We consider luminescence in photo-excited neutral $C_{60}$ using the Su-Schrieffer-Heeger model applied to a single $C_{60}$ 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 "dimerisation" 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.

PACS Numbers : 78.65.Hc, 74.70.Kn, 36.90+f
In a recent experiment, Matus, Kuzmany and Sohmen measured luminescence from $C_{60}$ films and interpreted their results in terms of an exciton polaron. The main purpose of this letter is to support the above author’s interpretation with some simple calculations and to clarify a few points.

We interpret the luminescence in $C_{60}$ within the Su-Schrieffer-Heeger (SSH) model applied to a single $C_{60}$ molecule. That is, we work with the Hamiltonian

$$H = \sum_{<i,j>} \{- (t - \alpha(X_{ij} - a)) \sum_\sigma [c_{i,\sigma}^\dagger c_{j,\sigma} + H.c.] + \frac{K}{2} (X_{ij} - a)^2 \} + U \sum_i n_i \bar{n}_i + \frac{1}{2} \sum_j m(\vec{r}_j^2/\dot{t})^2.$$

(1)

Here $\vec{r}_j$ 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 polymers leads us to two approximations: 1) We neglect intermolecular hopping (we discuss this assumption later). 2) We set $U=0$ (explicit electron-electron interaction is neglected). When considering vibrational properties of conducting polymers this is a good zeroth order approximation.

A number of authors have treated the above Hamiltonian 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 $T_{1_u}$ orbital. That is, the lattice distorts in the sense that the dimerisation (the difference in the two different bond lengths) is virtually destroyed on a ring circling the $C_{60}$ 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 $C_{60}$ is then as follows: By a complex dynamical process the photoexcited $C_{60}$ 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 dimerised, 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 \( l_1 = 1.40 \) Å and \( l_2 = 1.45 \) Å. For the first excited state calculations with the SSH model tell us the bond length pattern is largely the same as that of the ground state other then on a ring circling the molecule. On this ring, consisting of twenty carbon atoms, the difference in bond lengths 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 \( \vec{r}_i \) on the ring

\[
\vec{r}_i = (i\tilde{a} + (-1)^i u) \hat{x}, \tag{2}
\]

where the index \( i \) (1 ≤ \( i \) ≤ 20) 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 \( \tilde{a} \), the renormalised bond length is equal to \( a \) - average bond length shrinkage, where \( a \) is the unrenormalised bond length. (For the parameter values we have adopted the h-h shrinkage ≈ .11 Å and the p-h shrinkage ≈ .16 Å, the average shrinkage being therefore ≈ .14 Å). In this choice of collective coordinate, \( u=0 \) approximates the distortion of the exciton polaron and \( u= (p-h \text{ bond shrinkage} - \text{h-h bond shrinkage})/4 \) approximates the ground state dimerisation. We emphasize that our collective coordinate is not an unreasonable approximation to the Hg(8) phonons [3] obtained from microscopic calculations [3]. In particular, these calculations show that the twenty carbon atoms on the ring are displaced almost
parallel to the x-axis.

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

$$1/2 \sum_{i=1}^{20} m(d\vec{r}_i/dt)^2 = 1/2 \sum_{i=1}^{20} m(du/dt)^2 = 1/2M(du/dt)^2.$$ (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

