

Characterisation of the UV, Visible and Near-IR Spectra of the Fulleride Anions C_{60}^{1-} , C_{60}^{2-} and C_{60}^{3-} , and Theoretical Analysis of the Spectra of C_{60}^{1+} , C_{60}^0 , C_{60}^{1-} , C_{60}^{2-} and C_{60}^{3-} by Self Consistent Field-X α -Scattered-Wave (SCF-X α -SW) Calculations

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The spectra of the electrogenerated C_{60}^{2-} , and C_{60}^{3-} ions reveal intense near-IR absorption bands similar to those observed in C_{60}^{1-} ; theoretical analysis of the spectra of C_{60}^z species ($z = 1+, 0, 1-, 2-, 3-$) by SCF-X α -SW calculations provides an explicit interpretation of the strong bands in the UV region, and establishes the nature of the characteristic near-IR bands observed for the cationic and anionic species.

As a three-dimensional delocalised molecule, C_{60}^0 is both a vivid optical chromophore and an electron donor-acceptor. The violet or brown solutions in organic media are dominated by three intense absorption bands, centred at 32 000, 40 000 and 46 000 cm^{-1} and are featureless in the near-IR. Interestingly, the frontier orbital $\pi-\pi^*$ promotion is optically forbidden, though this weak absorption can be located at 16 300 cm^{-1} (2.02 eV)[†] in concentrated solutions. The spectrum of C_{60}^{1-} has been reported in solution at room temperature^{3,4} and in frozen matrices.^{5,6} The three intense UV bands are substantially unchanged from those of C_{60}^0 , but a new band emerges near 9300 cm^{-1} . We now report that the C_{60}^{2-} and C_{60}^{3-} radical anions, along with the C_{60}^{1-} species, have been reversibly generated electrochemically in CH_2Cl_2 at $-60^\circ C$, and in pyridine at $-40^\circ C$, and their optical spectra recorded in a cryostatted optically transparent thin-layer electrode (OTTLE) cell. Fig. 1 illustrates the highly characteristic near-IR spectra of C_{60}^{1-} , C_{60}^{2-} and C_{60}^{3-} .

Table 1 lists the experimental spectroscopic data in the near-IR region for the anionic species.

In each case the leading band is typical of a fully allowed transition, with a rapidly diminishing vibronic progression on the blue edge of the sharp origin.⁷ The near-IR spectrum of C_{60}^{3-} exhibits three absorption bands of comparable intensity, which is not expected for a 4A_u (t_{1u}^3) ground state, although studies on the superconducting compound K_3C_{60}

indicate that the dynamic Jahn-Teller effect is at a maximum for C_{60}^{3-} .⁸ Jones *et al.* have also provided ESR evidence for electron pairing in a distorted C_{60}^{3-} ground state.⁹ This may account for the unexpected complexity of the near-IR manifold. Our data do not exclude the possibility of specific ion pairing of C_{60}^{3-} by electrolyte cation (Bu_4N^+), or with H^+ ions (from traces of moisture), or of labile oligomerisation. All of these could complicate the spectrum of the three-electron reduced species, as could reaction with CH_2Cl_2 . The reductions in pyridine give identical spectra for C_{60}^{1-} and C_{60}^{2-} but the C_{60}^{3-} spectrum lacks the lowest energy component. We stress that the C_{60}^{2-}/C_{60}^{3-} transformation was electrosynthetically reversible in both solvents.[‡]

The wealth of new spectroscopic data has encouraged us to calculate the electronic structures and transition energies for each of the species C_{60}^+ , C_{60}^0 , C_{60}^{1-} , C_{60}^{2-} and C_{60}^{3-} within the SCF-X α -SW approximation.^{10,11} § Fig. 2(a) illustrates how the major spectral features of C_{60}^0 arise as a consequence of the calculated valence-level arrangement. There is pleasing agreement with the parallel calculation of Saito and Oshiyama for C_{60}^0 .¹⁸

[‡] The solution of C_{60}^0 in CH_2Cl_2 -0.5 mol dm^{-3} Bu_4NBF_4 was cycled repeatedly through these oxidation states with no loss of spectral intensity. Near-IR isosbestic points were found at 8875 and 10 100 cm^{-1} for C_{60}^{1-}/C_{60}^{2-} and at 10 300 and 12 500 cm^{-1} for C_{60}^{2-}/C_{60}^{3-} .

