapolates between the ground state and first excited state classical lattice configurations. In the case of C_{60} , the ground state of the lattice is dimerized, the bonds separating hexagons from hexagons, $h-h$ bonds, have a length l_1 , and the bonds separating pentagons from hexagons, $p-h$ bonds, have a length l_2 . Experiment gives a value of $l_1 = 1.40 \text{ \AA}$ and $l_2 = 1.45 \text{ \AA}$.⁹ For the first excited state, calculations with the SSH model tell us that the bond length pattern is largely the same as that of the ground state other than on a ring circling the molecule. On this ring, consisting of 20 carbon atoms, the difference in bond length between the $h-h$ and $h-p$ bonds is suppressed. We therefore choose a collective coordinate u so that carbon atoms not on the ring are fixed and for r_i on the ring

$$r_i = [\bar{a} + (-1)^i u] \hat{x} \quad (1 \leq i \leq 20), \quad (2)$$

where the index i labels the carbon atoms on the ring. Here we treat the ring as a chain along the x axis with periodic boundary conditions. This is a simple and reasonable approximation since the quantity entering into the total energy is the bond length difference. The parameter \bar{a} , the renormalized bond length, is equal to a minus the average bond length shrinkage, where a is the unrenormalized bond length. (For the parameter values we have adopted the $h-h$ shrinkage $\approx 0.11 \text{ \AA}$ and the $p-h$ shrinkage $\approx 0.16 \text{ \AA}$, the average shrinkage being therefore $\approx 0.14 \text{ \AA}$.) In this choice of collective coordinate, $u = 0$ approximates the distortion of the exciton polaron and $u = (p-h \text{ bond shrinkage} - h-h \text{ bond shrinkage})/4$ approximates the ground-state dimerization. We emphasize that our collective coordinate is not an unreasonable approximation to the Hg(8) phonons¹⁰ obtained from microscopic calculations.¹¹ In particular, these calculations show that the 20 carbon atoms on the ring are displaced almost parallel to the x axis.

It may seem somewhat counterintuitive that we are considering lattice motions restricted to the 20 carbon atoms on the ring. However, this is quite a plausible approximation since the electronic states that interact most strongly with the lattice are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular

orbital (LUMO). In the situation we are considering, the HOMO and LUMO correspond to the lower and upper gap states, respectively. When we look at single-particle states when the exciton polaron is present, we find the upper (lower) gap state has a probability of 0.72 (0.75) of being on the 20 carbon atoms of the ring. Therefore, the HOMO and LUMO are peaked on the ring and the dynamics for the ring is the most important part of the lattice dynamics for electron-phonon interactions.

We can give a slightly more formal justification of our choice of collective coordinate as follows: The process of going from the exciton polaron to the dimerized lattice can be viewed as a tunneling process,¹² i.e., more pictorially, imagine going from a higher valley to a lower valley. To go from one valley to another the most efficient path is such that the gradient of the total energy is parallel to the path. Explicit calculations for nondegenerate conducting polymers¹³ show that such a path is well approximated by a straight line connecting the two "valleys," in our case the exciton polaron and the dimerized lattice. Since the exciton polaron and the dimerized lattice configurations differ principally on the 20 carbon atoms on the ring our collective coordinate consequently only involves "moving" the 20 carbon atoms on the ring.

We proceed to examine the consequences of our collective coordinate. The lattice kinetic energy [Eq. (1)] then reads in terms of the collective coordinate u

$$\frac{1}{2} \sum_{i=1}^{20} m \left[\frac{dr_i}{dt} \right]^2 = \frac{1}{2} \sum_{i=1}^{20} m \left[\frac{du}{dt} \right]^2 = \frac{1}{2} M \left[\frac{du}{dt} \right]^2, \quad (3)$$

where $M = 20m$ is the mass of 20 carbon atoms. With this kinetic energy it is easy to write down the collective-coordinate Schrödinger equation,

