Electronic and infrared spectra of C_{60}^+ and C_{60}^- in neon and argon matrices

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The electronic transitions of C_{60}^+ and C_{60}^- isolated in 5 K neon matrices were detected with well-resolved vibrational structure after NeI irradiation of C_{60} during deposition. On the basis of a C_{60}^+ spectrum obtained by growing a matrix with a mass-selected C_{60}^+ ion beam, overlapping peaks in the electronic spectra were assigned to either C_{60}^+ or C_{60}^-. The vibrational frequencies 1406 and 1332 cm^{-1} for C_{60}^+, and 1386 and 1202 cm^{-1} for C_{60}^-, were identified in a neon matrix from the infrared spectrum. C_{60}^- was also detected after codepositing Na and K with C_{60}, without irradiation. Relevance of the data to interstellar observations is discussed.

1. Introduction

C_{60} has been the most widely studied molecule of the last few years. There are a number of review articles describing the properties of this fascinating molecule [1–4]. However, we focus here on the spectroscopy of the cation and anion of C_{60}.

C_{60}^+ and C_{60}^- are highly symmetric systems with incompletely filled degenerate molecular orbitals in the ground and excited electronic states. According to the Jahn–Teller theorem such systems are subject to symmetry lowering by static or dynamic distortions. This was studied theoretically, for the anion as well as cation, and the energy differences of the resulting structures were calculated [5–7]. The distortions also explain the broadness of the C_{60}^- ESR signal [8,9].

In this work electronic spectra of C_{60}^+ and C_{60}^-, better resolved than previously reported [10,11], as well as their infrared spectra are presented. The knowledge of the origin of the electronic transitions of the ions as well as of some of the infrared frequencies is of interest in connection with astrophysical observations and conjectures of the occurrence of these species in extra-terrestrial environments [12,13]. There is also considerable interest in C_{60}^{x-} anions due to the superconductivity in alkali metal-doped C_{60} solids [14–17]. In connection with the latter state-

ment we were able to observe the electronic transition of C_{60}^- by codepositing K, or Na, with C_{60} without irradiation.

2. Experimental

The C_{60} sample was separated from carbon soot by extraction in toluene and purified by column chromatography [18]. The mass spectrum of the sample showed traces of C_{70}. To remove the volatile solvents the C_{60} samples were heated under vacuum to 250°C for several hours.

Three types of experiments were carried out.

(1) C_{60} (oven temperature: 480°C) was codeposited with Ne or Ar on a rhodium mirror held at 5 or 10 K, respectively, while irradiating with NeI photons.

(2) The same experiment as (1) was conducted but with the addition of CCl_4 to the argon matrix, or by codepositing Na (oven temperature: 220°C) with Ar and C_{60}.

(3) Codeposition of a mass-selected C_{60}^+ ion beam (10–20 nA) with neon [19]. In the experiments (1) and (2) C_{60}^- was formed by electron capture.

The apparatus used in this study was the same as described in ref. [19]. Absorption spectra in the range from 600–20000 cm^{-1} were measured using a

Fourier transform spectrometer. In the case of the experiments with mass-selected C_{60}^+ ions, the transmission spectrum was measured with the wave-guide technique [20].

3. Results and discussion

3.1. Electronic absorption of C_{60}^+

The electronic absorption spectrum of C_{60}^+ was first recorded by Kato et al. [10] after γ-irradiation of a glassy solution of C_{60}. It exhibited poorly resolved vibrational structure. A better resolved spectrum was obtained by ArI photoionization of C_{60} isolated in an argon matrix, whereby C_{60}^+ and C_{60}^- were produced simultaneously [11]. The lowest-energy electronic absorption of these ions lies in the near-infrared region and the band systems overlap. Identification of the C_{60}^+ absorption peaks was achieved by codeposition of C_{60} with CCl_4, which works as an electron scavenger and suppresses C_{60}^- formation.

