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D-Term Scattering in the Resonance Raman Spectrum of C_{60}

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To date, D-term or non-adiabatic scattering[1] in a resonance Raman (RR) spectrum has been observed only in a small number of transition metal complexes: some metalloporphyrins and mixed-valence compounds.[2] We now report its observation in C_{60}. This is phenomenologically significant and is also important because interpretation of the enhancement mechanism illustrates the presence of substantial non-adiabatic vibronic coupling, through D-term scattering, between certain excited electronic states of C_{60}. The mixing of electronic excited states is important in understanding the photophysics and photochemistry of fullerenes and for gaining insight into the conductivity and superconductivity of fullerene-based materials. C_{60} also presents the first opportunity to observe resonance intensity enhancement of a Raman band assigned to a mode of h_g (5-fold degenerate) symmetry. This has been observed in the resonance Raman spectrum of C_{60} in toluene for the h_g mode at 1421 cm^{-1}.

D-Term contributions to Raman scattering intensity become important when there is a breakdown in the Born−Oppenheimer approximation.[2−5] They must be considered for systems that have two close-lying excited electronic states involved in intersystem crossing. D-Term scattering is characterized by the greater intensity of a vibrational band when the incident radiation is in resonance with a 0−1 transition compared to when it is in resonance with the corresponding 0−0 transition. In metalloporphyrins, this behavior is seen for a_{2g} modes that vibronically couple the Q state to the higher energy Soret state.[3,5] Analogous to the Q and Soret states of metalloporphyrins are the A and C electronic states of C_{60}.[6] The A state transition arises from the weakly allowed HOMO−LUMO ($1^1T_{1u}-1^1A_g$) and is known as the A_0 transition. The C state transition ($3^1T_{1u}-1^1A_g$) lies to higher energy and is strongly allowed. Like the Q state of metalloporphyrins, the A state of C_{60} also has a 0−1 vibronic side band, the first of which is the ${}^1T_{1u}-1^1A_g + h_g$ squashing mode, or the A_1 transition. In toluene, the A_0, A_1, and C transitions occur at 411, 407, and 336 nm, respectively.

Previously, the only reported work on RR scattering by C_{60}, in both solid state[7] and solution,[8] had been on the pentagonal pinch and breathing a_g vibrational transitions. Detailed studies[9] on the solvent effects on the electronic transitions of C_{60} have enabled us to tune the energies of the A_0 and the A_1 transitions, respectively, with the excitations at 413.10 and 406.67 nm available with the Kr^+ laser. Band analysis of the electronic absorption spectrum in toluene[9−11] (Figure 1) reveals that the laser line at 406.67 nm is at ~95% peak resonance with the A_1 transition and at ~15% peak resonance with the A_0 transition, while the line at 413.10 nm is at ~65% peak resonance with the A_0 transition but is not in resonance with the A_1 transition. Upon resonance with the A_0 (0−0) and A_1 (0−1) transitions, the Raman spectra show that the band for the non-totally symmetric h_g mode[12] at 1421 cm^{-1} has an unusual excitation response. When the excitation line is at 413.10 nm and in resonance with the A_0 transition, this h_g transition becomes resonance enhanced. When the excitation line is at 406.67 nm and in resonance with the A_1 transition, the intensity of this h_g band grows even more markedly, especially with respect to that of the a_g pentagonal pinch mode at 1468 cm^{-1} (Figure 2). Excitation outside the A state manifold, using 457.94-nm radiation of an Ar^+ laser, is characterized by the absence of the h_g transition at 1421 cm^{-1}. A different resonance enhancement mechanism must operate.

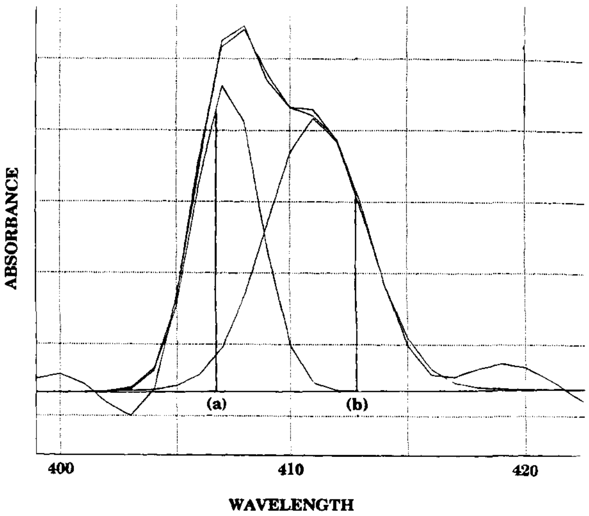

Figure 1. Band analysis of the electronic spectrum of C_{60} in toluene in the region 400−420 nm at room temperature. The wavelengths of the excitation laser lines at 406.67 and 413.10 nm are shown by vertical lines a and b, respectively.

