

## Reversible Alkali-metal Reduction of C<sub>60</sub> in Liquid Ammonia; First Observation of Near-infrared Spectrum of C<sub>60</sub><sup>5-</sup>

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A new method for the homogeneous redox manipulation of alkali-metal fullerides with a solution of rubidium in liquid ammonia at -40 °C has been used to prepare the C<sub>60</sub><sup>2-</sup>, C<sub>60</sub><sup>3-</sup>, C<sub>60</sub><sup>4-</sup> and C<sub>60</sub><sup>5-</sup> ions, the near IR spectra being recorded at various stages of the titration; the excitation energy of the main band in C<sub>60</sub><sup>5-</sup> (10 500 cm<sup>-1</sup>) is close to that of C<sub>60</sub><sup>1-</sup> and the principal band in the C<sub>60</sub><sup>2-</sup> spectrum.

The discovery of superconductivity in various alkali-metal-doped fullerides<sup>1,2</sup> has promoted intense study into the electronic properties of these materials. Up to six reversible reduction waves have been detected electrochemically,<sup>3-8</sup> while the characteristic near-IR spectra of the soluble anions C<sub>60</sub><sup>n-</sup> ( $n = 1,2,3,4$ )<sup>5,8-11</sup> have been observed using optically transparent thin-layer electrosynthetic (OTTLE) techniques. This spectral information, in conjunction with calculations, provides information about the electronic structure of the anions of C<sub>60</sub>, which is important for the understanding of the mechanism of superconductivity in fulleride salts. We report

here the first observation of the near-IR absorption spectrum of the C<sub>60</sub><sup>5-</sup> anion, produced by a novel solution-phase technique using rubidium in liquid ammonia, and monitored by near-IR spectroscopy.

The method takes advantage of the newly-discovered solubility of alkali-metal fullerides in ammonia at low temperatures. A full description of apparatus which was constructed to enable the preparation of alkali-metal compounds of C<sub>60</sub> in liquid ammonia will appear in a subsequent publication.<sup>12</sup> The glass vessel consists of three chambers, two of which are calibrated and contained respectively reagent solutions of

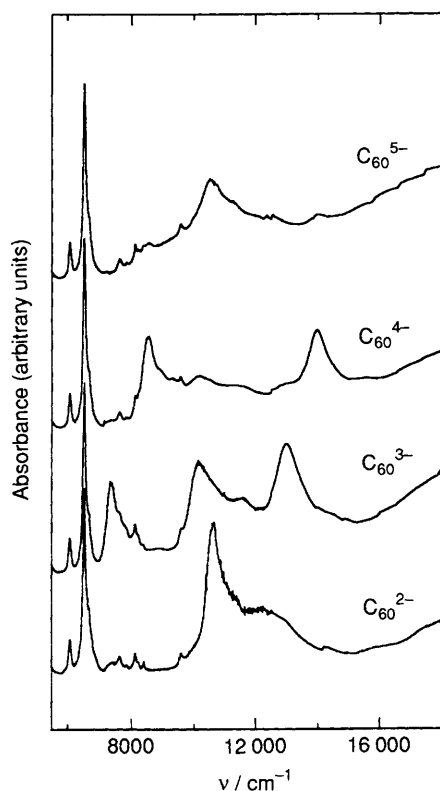


Fig. 1 The electronic spectrum in the near-IR of  $C_{60}^{5-}$ ,  $C_{60}^{4-}$ ,  $C_{60}^{3-}$  and  $C_{60}^{2-}$ , at various stages of the titration of  $C_{60}$  with Rb-liquid ammonia at  $-40^\circ\text{C}$ . Bands below *ca.*  $7000\text{ cm}^{-1}$  are due to the liquid ammonia

rubidium dissolved in liquid ammonia and finely-divided  $C_{60}$  in suspension in liquid ammonia. Metered amounts of these solutions were progressively added to the third chamber, to which was appended a quartz cuvette for spectroscopic measurements. With this equipment, it was possible to 'titrate' aliquots of the rubidium-ammonia solution into the suspension of  $C_{60}$  in ammonia and to observe successive reductions spectroscopically. Subsequent reversal to less-reduced states can be performed by further addition of  $C_{60}$ -ammonia. Spectroscopic monitoring was found to be more precise and informative than relying on stoichiometric addition (although this is also possible using the same apparatus). The three chambers are jacketed and may be maintained at a temperature as low as  $-60^\circ\text{C}$  by the circulation of methanol. A stream of chilled, dry nitrogen prevented boiling of the solvent in the cuvette and frosting of the windows.