In the present study the lowest electronic absorption of C_{60}^+ was detected after NeI irradiation of C_{60} during deposition (fig. 1, trace (b)) or after codepositing Ne with a mass-selected C_{60}^+ ion beam of 10–20 nA (fig. 1, trace (a)). In both cases the vibra-
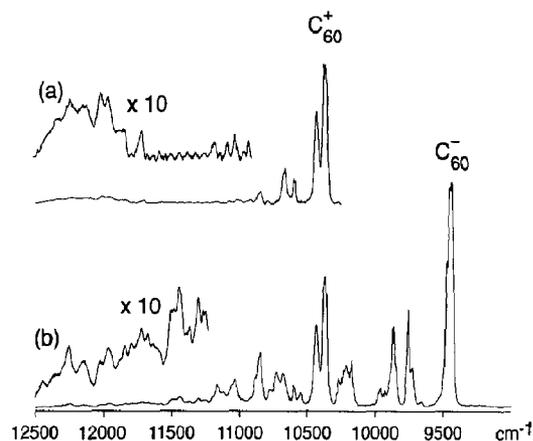

Fig. 1. Electronic absorption spectrum of: (a) C_{60}^+ obtained by growing a neon matrix with a mass-selected ion beam; (b) C_{60}^+ and C_{60}^- generated in a neon matrix upon NeI irradiation during deposition of C_{60} with neon.

tional structure is discernible. On the basis of the mass-selected C_{60}^+ spectrum we are able to unambiguously assign the vibrational progressions to either C_{60}^+ or C_{60}^-. The origin band of the C_{60}^+ electronic transition lies at 10368 cm^{-1} in the neon matrix and is blue-shifted by 90 cm^{-1} with respect to that in argon [11]. The latter is further blue-shifted by 80 cm^{-1} in comparison to that in a freon matrix [10].

Semi-empirical [21,22] and ab initio [23] calculations for C_{60} predict a fivefold degenerate h_u symmetry for the HOMO orbital and, thus, a ^2H_u ground state of C_{60}^+. Ejection of one electron from the lower-lying orbitals gives ^2H_g and ^2G_g excited electronic states of C_{60}^+. Both states are accessible from the ground state by dipole-allowed electronic transitions and their energies are calculated by INDO to be 8600 and 8900 cm^{-1} respectively [5].

The electronic absorption spectrum of C_{60}^+ should show the excitation of the totally symmetric modes in single quanta with other symmetry vibrations, possibly excited by two quanta. Though there are no theoretical calculations of vibrational frequencies of C_{60}^+, their values should not differ drastically from those of C_{60}. If we compare the frequencies of the a_g modes of C_{60} ($\nu_1 = 1469$ cm^{-1}, $\nu_2 = 497$ cm^{-1} [24,25]) with those inferred from the electronic spectrum of C_{60}^+ (table 1) we see that I_h symmetry is not appropriate in describing the spectroscopic behavior of C_{60}^+ in rare-gas matrices. The ground ^2H_u as well as excited ^2H_g and ^2G_g electronic states of C_{60}^+ undergo a dynamic or static Jahn–Teller distortion along h_g and g_g normal coordinates leading to lower D_{5d}, D_{3d} or D_{2h} symmetry [26]. An INDO calculation on C_{60}^+ in these geometries yields a 8.1 kcal/mol stabilization energy (with respect to I_h symmetry) for an $^2A_{1u}$ ground state in D_{5d} symmetry [5].

In D_{5d} symmetry the $^2E_{1g} \leftarrow ^2A_{1u}$ transition of C_{60}^+ is calculated at 8630 cm^{-1}, close to the observed absorption band system (origin at 10368 cm^{-1} in neon matrix). The eight h_g modes (in I_h symmetry) yield an a_{1g} component in the reduced D_{5d} geometry. Table 1 lists a collection of frequencies of the vibrational peaks associated with the C_{60}^+ electronic band system in 5 K Ne and 10 K Ar matrices. These were identified by the different measurements outlined in section 2. In trace (a) of fig. 1, using mass-selected C_{60}^+ deposition, most of the bands are clearly seen.