§ The coordinates were calculated from the optimised bond lengths of Lüthi and Almlöf¹² (C-C 1.453 and 1.369 Å). The atomic exchange parameters were taken from Schwarz,¹³ and the starting potential was generated from a superposition of Herman-Skillman¹⁴ atomic potentials. The wavefunction was expanded using spherical harmonics up to $L = 1$ on carbon and $L = 6$ on the outer sphere. The Norman criterion¹⁵ was used to determine sphere radii. A Watson sphere¹⁶ of charge +1, +2, +3 and +4 was used for C_{60}^0 , C_{60}^{1-} , C_{60}^{2-} and C_{60}^{3-} respectively. The potential was converged using D_{5h} symmetry, and in each case, the converged ground state potential was used to perform Slater-type transition-state calculations¹⁷ for the excited states.

[†] For closed shell systems, the optical transition energy, $h\nu$, can be approximated by $h\nu = (1 + \rho)\Delta E$,¹ where ΔE is the difference between oxidation and reduction potentials, and ρ is a vibronic coupling constant, typically 0.3 or less. The reduction of C_{60}^0 is observed at -0.45 V vs. the saturated calomel electrode, and Kadish² reports the onset of oxidation at $+1.76$ V, which indicates that $\rho + 1$ is close to unity. We suggest that ρ approaches zero because internal and external reorganisation is likely to be small in such a constrained, non-polar molecule.

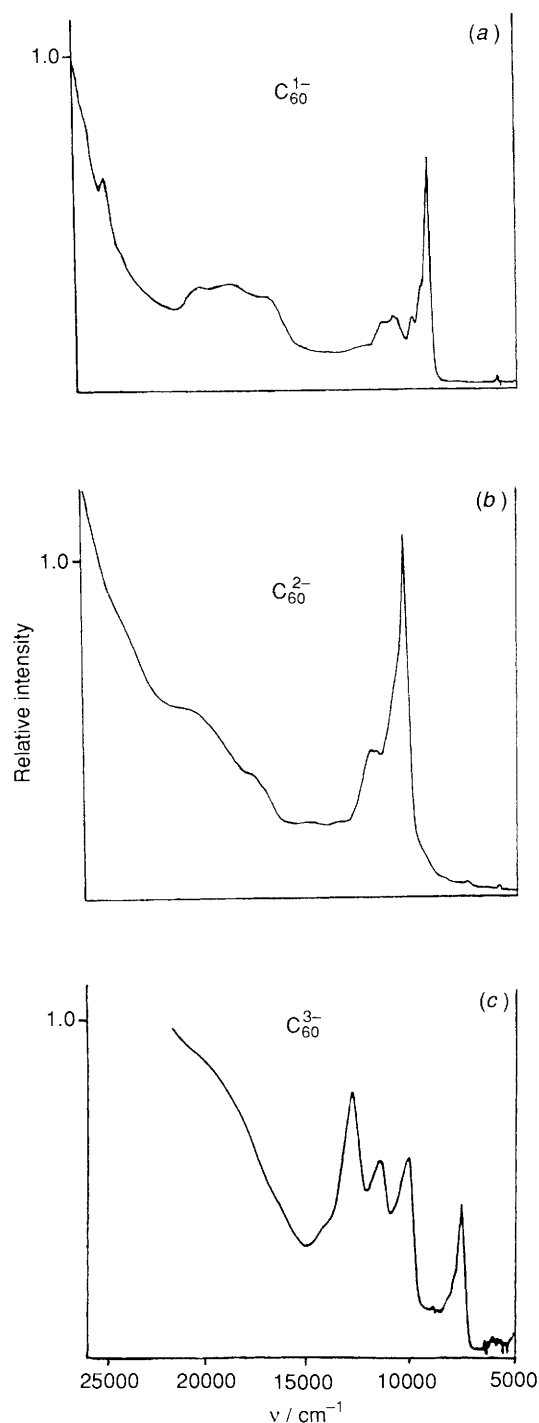


Fig. 1 Near-IR spectra of (a) C_{60}^{1-} , (b) C_{60}^{2-} and (c) C_{60}^{3-} in CH_2Cl_2 at $-60^\circ C$

Table 1 Near-IR bands observed for C_{60}^{n-} ($n = 1, 2, 3$) in CH_2Cl_2

	ν/cm^{-1}	$\epsilon/dm^3 mol^{-1} cm^{-1}$	Configuration
C_{60}^{1-}	9300	12000	$5t_{1u}^1 \rightarrow 2t_{1g}^1$
	10730	3560	
C_{60}^{2-}	10500	18750	$5t_{1u}^2 \rightarrow 5t_{1u}^1 2t_{1g}^1$
	11900	7688	
C_{60}^{3-}	7400 ^a	6700	$5t_{1u}^3 \rightarrow 5t_{1u}^2 2t_{1g}^1$
	10100	8000	
	11400	8000	
	12900	11250	

^a Absent in pyridine solution.