As a preparative technique, this arrangement has major advantages over electrochemical syntheses in that the volatile solvent is readily removed, and no workup is required to remove supporting electrolytes. A sample of  $\text{Rb}_3\text{C}_{60}$  prepared in this way has undergone preliminary testing by microwave susceptibility measurements and was found to exhibit superconductivity, although the exact  $T_c$  has not yet been determined.

Spectra obtained for the 2-, 3-, 4- and 5- states are shown in Fig. 1, with peak wavenumbers, approximate absorptivities and comments listed in Table 1. The remarkable similarity of the spectra for  $C_{60}^{2-}$ ,  $C_{60}^{3-}$  and  $C_{60}^{4-}$  shown here to those previously observed using OTTLE techniques with dichloromethane,<sup>8</sup> pyridine<sup>8</sup> and benzonitrile<sup>10</sup> as solvent, is evidence for the relative unimportance of both ion-pairing, where supporting electrolytes were employed, and solvent effects. To our knowledge, this is the first report of the spectrum of  $C_{60}^{5-}$ .

Authentication of this spectrum was provided by several facts: the species could be observed to coexist with that of  $C_{60}^{4-}$ , and therefore, from the known reduction potentials, could not

Table 1 Major near-IR bands observed for  $C_{60}^{n-}$  ( $n = 1, 2, 3, 4, 5$ ) in solution

Species	$\nu/\text{cm}^{-1a}$	$\nu - \nu_0/\text{cm}^{-1}$	$\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1b}$	Comments <sup>c</sup>
All	5000–7000			Liquid ammonia bands
$C_{60}^{1-d}$	9300	0	—	FC max $t_{1u}^1 \rightarrow t_{1g}^1$
	9650	350	—	$T_{2u}, G_u$
	10080	780	—	$H_u, H_g, T_{2u}$
	10750	1450	—	$A_g, T_{1u}, G_u, H_g$
	10950	1650	—	$T_{2u}, H_g, H_u$
$C_{60}^{2-}$	(7390)		Weak	Probable 3- peak
	10600	0	5600	FC max $t_{1u}^2 \rightarrow t_{1u}^1 t_{1g}^1$
	10900	300	Medium	Shoulder, $G_u, H_g$
	11350	750	Medium	Shoulder, $H_u, H_g, T_{2u}$
	12300	1700	2500	$H_g, H_u$ /or FC max
	(12890)		Medium	Shoulder, probable 3- peak
$C_{60}^{3-}$	7370	0	52000	FC max $t_{1u}^3 \rightarrow t_{1u}^2 t_{1g}^1$
	8780	1400	Weak	$A_u, T_{1u}, H_g$
	10150	0	6300	FC max
	11550	1400	4200	$A_u, T_{1u}, H_g$
	13000	0	7400	FC max
	14400	1400	3400	$A_u, T_{1u}, H_g$
$C_{60}^{4-}$	(7370)		Weak	Probable 3- peak
	8500	0	5500	FC max $t_{1u}^4 \rightarrow t_{1u}^3 t_{1g}^1$
	8900	400	Medium	$G_g, H_u, H_g$
	(10200)		3200	Probably 3-
	(11600)		2600	Probably 3-
	14000	0	6000	FC max
15600	1600	Medium	$G_g, H_g$	
$C_{60}^{5-}$	(8550)		Weak	Probable 4- peak
	10500	0	7180	FC max $t_{1u}^5 \rightarrow t_{1u}^4 t_{1g}^1$
	11250	750	Weak	Shoulder $T_{2u}, H_g, H_u$
	12100	1600	Weak	Shoulder $G_g, H_g$