In the vicinity of the 0_0^0 band of C_{60}^+ there is a

Table 1
Wavenumbers (cm^{-1}) of the observed absorption peaks in the spectrum of C_{60}^+ isolated in argon and neon matrices

Ar matrix	Δ	Δ'	Ne matrix [a]	Δ	Δ'	Assignment [b]
10282	0		10368 [c]	0		0^0_0
10355 [d]	87	0	10435	67	0	$0^{0'}_0$
10526	244		10603	235		$\nu_8(h_g)$
10600		245	10667		232	$\nu'_8(h_g)$
			10792	424		$\nu_7(h_g)$
10770		415	10845		410	$\nu'_7(h_g)$
			10922		487	$\nu'_2(a_g)$
			11082		647	$\nu'_6(h_g)$
11090		735	11165		730	$\nu'_5(h_g)$
11644		1289	11715		1280	$\nu'_3(h_g)$
			11841		1406	$\nu'_2(h_g)$
11882	1600		11955	1586		$\nu_1(h_g)$
			12012		1577	$\nu'_1(h_g)$

[a] Wavenumbers taken from mass-selected spectrum.
[b] Using C_{60} mode numbering [24,25]; see also text.
[c] Multiplet components at 10359, 10368, 10372 and 10377 cm^{-1}.
[d] Shoulder.

strong peak 67 cm^{-1} to higher energy in the neon matrix which is seen merely as a shoulder in argon. The energy spacing of 67 cm^{-1} is too small for a vibrational mode of C_{60}^+. This is probably because the spectrum comprises two overlapping electronic transitions with origins at 10368 and 10435 cm^{-1} (the latter forming longer progressions), corresponding to two slightly different C_{60}^+ structures trapped by the matrix environment, one of which has D_{5d} geometry. The relative intensities of these two band systems depend on experimental conditions. In the case of mass-selected ion deposition the system with the blue-shifted origin becomes slightly more intense than in photoionization experiments. The stabilization of distorted structures for degenerate states of symmetric cations, e.g. CH_4^+, $C_6H_6^+$, in rare-gas matrices is shown by their ESR spectra [27].

Alternative explanations are that the two peaks correspond to spin–orbit components in the excited degenerate state of C_{60}^+ [11] or that the second peak is a phonon band (neon Debye frequency: 75 cm^{-1} [28]). However, if the peak displaced by 67 cm^{-1} is a phonon sideband, it is surprising, in view of its high intensity, that higher excited phonon modes are not discernible.

C_{60}^+ as a potential interstellar molecule [12,13] could be detected by its electronic absorption in the near infrared. In order to estimate the location of its absorption in the gas phase, the known gas-neon matrix shifts of unsaturated hydrocarbons ($H(C\equiv C)_nH^+$, $n=2$, 3, 4) were compared [29]. These are 100–150 cm^{-1} to higher energies in the gas phase. Thus the origin of the C_{60}^+ gas-phase transition should lie in the 965–951 nm range. However, spectral observations of diffuse interstellar bands are presently not available at these wavelengths.

For the purpose of interstellar observations, the mean oscillator strength of the overlapping band systems of C_{60}^+ was evaluated to be 0.003–0.006. This value was calculated using the published extinction coefficient of the anion, $(3\pm1)\times10^4$ dm^3 mol^{-1} cm^{-1} in a freon matrix [10], assuming equal concentrations of C_{60}^+ and C_{60}^-, with the formula $f=4\epsilon_0 m_e c^2 \ln(10)(N_A e^2)^{-1}\int\epsilon(\tilde{\nu})\,d\tilde{\nu}$. The integrated oscillator strength thus estimated is an order of magnitude smaller than a theoretical value [5]. Furthermore, C_{60}^+ shows no other absorption bands in the 300–900 nm range with $\epsilon > 1000$ dm^3 mol^{-1} cm^{-1}. This conclusion can be drawn on the basis of matrix measurements with a mass-selected C_{60}^+ ion beam, where C_{60} absorption is absent in contrast to γ-irradiation or photoionization experiments.

3.2. Electronic absorption of C_{60}^-

C_{60} has a high electron affinity, 2.60 eV [30], and C_{60}^-, as well as C_{60}^{2-}, have been observed in the gas phase [31]. In addition the C_{60}^{n-} ions ($n \leqslant 6$) were generated in solution upon cathode reduction of C_{60} and the electronic absorption spectra of C_{60}^{n-} ($n=1-3$) were reported [32–35].