The enhancement of the intensity of a non-totally symmetric

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(1) Light scattering theory predicts that four terms will contribute to the Raman scattering intensity under resonance conditions: the A, B, C, and D terms of the polarizability tensor.[2] The A and B terms are most common, accounting for almost all instances. C-Term scattering has never been observed, while D-term is very rare.[2] The B- and D-term mechanisms represent vibronic coupling between electronic excited states.[2−5]

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(10) C_{60} was prepared and purified according to literature methods,[11] and its purity was established by ${}^{13}C$ NMR spectroscopy. UV−vis and Raman spectra were recorded for saturated solutions in toluene (Merck) using a Cary 5E UV−vis−near-IR spectrophotometer at 0.5-nm resolution (1-cm path length Infrasil cuvette) and a Jobin-Yvon U1000 double monochromator, respectively. Spectra Physics 2025-11 Kr^+ and 2020 Ar^+ lasers provided 406.67, 413.10, and 457.94 nm excitation frequencies, respectively, and the light scattered was sampled from a quartz spinning cell at 90° to the incident 20-mW radiation at 1-cm^{-1} resolution. Band analysis of both the electronic and RR spectra was performed using the WIN-IR curve-fitting program (Bio-Rad WIN-IR Version 2.04 based on GRAMS/386, Galactic Industries Corp., Copyright 1991−1993). The error in the position of the A_0 and A_1 transitions is ±30 cm^{-1}, while it is ±10% for the Raman intensities.

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(12) The h_g mode was predicted from calculations at 1465 cm^{-1} (Negri, F.; Orlandi, G.; Zerbetto, F. *Chem. Phys. Lett.* **1988**, *144*, 31) and found at 1422 cm^{-1} (Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Spectrochim. Acta Sect. A* **1991**, *47*, 1289−1291).

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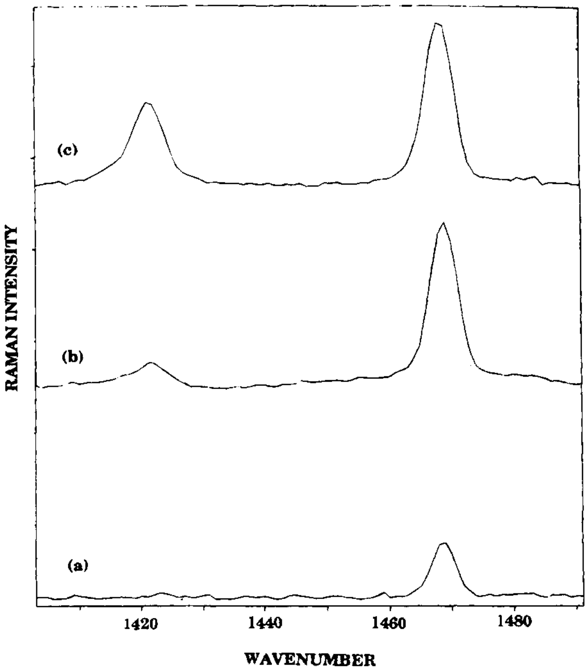

Figure 2. Resonance Raman spectra of C_{60} in toluene at room temperature in the region 1400–1500 cm^{-1}, showing the growth of the h_g band at 1421 cm^{-1} as a function of excitation energy: (a) 457.94, (b) 413.10, and (c) 406.67 nm. The band at 1468 cm^{-1} is the a_g pentagonal pinch mode. The solvent spectrum has been subtracted for clarity.

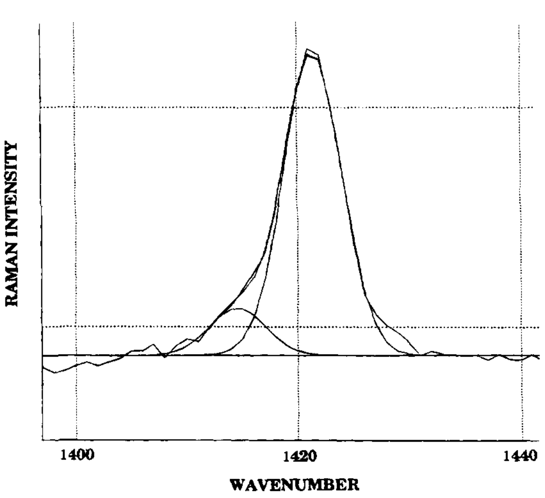

Figure 3. Band analysis of the h_g vibrational transition of C_{60} in toluene at 1421 cm^{-1} with 406.67-nm excitation, showing the splitting of this transition at 1415 cm^{-1}.