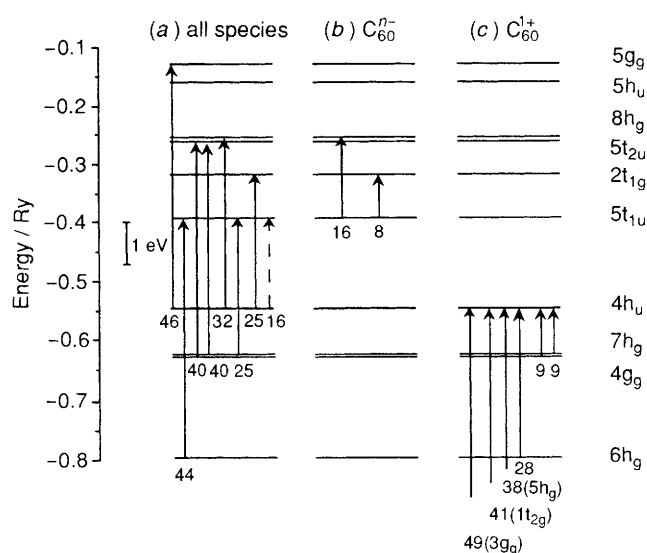


Fig. 2 Transitions contributing to the observed electronic spectra of C_{60}^0 and its ions: (a) transitions in the UV for C_{60}^0 and all derivatives; (b) additional transitions for C_{60}^{n-} arising from promotion from the partially occupied t_{1u} orbital and (c) additional transitions for C_{60}^{1+} arising from promotions into the partially occupied $4h_u$ orbital. \longrightarrow indicates forbidden transition. Approximate transition energies ($\times 10^3 cm^{-1}$) are shown under relevant arrows. $1 Ry \approx 13.61 eV$.

Table 2 Energies/ cm^{-1} of transitions shown in Fig. 2(a, b)

	C_{60}^{+}	C_{60}	C_{60}^{1-}	C_{60}^{2-}	C_{60}^{3-}
$4h_u \rightarrow 5g_g$	45 300	45 500	45 800	46 000	46 200
$6h_g \rightarrow 5t_{1u}$	44 500	44 200	43 900	43 600	43 300
$4g_g \rightarrow 5t_{2u}$	40 300	40 400	40 500	40 700	40 900
$7h_g \rightarrow 5t_{2u}$	39 800	40 000	40 100	40 200	40 300
$4h_u \rightarrow 8h_g$	31 600	31 700	31 700	31 800	31 900
$7h_g \rightarrow 5t_{1u}$	25 500	25 500	25 600	25 600	25 700
$4h_u \rightarrow 2t_{1g}$	24 900	24 900	24 900	24 800	24 800
$4h_u \rightarrow 5t_{1u}^a$	16 500	16 500	16 600	16 600	16 700
$5t_{1u} \rightarrow 8h_g$	—	—	15 200	15 200	15 200
$5t_{1u} \rightarrow 2t_{1g}$	—	—	8 300	8 200	8 100

^a Optically forbidden.

Figs. 2(b and c) show that low-energy (near-IR) transitions are readily anticipated in both C_{60}^{n-} and C_{60}^{1+} .

In the 46 000 to 40 000 cm^{-1} region, where two bands are seen, Fig. 2(a) shows four possible transitions. The observed band at 46 000 cm^{-1} coincides with the $4h_u \rightarrow 5g_g$ transition, while that at 40 000 cm^{-1} coincides with the $7h_g \rightarrow 5t_{2u}$ and $4g_g \rightarrow 5t_{2u}$ transitions (Table 2), but the possibility of a contribution from the $6h_g \rightarrow 5t_{1u}$ transition to one of these bands cannot be excluded.¶