The spectrum of C_{60}^- isolated in a 5 K neon matrix extends from 9449 cm^{-1} (origin) to 12300 cm^{-1} and has a rich vibrational structure (fig. 1, trace (b)). The 0_0^0 band shows a multiplet structure with separations of 6, 7 and 24 cm^{-1}. A multiplet structure is also apparent in a good quality argon matrix, where C_{60} ions were produced by photoionization with a sealed Xe discharge lamp. This structure can be due to different distorted geometries stabilized by the matrix environment (vide infra). As with C_{60}^+, the 0_0^0 transition of C_{60}^- in neon is blue-shifted by 90 cm^{-1} relative to the argon matrix value [11]. Many weaker peaks not seen in the previously reported spectrum (the present absorption is ≈ 10 times stronger – fig. 1) are apparent and are distinguished from those of C_{60}^+ by reference to the data obtained by mass selection.

According to theoretical calculations [21–23,36], the ground state of C_{60}^- has $^2T_{1u}$ symmetry, which corresponds to a singly occupied LUMO of C_{60}. The first- and second-excited electronic states, which can be reached from the ground state in a dipole-allowed transition, have $^2T_{1g}$ and ^2H_g symmetry. They are estimated, on the basis of calculated orbital energies of C_{60} [23], to lie 1.62 and 3.1 eV above the ground state. On the other hand, a PPP CI calculation on C_{60}^- gives the energies of these states at 0.37 and 2.58 eV [37]. The 0_0^0 transition in a neon matrix is found at 1.17 eV.

The Jahn–Teller distortion of the ground $^2T_{1u}$ and excited $^2T_{1g}$ states of C_{60}^- leads to symmetry lowering to D_{5d} or D_{3d} [38]. Ab initio calculations at optimized D_{5d}, D_{3d} and D_{2h} geometries [7], give a similar energy for all distorted structures, which lie 2 kcal/mol below C_{60}^- in I_h symmetry.

The theoretical results and the fact that the electronic absorption of C_{60}^- has rich vibrational structure (fig. 1, trace (b)), suggest that the symmetry is lower than I_h. Thus the observed near-infrared absorption can be interpreted as the $^2E_{1g} \leftarrow ^2A_{2u}$ elec-

tronic transition in D_{5d} symmetry. As all h_g modes (in I_h) yield a totally symmetric component (a_{1g}) in D_{5d} symmetry, the observed vibrational pattern of the electronic absorption spectrum can be assigned to progressions and a combination of the a_{1g} modes in the excited state (table 2).

3.3. Infrared spectra of C_{60}^+ and C_{60}^-

In addition to the electronic absorption of C_{60}^+ and C_{60}^-, NeI irradiation during deposition of C_{60} produces new peaks in the 1450–1100 cm^{-1} region (fig. 2). It was demonstrated by Jacox's group [39,40], that NeI photoionization of matrix-isolated species generates ions in a concentration sufficient to measure their infrared spectra. New peaks which appeared in the infrared spectrum of matrix-isolated C_{60} are attributed to C_{60}^+ and C_{60}^- (fig. 2, trace (b)).

As the C_{60} ions appear to have symmetry lower than I_h in rare-gas matrices, more than the four t_{1u} modes (in I_h) should be infrared active for each species. One expects that the strongest infrared transitions of C_{60} ions are those which are allowed in I_h symmetry. Two vibrations lie below 600 cm^{-1} and are out of the range of our detector. The other two vibrations should fall in the range 1450–1100 cm^{-1}. If we eliminate the known C_{60} peaks at 1432 and 1185 cm^{-1} [24], and the peaks at 1264 cm^{-1} (unidentified) and 1308 cm^{-1} (CH$_4$), which are present in the matrix before NeI irradiation, the four bands at 1406, 1386, 1332, 1201 cm^{-1} are associated with C_{60} ions (fig. 2).

To our knowledge there are no theoretical calculations of the vibrational frequencies of C_{60}^+, and the t_{1u} modes are not given in the C_{60}^- calculation [41]. As the presently attainable ion concentration with the mass-selected method is too low, it is not applicable for the infrared studies in matrices. However, the relative concentrations of C_{60}^+ and C_{60}^- can be altered by codepositing C_{60} with either alkali metals (K, Na) or with CCl$_4$, NO$_2$.

The observed electronic absorptions are shown in fig. 3, and the corresponding infrared spectra in fig. 4. The intensities of the infrared peaks at 1386 and 1201 cm^{-1} increase after the addition of alkali metals and decrease after the addition of electron scavengers to the matrix, and are thus assigned to C_{60}^-.