$$-\frac{\hbar^2}{2M} \frac{d^2\psi}{du^2} + V(u)\psi = E\psi. \quad (4)$$

$V(u)$, the adiabatic potential energy, is computed as the total energy of the SSH Hamiltonian for a fixed value of u . In Fig. 1 we have plotted the adiabatic potential energy for the electronic ground state and the first excited state. Of course, to obtain such a curve we have used parameter values for t , α , and K . For polyacetylene, we find that $t = 1.35 \text{ eV}$, $\alpha = 7.0 \text{ eV/\AA}$, and $K = 53 \text{ eV/\AA}^2$ work rather well to reproduce the experimental optical properties and dimerization. If we use these parameter values for C_{60} we obtain a bond length difference that is slightly too large (i.e., 0.06 \AA) and an optical gap that is somewhat too large ($\approx 2.2 \text{ eV}$).⁸ We expect α to show the most significant variation in going from one π electron system to another. By fixing a value of α , the bond length difference is determined since we determine the bond lengths by finding the minimum value of the energy of the Hamiltonian (1), treating the X_{ij} 's as classical degrees of freedom. Therefore we only have one free parameter to fit both the bond length difference and the energy gap. We have consequently adjusted α to give the experimental bond length difference by decreasing α to 6.3 eV/\AA . Such a value of α reduces the classical gap (see below for further discussion of this point) to 1.96 eV in better agreement with the experimental optical gap of

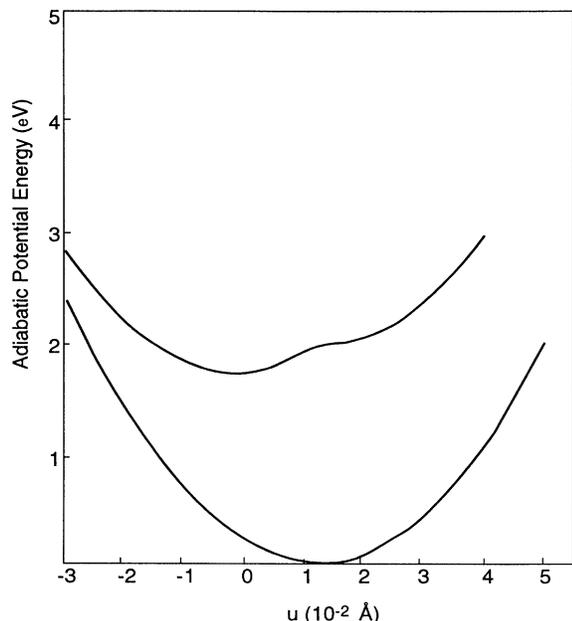


FIG. 1. Adiabatic potential energy vs collective coordinate u . For our parameter values $u = 0.0125 \text{ \AA}$ corresponds to a dimerized lattice and $u = 0$ corresponds to the exciton polaron.

1.9 eV.¹ In any case, we should not expect quantitative agreement for an electronic property (the energy gap) without explicitly including electron-electron interaction or broadening from intermolecular hopping.

By solving the collective-coordinate Schrödinger equation in the lower adiabatic potential we obtain a series of discrete levels separated by about 0.21 eV. The energy differences between these levels should correspond to the energy difference between vibronic peaks in luminescence. There is consequently reasonable agreement between our calculation and experiment since Matus, Kuzmany, and Sohmen¹ report prominent peaks at 1.70 and 1.52 eV; that is an energy difference of 0.18 eV. According to our calculation, there should be additional equally spaced peaks. We attribute the absence of such peaks (which we calculate to have smaller intensity, see below) to experimental uncertainties, material problems, etc. An earlier measurement of luminescence in C₆₀ films by Reber *et al.*,¹⁴ in fact, seems to resolve three peaks differing in energy by ≈ 0.17 eV. Preliminary results of Iwasa, Koda, and Koda¹⁰ also indicate the presence of additional peaks. Our value of energy-level differences of 0.21 seems relatively insensitive to parameter choices, for example, if we let $\alpha = 7.0 \text{ eV/\AA}$ we get a level spacing of 0.2 eV.

A consequence of our theory is that the energy difference between peaks in luminescence should depend on the isotope of carbon present in the C₆₀ molecule. Since the adiabatic potential is very close to harmonic (for the lower curve) the energy spacing depends on the mass of the carbon atom m like $m^{-1/2}$. It therefore may be interesting to do experiments on luminescence in C₆₀ films made using C^{13,15}.

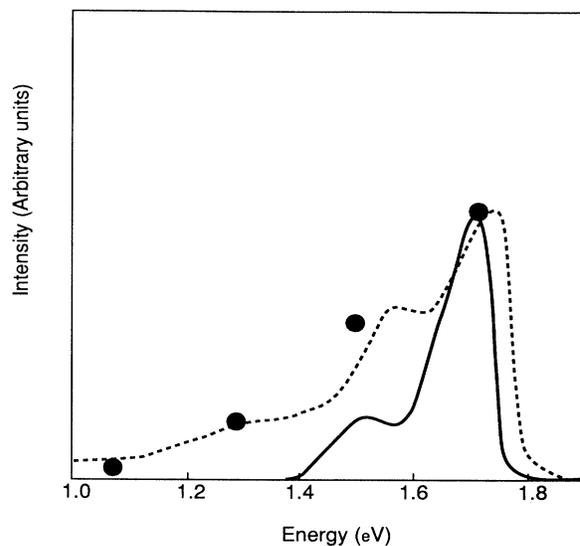


FIG. 2. Relative intensity of luminescence vs energy. The large dots are our calculation, the dashed curve is an envelope of the experimental data from Reber *et al.* (Ref. 14), and the solid curve is from the experiment of Matus, Kuzmany, and Sohmen (Ref. 1).