The band found at 32 000 cm^{-1} can be assigned to the $4h_u \rightarrow 8h_g$ transition. The optically forbidden frontier orbital gap transition from $4h_u \rightarrow 5t_{1u}$ is calculated to occur at 16 500 cm^{-1} , which coincides well with experiment. Between these features, the experimental spectrum of C_{60}^0 displays only a very sharp, weak band at 24 800 cm^{-1} , and a much broader, weaker feature in the region 16 000 to 22 000 cm^{-1} . The calculations predict two allowed transitions at 25 000 cm^{-1} , due to the $4h_u \rightarrow 2t_{1g}$ and $7h_g \rightarrow 5t_{1u}$ transitions. Since only

¶ Preliminary calculations of oscillator strengths have been performed (Noodleman's procedure¹⁹ which indicate that the intensities of the $7h_g \rightarrow 5t_{2u}$ and $4g_g \rightarrow 5t_{2u}$ transitions are negligible. This leads us to assign the two bands at 46 000 and 40 000 cm^{-1} to the $4h_u \rightarrow 5g_g$ and $6h_g \rightarrow 5t_{1u}$ transitions.

one band is observed, we conclude that only one of these transitions has non-negligible intensity. There is the possibility of considerable configuration interaction between the T_{1u} states arising from the two almost isoenergetic excited configurations, $4h_u^9 2t_{1g}^1$ and $7h_g^9 5t_{1u}^1$, which may affect both energies and intensities in this region of the spectrum.²⁰

The near-IR spectrum of C_{60}^{1-} defines the energy interval between the $5 = t_{1u}^1$ and $2 = t_{1g}^1$ configurations as 9300 cm^{-1} , thereby empirically mapping the frontier orbital gap of the anion (Fig. 2(b)). In view of the excellent agreement between the SCF-X α -SW calculations and the observed spectrum in the range $15\,000\text{--}50\,000\text{ cm}^{-1}$, it is reassuring that for each of the radical anions C_{60}^{n-} ($n = 1, 2, 3$), a new absorption band system is predicted at about 8200 cm^{-1} (Table 2). No other well-defined new features are observed for the anions, but there is a marked increase in intensity in the region of $17\,000\text{ cm}^{-1}$, which may reflect the $5t_{1u} \rightarrow 8h_g$ transition.

The spectrum of the C_{60}^{1+} cation in the UV region has not been reported. We predict that bands similar to those observed in the neutral and anionic species will be observed in the region $15\,000\text{--}50\,000\text{ cm}^{-1}$, but there will be additional features due to transitions into the now partially occupied $4h_u$ orbital [Fig. 2(c)], occurring at $28\,050$, $38\,000$, $40\,700$ and $48\,900\text{ cm}^{-1}$. The strong band observed in the near-IR at $10\,200\text{ cm}^{-1}$ has been assigned to the $7h_g \rightarrow 4h_u$ transition,⁵ in accord with our calculations, which predict the transitions from the almost isoenergetic $7h_g$ and $4g_g$ orbitals into $4h_u$ orbital to lie in the near-IR region at 9010 and 9450 cm^{-1} , respectively.

The invariance of the major spectral features and of the calculated transition energies across the series C_{60}^0 to C_{60}^{3-} indicates that the relative ordering of orbitals is insensitive to charge. The measured frontier orbital separations, $7h_g \rightarrow 4h_u$ (in C_{60}^{1+}) and $5t_{1u} \rightarrow 2t_{1g}$ (in C_{60}^{1-}) will therefore be very similar to the corresponding separations in C_{60}^0 , where the those transitions are not directly observable, but the $4h_u \rightarrow 5t_{1u}$ transition is. Compiling this empirical information regarding energy level separations indicates that both the $7h_g \rightarrow 5t_{1u}$ and $4h_u \rightarrow 2t_{1g}$ separations are close to $25\,000\text{ cm}^{-1}$, as predicted by the calculations. This lends further weight to our assignment of the band at $24\,800\text{ cm}^{-1}$.

In summary, the electronic spectra of C_{60}^{1-} , C_{60}^{2-} and C_{60}^{3-} have been observed in the $5000\text{--}50\,000\text{ cm}^{-1}$ range in solution, that of C_{60}^{3-} showing unexpected complexity in the

near-IR region, and MO calculations have led to a new and self consistent assignment of the spectrum of C_{60}^0 and its several known ions.

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|| The oscillator strength for $4h_u \rightarrow 2t_{1g}$ is calculated to be negligible, supporting the conclusion of Leach *et al.*²¹ that the band at $24\,800\text{ cm}^{-1}$ is due to $7h_g \rightarrow 5t_{1u}$ transition.