Table 2
Wavenumbers (cm^{-1}) of the observed absorption peaks in the spectrum of C_{60}^- isolated in neon and argon matrices. Weak peaks are marked with "w"

Ar matrix	Ne matrix	Δ (Ne matrix)	Assignment [a]	C_{60} ground state frequencies [24,25]
9363	9443 9449 9455 9479	0	0_0^0	
9592	9655w 9671w 9678w	222		
9678	9726 9734 9758 9764 9773	309	ν_8	270(h_g)
9790	9850 9865 9869	416	ν_7	431(h_g)
	9872w 9889w 9930w 9943w			
9895	9964 9971	514	ν_2	497(a_g)
10129	10173 10213 10273	764	ν_5	773(h_g)
	10555	1106	ν_4	1099(h_g)
10661	10728	1279	ν_3	1248(h_g)
	10771	1322		
10770	10848 10859 [b] 10882	1399	ν_2, ν_1	1426(h_g), 1469(a_g)
	11022			
10957	11033	1584	ν_1	1574(h_g)
	11056			
	11122	1673	$\nu_3 + \nu_7$	
	11254	1805	$\nu_2 + \nu_7$	
	11268			
	11305	1857	$\nu_4 + \nu_5$	
	11368	1920	$\nu_2(a_g) + \nu_2(h_g)$	
	11430w			
	11445w±5	1993	$\nu_1 + \nu_7$	
	11508w±5	2057	$\nu_3 + \nu_5$	
	11670w±5	2251		
	11785w±5	2336	$\nu_1 + \nu_5$	
	11844w±5	2396	$\nu_3 + \nu_4$	
	12029w±5	2564	$2\nu_3$	
	12252w±5	2803	$2\nu_2$	

[a] To a_{1g} modes in D_{5d} symmetry.
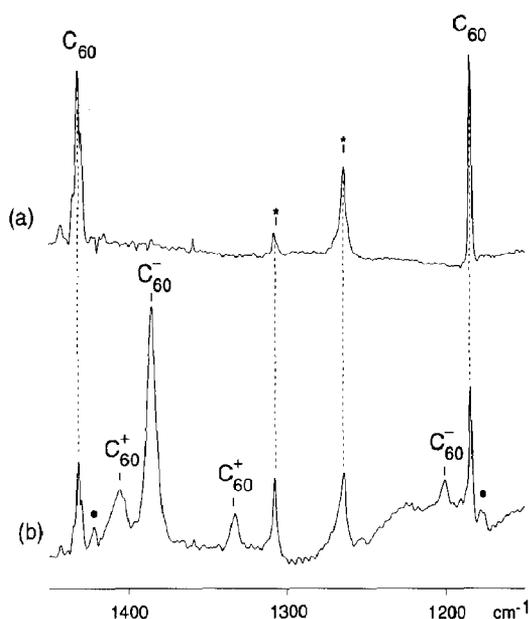[b] Overlaps with C_{60}^+ band.

Fig. 2. Section of the infrared spectrum of: (a) C_{60} isolated in a neon matrix; (b) after NeI irradiation of during deposition. Peaks at 1178 and 1422 cm^{-1} (marked with a dot) are further candidates for either C_{60}^+ or C_{60}^-. Impurities are marked with a star (see text).
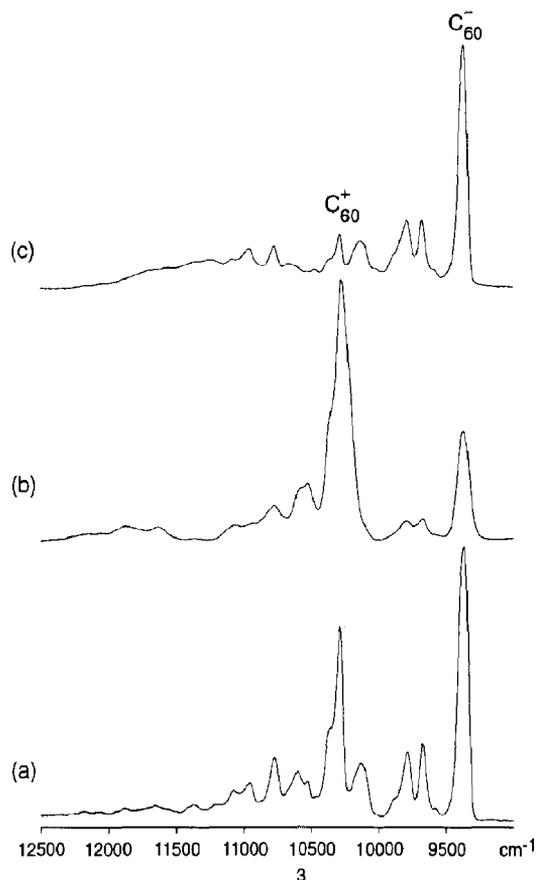

