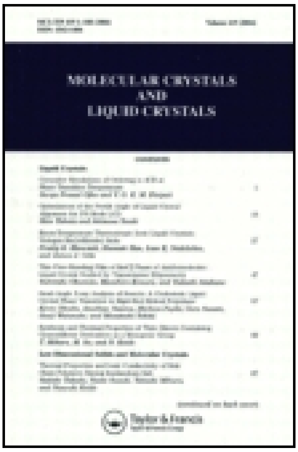

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Extrinsic Nature of the 2.5 eV Raman Resonance in C_{60}

S. Guha [a], J. Lorentzen [a], K. Sinha [a], J. Menéndez [a], G. B. Adams [a], J. B. Page [a] & O. F. Sankey [a]

[a] Department of Physics and Astronomy, Arizona State University, Tempe, AZ, 85287-1504

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EXTRINSIC NATURE OF THE 2.5 eV RAMAN RESONANCE IN C_{60}

S. GUHA, J. LORENTZEN, K. SINHA, J. MENÉNDEZ, G.B. ADAMS, J.B. PAGE, AND O.F. SANKEY
Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287-1504

Abstract We present experimental evidence that the resonance near 2.5 eV observed in the Raman excitation profile of C_{60} is induced by the interactions of the C_{60} molecule with the surrounding medium and is not to be expected in isolated molecules.

In icosahedral C_{60}, the separation between the HOMO (h_u) and the LUMO (t_{1u}) lies in an energy range near 2 eV which is easily accessible with light sources in the visible. Unfortunately, the transition between h_{1u} and t_{1u} is optically forbidden. In C_{60} dissolved in hexane, a very weak and broad optical absorption band has been observed in the 1.9 - 2.8 eV energy range.[1] This band has been assigned to vibrational-assisted transitions between the HOMO and the LUMO. A similar but stronger band is observed in experiments on solid C_{60} films.[2] Features near 2.5 eV become very prominent in electro-absorption[3] (EA) and Resonant Raman Scattering (RRS) experiments[4-6] in solid C_{60} films. In both instances, symmetry-breaking mechanisms have been invoked to explain their observation. In the case of EA, the applied electric field is expected to break the parity selection rules. In the case of RRS, the observation of a resonance near 2.5 eV has been assigned[4] to the weak coupling between neighboring buckminsterfullerenes in the crystalline lattice. The strength of the EA and RRS features is not surprising in view of the *derivative* character of these techniques. An alternative explanation for the RRS data, however, has been proposed by Matus *et al.*[5] These authors assign the Raman resonance near 2.5 eV to the allowed transition between the h_u HOMO and the t_{1g} LUMO+1 state. This assignment was ruled out by Sinha *et al.*[4] because the resonance was not observed in C_{60} dissolved in CS_2. In this paper, we present additional experimental evidence that the Raman resonance near 2.5 eV is caused by external perturbations and does not appear in isolated C_{60} molecules. We show that a resonance near 2.5 eV is observed in *frozen* solutions of C_{60} in CS_2. This resonance disappears as the solution melts.

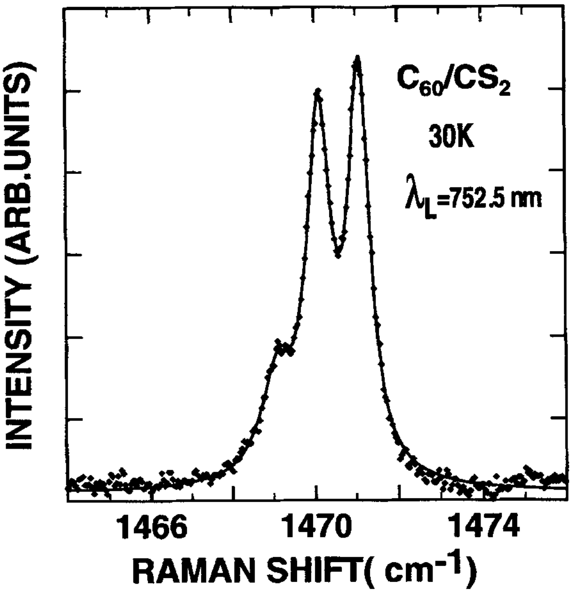

Figure 1 The Raman spectrum of C_{60} in the vicinity of the pentagonal-pinch totally symmetric A_g mode.

Solutions of C_{60} in CS_2 were prepared by dissolving a few milligrams of commercially available high-purity C_{60} in 2 ml of CS_2. Typical molar concentrations were in the 0.003 - 0.006 M range. The solutions were placed in a cryogenic dewar, and the Raman spectra were obtained using most of the visible lines of an Ar+ and a Kr+ laser. The scattered light was detected with a SPEX 1404 0.85 m double monochromator equipped with a CCD array detector.