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

$V(u)$, the adiabatic potential energy is computed as the total energy of the SSH Hamiltonian for a fixed value of $u$. In figure 1 we have plotted the adiabatic potential energy for the electronic ground state and first excited state. Of course, to obtain such a curve we have used parameter values for $t, \alpha$ and $K$. For polyacetylene, we find $t=1.35$ eV, $\alpha=7.0$ eV/Å and $K=53$ eV/Å$^2$ work rather well to reproduce the experimental optical properties and dimerisation. If we use these parameter values for $C_{60}$ we obtain a slightly too large bond length difference (ie. .06 Å ) and a somewhat too large optical gap ($\approx$2.2 eV). We have consequently adjusted $\alpha$ to give the proper dimerisation by decreasing $\alpha$ to 6.3 eV/Å. Such a value of $\alpha$ reduces the naive gap (see below) to 1.96 eV in better agreement with the experimental optical gap of 1.9eV \cite{matus95}. By solving the collective coordinate Schrödinger equation in the lower adiabatic potential we obtain a series of discrete levels separated by about .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 Sohmen\cite{matus95} report prominent peaks at 1.70 and 1.52 eV, that is an energy difference of .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 $C_{60}$ films by Reber et al.\cite{reber93}, in fact, seems to resolve 3 peaks differing in energy by $\approx$.17 eV. Preliminary results of Iwasa et al.\cite{iwasa95} also indicate the presence of additional peaks. Our value of energy level differences of .21 seems relatively insensitive to parameter choices, for example if we let $\alpha=7.0$ eV/Å we get a level spacing of .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 $C_{60}$ 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 $C_{60}$ films made using $C^{13}$.

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

$$\omega^4 \left| \int_{-\infty}^{\infty} \psi_i^*(s) \psi_f(s) Q(s) ds \right|^2.$$  \hspace{1cm} (5)

where $\psi_i, \psi_f$ are the initial and final vibrational wavefunctions and $Q(s)$ is the electronic matrix element for the lattice configuration with 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 doesn’t enter, we need only consider the quantity

$$\omega^4 \left| \int_{-\infty}^{\infty} \psi_i^*(s) \psi_f(s) ds \right|^2.$$  \hspace{1cm} (6)

A straightforward calculation yields figure 2. In figure 2, the solid circles are our calculation, while the solid curve is the experiment of Matus, Kuzmany and Sohmen and the dashed curve is the experiment of Reger et al. 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 wavefunction in the first adiabatic potential makes a transition to various vibrational wavefunctions in the second adiabatic potential. We have plotted the absorption in figure 3. The most intense absorption occurs at 1.9 eV. This is in apparent agreement with the onset of absorption reported in ref.1.

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 $C^{13}$.

This work was partially supported by the Sam Houston State University research enhancement fund, the Robert A. Welch Foundation and by the Texas Center for superconductivity at the University of Houston under Prime Grant No. MDA 972-88-G-002 to the University of Houston from the Defense Advanced Research Projects Agency and the State of Texas. One of the authors (K.H.) thanks Dr. S. Abe for many fruitful discussions. We also acknowledge helpful conversations with Professor W. P. Su (with K. H. at the Electrotechnical Technical Lab and at ICSM’92) and Dr. Y. Iwasa.
References

[1] M. Matus, H. Kuzmany, and E. Sohmen, Phys. Rev. Lett. 68, 2822(1992).

[2] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su Rev. Mod. Phys., 781(1988).

[3] K. Harigaya, J. Phys. Soc. Jpn., 4001(1991); B. Friedman Phys. Rev. B, 1454(1992); K. Harigaya Phys. Rev. B, 13676 (1992).

[4] B. Friedman and W. P. Su Phys. Rev. B, 5152(1989).

[5] Y. Iwasa, T. Koda, and S. Koda, C$_{60}$ Symposium (Tokyo) July 14,15 1992; International Symposium on Science and Technology of Synthetic Metals (ICSM’92) (Göteborg) Aug. 12-18, 1992.

[6] G. B. Adams et al., Phys. Rev. B, 4052(1992).

[7] C. Reber et al., J. Phys. Chem., 2127(1991).

[8] C. C. Chen, and C. M. Lieber, J. Am. Chem. Soc., 3141(1992).
FIGURE CAPTIONS

Figure 1. Adiabatic potential energy vs collective coordinate $u$. For our parameter values $u=.0125\,\AA$ corresponds to a dimerised lattice and $u=0$ corresponds to the exciton polaron.

Figure 2. Relative intensity of luminescence vs energy. The large dots are our calculation, the dashed curve is an envelop of the experimental data from Reber et al. and the solid curve is from the experiment of Matus, Kuzmany, and Sohmen.

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

Note: Figures will be sent by the conventional mail. Please send your request to harigaya@etl.go.jp.