transition with 406.67- and 413.10-nm excitation can be explained only by the mixing of the resonant excited state with a second excited state through vibronic coupling with that vibrational mode.[2-5] We postulate that the A state steals intensity from the C state via vibronic coupling. Consistent with this postulate, Leach *et al.*[6] have shown that the ratio of observed and calculated oscillator strengths, $f_{\text{obs}}/f_{\text{calc}}$, is ~20% lower for the C state than for the other allowed transitions. Group theory calculations show that a_g and h_g vibrational modes can couple the A and C excited electronic states, each having T_{1u} symmetry, *viz.* eq 1:

$$T_{1u} \otimes T_{1u} = A_g + [T_{1g}] + H_g \tag{1}$$

Vibronic coupling between excited states may occur by either *B*-term or *D*-term scattering mechanisms. However, for *B*-term scattering, the intensities of the h_g mode at both A_0 and A_1 resonances are the same within the adiabatic approach.[2-5] When non-adiabatic *D*-term scattering mechanisms operate, the expression for the ratio of the intensities for A_0 and A_1 resonant conditions is eq 2:[3]

$$\frac{I_{A_1}}{I_{A_0}} = \left(\frac{\Delta\nu_{AC} + \nu_{h_g}}{\Delta\nu_{AC} - \nu_{h_g}}\right)^2 \tag{2}$$

where I_{A_1} and I_{A_0} are the intensities of the h_g band (1421 cm^{-1}) resulting from resonances with the A_1 and A_0 electronic transitions, respectively. The term $\Delta\nu_{AC}$ is the A–C energy spacing (cm^{-1}), and the ν_{h_g} term is the energy of the h_g transition (cm^{-1}). In toluene, the A–C energy spacing is ~5430 cm^{-1}, and the h_g vibrational energy is ~1420 cm^{-1}. The measured value of I_{A_1}/I_{A_0} is 3.5, which is within experimental error of the value of 2.9 calculated from eq 2 for *D*-term scattering. The value of I_{A_1}/I_{A_0} would better approach the calculated value were a tunable laser source used; however, the important consideration here is that the 406.67- and 413.10-nm lines are exciting essentially only into the A_1 and A_0 transitions, respectively. Clark and Dines[2] suggest that non-adiabatic coupling can arise when the coupled excited states are close together such that their energy spacing is comparable to the vibrational band energy. The energy separation here is less than that observed for the *D*-term scattering of a_{2g} modes in nickel etioporphyrin, as reported by Shelnutt *et al.*[5] and calculated by Rousseau.[3]

The other interesting feature of the resonance Raman spectra of C_{60} is that at 406.67-nm excitation (Figure 3), the h_g vibration is split in toluene and other aromatic solvents but not split in the solid state.[13] The assumed splitting of this h_g band can be interpreted in a number of ways. One recent interpretation suggests that asymmetry arises from ^{13}C splitting.[14] Other interpretations are that the symmetry of C_{60} is slightly lowered in aromatic solvents, removing degeneracy of this h_g transition, or that there are at least two distinct forms of C_{60} on the resonance Raman time scale (10^{-8}–10^{-6} s). That the aromatic solvents interact reasonably strongly with C_{60}, as shown by shifts in the electronic spectra,[9] suggests that the solvent-induced lowering of symmetry is the probable reason for this observation. In addition, because there are not additional bands due to nondegenerate a_g modes, the most reasonable explanation is that there is only one chemical form of C_{60} on the Raman time scale. Enrichment or depletion of the ^{13}C content of C_{60} may be required to differentiate between these possibilities.

Using the solvatochromic dependence of the electronic spectrum of C_{60} to shift the A_0 and A_1 transitions in and out of resonance with the 413.10- and 406.67-nm lines, respectively, a pseudoexcitation profile has been completed and will be reported elsewhere. The low-energy h_g squashing vibrational transition (264 cm^{-1}) shows an interesting intensity response to the 406.67- and 413.10-nm excitations. Previously, this mode has not been reported for RR spectra in solution. Other work has revealed that the a_g pentagonal pinch (1468 cm^{-1}) and the a_g breathing (490 cm^{-1}) vibrational transitions have different excitation responses for A_0 and A_1 resonances despite being of the same symmetry. These results indicate that other RR scattering mechanisms are involved, which include *A*-term, *B*-term, and *A*-term/*B*-term interference scattering, plus Jahn–Teller effects, and are being explored in detail.

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