Figure 1 shows a typical Raman spectrum corresponding to the 1470 cm^{-1} pentagonal-pinch A_g mode from a frozen solution. Three closely spaced peaks are clearly resolved. These peaks can be assigned to C_{60} molecules with different isotopic composition. A complete analysis of the isotopically split lines has been submitted elsewhere. As the solution melts, the peaks broaden and the isotopic structure is no longer resolved.

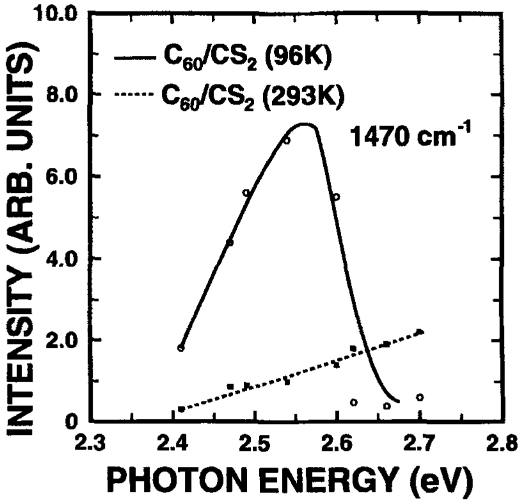

Figure 2 Raman excitation profiles for the pentagonal pinch mode of C_{60} in frozen and room-temperature solutions in CS_2.

Figure 2 shows Raman excitation profiles for the pentagonal pinch mode in frozen and room-temperature solutions. The Raman intensities were normalized to the 650 cm^{-1} Raman peak of CS_2. A clear resonance - similar to the one previously obtained at room temperature in crystalline films - is observed in frozen solutions. However, at room temperature one obtains the pre-resonant line shape that might be expected for isolated C_{60} molecules if the first strong optically allowed transition is placed at 3.6 eV, as is suggested by the optical absorption data. The interpretation of Fig. 2 is straightforward.

When the solution is frozen, the solvent-C_{60} interaction breaks the inversion symmetry that prevents the HOMO-LUMO transition in the isolated molecule, in much the same way that C_{60} - C_{60} coupling renders the transition allowed in the solid.[4] As the solution melts, the rapidly moving C_{60} and CS_2 lead to an almost spherical perturbation which preserves the selection rule forbidding the transition. If the transition responsible for the Raman resonance were optically allowed, one should observe a resonance in frozen as well as in room temperature solutions.

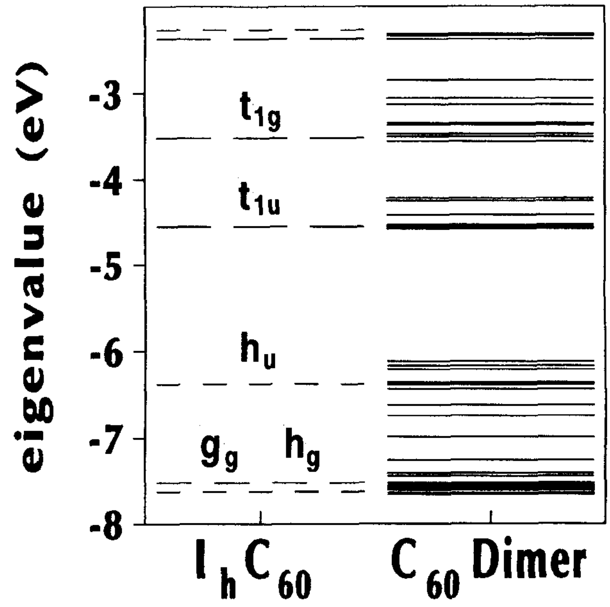

Figure 3 Energy level diagram near the HOMO-LUMO gap for molecular C_{60} and the C_{60}-C_{60} dimer. The number of repeated horizontal dashes indicates the degeneracy of the states.

Under moderate photoexcitation in the visible, C_{60} polymerizes.[7] Fig. 3 shows the predicted lineup of molecular orbitals for a C_{60}-C_{60} dimer compared to C_{60}, calculated using the first-principles approach of Adams et al. (Ref. 8) The six lowest unoccupied states (in order of increasing energy) belong to the b_{1u}, a_g,