We next turn to the intensity of the luminescence. The intensity of the luminescence is proportional to (with an energy independent constant)

$$\omega^4 \left| \int_{-\infty}^{\infty} \psi_i^*(s) \psi_f(s) Q(s) ds \right|^2, \quad (5)$$

where ψ_i , ψ_f are the initial and final vibrational wave

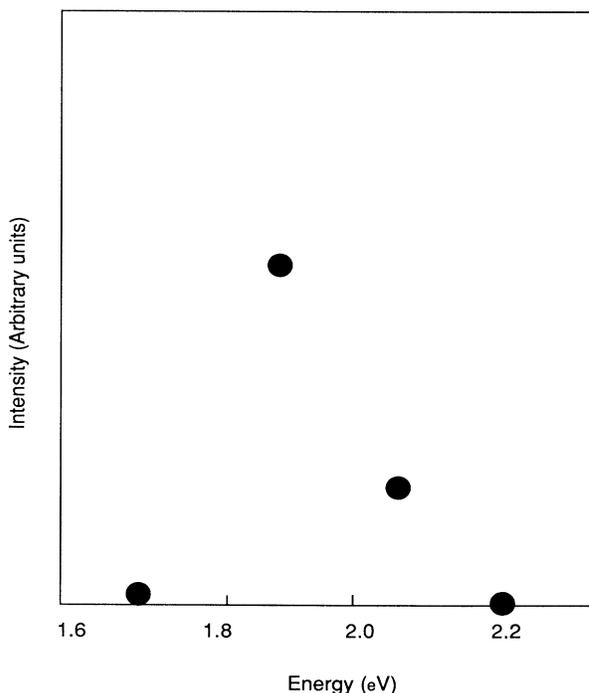


FIG. 3. Relative intensity of absorption vs energy. The large dots are our calculation.

functions, and $Q(s)$ is the electronic matrix element for the lattice configuration with a fixed collective coordinate s . The difficulty here is that in the dipole approximation for an isolated C_{60} molecule (and our collective coordinate) $Q(s)$ is zero. We expect that oxygen impurities, coexisting C_{70} , and/or solid-state physics effects (other C_{60} molecules) will make $Q(s)$ nonzero even in the dipole approximation. Such effects are not simple to estimate; fortunately $Q(s)$ is probably only weakly s dependent. Therefore, we can treat $Q(s)$ as a constant and pull it out of the integral. In calculating relative intensities, Q then does not enter; we need to consider the quantity

$$\omega^4 \left| \int_{-\infty}^{\infty} \psi_i^*(s) \psi_f(s) ds \right|^2. \quad (6)$$

A straightforward calculation yields Fig. 2. In Fig. 2, the solid circles are our calculation, while the solid curve is the experiment of Matus, Kuzmany, and Sohmen,¹ and the dashed curve is the experiment of Reger *et al.*¹⁴ Our calculation is by no means in perfect agreement with experiment; it does, however, seem to be not unreasonable especially for such a simple theory. (Actually our calculated relative intensities agree remarkably well with the experiment of Reger *et al.*)

Lastly, we consider absorption. Our model for absorption is that the lowest vibrational wave function in the first adiabatic potential makes a transition to various vibrational wave functions in the second adiabatic poten-

tial. We have plotted the absorption in Fig. 3. The most intense absorption occurs at 1.9 eV. It is probably beyond the accuracy of our simple theory to calculate the onset of absorption due to the effects (as previously mentioned) of direct electron-electron interaction and intermolecular hopping. However, we do believe it is reasonable to compare our theory to the peak in the photocurrent measured by Mort *et al.*¹⁶ For low-energy photons the photocurrent peaks at 1.9 eV in apparent agreement with our calculated most intense absorption.

In conclusion, we have considered luminescence within a simple model. Our model agrees well with the existing experimental energy differences and there is fair agreement with the relative intensity. We predict that more extensive experiments will see more peaks in luminescence and an isotopic shift for the luminescence peaks if C^{12} is replaced by C^{13} .

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