Fig. 3. The electronic absorption spectra of: (a) C_{60}^+ and C_{60}^- produced in an argon matrix after photoionization with NeI photons; (b) after NeI photoionization of C_{60} codeposited with CCl$_4$; (c) NeI photoionization of C_{60} codeposited with K.

The ones at 1406 and 1332 cm^{-1} have the opposite behavior and are taken to be of C_{60}^+. The frequency shift for C_{60} ions going from neon to argon matrix (1–2 cm^{-1}) with respect to neutral C_{60} (no shift) supports the assignment due to the stronger interactions of ions. The infrared frequencies of the C_{60}^- modes obtained presently (1386, 1201 cm^{-1}) differ considerably from those assigned to the t_{1u} modes (1422, 1183 cm^{-1}) of C_{60}^-, apparently produced in a thin film of an iridium–C_{60}-complex on a surface [42]. The latter frequencies are however identical with those of C_{60} itself.

Finally a comparison of the inferred vibrational frequencies of C_{60}^+ with interstellar infrared bands is appropriate. The latter show distinct peaks at 885, 1163, 1299 and 1613 cm^{-1} [43]. However none of these coincide with the two frequencies inferred for C_{60}^+.

3.4. Spectra of C_{60} codeposited with alkali metals

The near-infrared spectrum of C_{60} codeposited with alkali metals (Na, K) in argon matrices, without irradiation, is identical to the electronic absorption of C_{60}^-. This indicates that an electron transfer process takes place in or on the surface of the matrix, where the alkali metals function as electron donors. As the ionization potential of potassium is 4.34 eV and the electron affinity of C_{60} is 2.60 eV [30], such a process would be endothermic in argon matrices. However, the stabilization energy can be obtained from the Coulomb interaction of ion pairs separated by 5–8 Å.

Fig. 4 (trace (d)) shows a section of the infrared spectrum of C_{60} codeposited with potassium in ar-
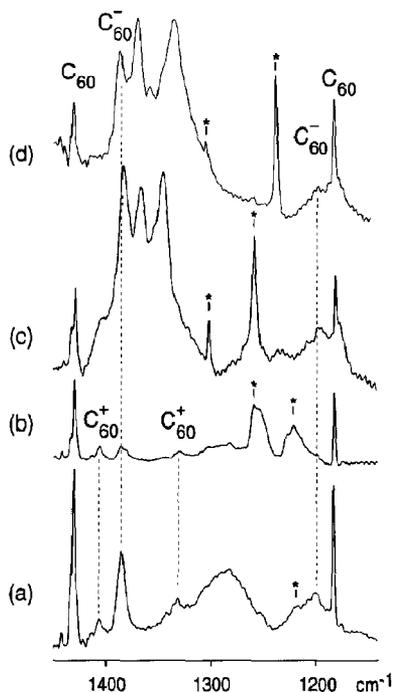
Fig. 4. Portion of the infrared spectrum of C_{60} ions isolated in an argon matrix: (a) after photoionization of the matrix with NeI photons; (b) after NeI irradiation of C_{60} while depositing with CCl_4; (c) after NeI irradiation during codeposition with Na; (d) C_{60} codeposited with K without irradiation. Impurities are marked with a star and the broad peak at ≈ 1300 cm^{-1} (trace (a)) is a measurement artefact.

gon matrix. A peak is seen at 1385 cm^{-1} which was attributed to C_{60}^- (see section 3.3). There are also a few other peaks in the vicinity, and their relative intensity pattern changes with sodium or potassium concentration. These can be interpreted either as a t_{1u} vibration of C_{60}^- perturbed to a varying degree by alkali metal cations or that they are differently charged C_{60}^- ions. However, no other electronic absorption (except for C_{60}^-) was observed, although these have been reported for C_{60}^{2-} and C_{60}^{3-} in solution [35].

Acknowledgement

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