b_{2u}, b_{3g}, b_{2g} and b_{3u} one-dimensional irreducible representations of the D_{2h} symmetry group of the dimer. It is apparent from Fig. 3 that these states are mainly derived from the three-fold degenerate t_{1u} states of two C_{60} molecules that form the dimer. The ten highest occupied levels (in order of decreasing energy) belong to the b_{3u}, b_{2g}, a_u, b_{3g}, b_{2u}, b_{1g}, a_u, b_{1g}, a_g and b_{1u} irreducible representations of D_{2h}. Unlike the case of the t_{1u}-related unoccupied states, the formation of the dimer mixes the occupied states very heavily. This can be seen in Fig. 3, where the occupied states of the dimer cannot be ascribed to a particular molecular orbital of C_{60}. Hence the ten highest occupied states indicated above will not only contain an icosahedral h_u component, but also significant h_g and g_g contributions. A total of 22 transitions between the 10 highest occupied dimer states and the six lowest unoccupied states are optically allowed. These transitions become allowed because of the mixing of even and odd occupied molecular orbitals and also because a transition between the h_u occupied state of a C_{60} molecule and the t_{1u} unoccupied state of the *other* C_{60} molecule in the dimer is not forbidden by symmetry. This means even without heavy mixing of the molecular orbitals of isolated C_{60} we would obtain allowed transitions, although their strength might be small depending on the overlap between the wave functions of the two molecules.

The above analysis argues that the origin of the allowed optical transitions in the dimer is conceptually the same as proposed for solid C_{60},[4] but since the bonding between the two C_{60} molecules is covalent, a stronger overlap between the states involved in the optical transition might be expected. However, a comparison of the calculated width of the t_{1u} conduction band in solid C_{60}, (~ 0.4 eV, see Ref. 9) with the total splitting of the t_{1u} manifold in the C_{60} dimer (0.35 eV, see Fig. 3), and a comparison of the widths of the valence band in the solid (0.6 eV according to Ref. 9) with the total separation of 1.6 eV between the occupied states in Fig. 3 shows that these quantities are of the same order of magnitude. Hence it is by no means obvious that a stronger Raman resonance should be expected. In fact, our experimental data suggests that the Raman resonance is weaker in polymerized C_{60}.

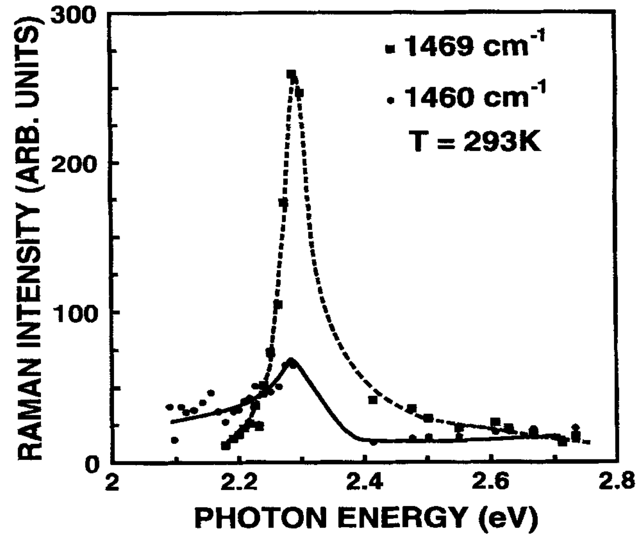

Figure 4 Raman excitation profiles for C_{60} and polymerized C_{60}. The relative magnitudes have not been corrected for the different absorption coefficients of the two materials.

Figure 4 shows Raman excitation profiles for the 1460 cm^{-1} Raman line assigned to polymerized C_{60} and the 1469 cm^{-1} line of pristine C_{60}. The data were obtained from the same film. Polymerized C_{60} was formed by increasing the laser power. The Raman intensities were measured relative to the 520 cm^{-1} Raman line of Si and normalized to the same incident power. No further corrections were applied. A resonance is clearly observed near 2.3 eV in the polymerized film, but the experimental data shows that the 1460 cm^{-1} remains considerably weaker than the 1469 cm^{-1} line for all laser wavelengths. A definitive comparison between the Raman intensities in pristine and polymerized C_{60} will not be possible until reliable absorption data become available. Photoluminescence experiments show emission from polymerized C_{60} at lower energies than in pristine C_{60}, and low-energy absorption peaks have been reported from irradiated solutions.[4] Thus it is reasonable to assume a higher absorption coefficient for the polymer, which would lead to a weaker apparent Raman resonance. More research is needed to extract accurate relative cross sections. From the available data, however, it is probably safe to conclude that the Raman cross section is not dramatically enhanced in the polymer, and this fact appears to be consistent with electronic structure calculations.

In summary, our experiments in frozen and room-temperature solutions of C_{60} in CS_2 provide additional evidence that the observed resonance in the Raman excitation profiles in C_{60} near 2.5 eV are extrinsic and cannot be assigned to an allowed optical transition in the isolated molecule. Results from polymerized films are consistent with this scenario, although a quantitative evaluation of Raman excitation profiles in polymerized films requires careful measurements of their absorption coefficient.

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