<sup>a</sup> Precision of measured wavenumbers is estimated to be  $\pm 30\text{ cm}^{-1}$  on the major peaks (designated as Frank-Condon maxima [FC<sub>max</sub>]). Not listed here are the two peaks common to each spectrum and assigned to overtone and combination bands of liquid ammonia. They are, with probable assignments:  $6085\text{ cm}^{-1}$  (weak),  $\nu_2 + \nu_3 + \nu_4$ ;  $6535\text{ cm}^{-1}$ ,  $2\nu_1$  (and  $2\nu_3, \nu_1 + \nu_3$ ). Parentheses indicate peaks probably due to other species. <sup>b</sup> It was only possible to determine approximate values for molar absorptivities due to uncertainties in solvent volumes, however this will be overcome in future experiments of this type. <sup>c</sup> Vibrational assignments were determined by accepting fundamental vibrations within  $\pm 50\text{ cm}^{-1}$  of the measured frequency difference. Experimental data<sup>20,21</sup> were used where available in preference to calculated values. <sup>d</sup> Values obtained in  $\text{CHCl}_2$  solution using OTTLE techniques from ref. 8. These are included to emphasise the similarities to the  $C_{60}^{2-}$  and  $C_{60}^{3-}$  spectra; solvent effects have been shown to be negligible. Experimental difficulties prevented the observation of the spectrum of the monoanion in liquid ammonia.

be the 6- species; it was possible to recover the 4-, 3- and 2- species sequentially from the postulated 5- state by further addition of an appropriate aliquot of  $C_{60}$ -ammonia. Finally the spectrum was observed to be very similar to that of  $C_{60}^{1-}$ , as would be expected given the complementary nature of the  $t_{1u}^1$  and  $t_{1u}^5$  states. Further addition of Rb-ammonia to the 5- species resulted in an abrupt change in the near-IR region, with the disappearance of the  $C_{60}^{5-}$  spectrum, and the appearance of a broad absorption, characteristic of solvated electrons and typical of the spectra of alkali metals in ammonia.<sup>13</sup> The  $C_{60}^{5-}$  spectrum was recoverable from this solution by comproportionation with addition of further  $C_{60}$ -ammonia.

The existence of absorbances in the near-IR of the anions of  $C_{60}$  can be predicted from MO diagrams<sup>14</sup> which show that the HOMO and LUMO orbitals for the anions are the closely

spaced, triply degenerate  $t_{1u}$  and  $t_{1g}$  orbitals respectively. Such simple diagrams account for the similarity of the  $C_{60}^{1-}$  and  $C_{60}^{2-}$  spectra if one assumes weak electron–electron interactions in  $C_{60}^{2-}$  but do not explain the multiple peaks observed for  $C_{60}^{3-}$  and  $C_{60}^{4-}$ . The features on the high-frequency side of the single major peaks of the spectra of  $C_{60}^{1-}$  and  $C_{60}^{2-}$  have provoked suggestions that the electronic state degeneracy is appreciably lifted by the Jahn–Teller effect.<sup>10</sup> It would appear, however, that in a molecule as large as  $C_{60}$  any such distortions would be small, and unlikely to cause splittings of the observed magnitude, except possibly in the case of  $C_{60}^{3-}$  ion, for which Jahn–Teller effects are at a maximum.<sup>15</sup>

A possible explanation<sup>9</sup> for at least some of the extra peaks is vibrational structure. We note that this structure in the spectra of  $C_{60}^{1-}$ ,  $C_{60}^{2-}$  and  $C_{60}^{5-}$  is similar though fine detail is limited for instrumental reasons. Some provisional vibrational assignments are given in Table 1 and it is, perhaps, of note that  $H_g$  fundamentals are involved in a number of the progressions. One immediately obvious point is that plausible assignments can be made using vibrations close in frequency to known<sup>16–18</sup> ground state fundamentals. This relative insensitivity of the excited state vibrational frequencies to  $C_{60}$  oxidation state mirrors what has been found for the ground state.<sup>19,20</sup> Further experiments at higher resolution are underway to elucidate the interpretation of this structure.

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