J. Am. Chem. Soc. 1995, 117, 6265−6272 6265

Determination of the Singlet−Triplet Energy Separation for C_{60}^{2-} in DMSO by Electron Paramagnetic Resonance

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Received January 27, 1995[⊗]

Abstract: *In situ* near-IR (NIR) spectra for C_{60}^{2-} generated electrochemically in DMSO (dimethyl sulfoxide) indicate 87 ± 10% conversion to C_{60}^{2-}. In the EPR spectra at 106 K a single line with a 2-G peak-to-peak line width is superimposed on signals with splittings of 11 and 30 G, which is similar to spectra reported in the literature. The total intensity for all of the signals observed at 106 K is less than 4% of the total C_{60}, which is too small for the ground state of C_{60}^{2-}. The spin lattice relaxation time for the sharp signal is about 0.6 s at 4 K, which is too long to permit study by continuous wave EPR spectroscopy. The temperature dependence of the intensity of the FID and of the spin echo for the sharp signal between 4.5 and 50 K corresponds to that expected for a doublet or triplet ground state species and not that expected for a thermally-populated excited state. The microwave power required to achieve a 90° pulse for the sharp signal is that characteristic of an $S = {}^1/_2$ system. Thus, the sharp EPR signal in DMSO is due to an $S = {}^1/_2$ species that is neither the ground state nor a thermally-accessible excited state of C_{60}^{2-}. The EPR data in DMSO are consistent with the conclusion reached previously for toluene:acetonitrile solutions, studied below 120 K, that the ground state of C_{60}^{2-} is diamagnetic. Above 135 K, a Lorentzian signal with a 30-G peak-to-peak line width grows in with increasing temperature and at 255 K corresponds to 6 ± 1% (calculated for $S = 1$) of the C_{60}^{2-} concentration determined by NIR. The temperature independence of the line width and the increase in signal intensity with increasing temperature distinguish this signal from the broad signals observed for C_{60}^{-} and C_{60}^{3-} in DMSO in this temperature interval. This signal is assigned to a thermally-populated excited triplet state of C_{60}^{2-} with a singlet−triplet splitting of 600 ± 100 cm^{-1}.

Introduction

Early in the studies of C_{60} it was noted that the LUMO is triply degenerate.[1−4] Electrochemical studies have demonstrated stepwise reduction of C_{60} to form anions by addition of 1 to 6 electrons to the LUMO.[5] Molecular orbital calculations for C_{60}^{2-} show multiple low-lying excited states and the assignment of a ground state is strongly dependent on how the configuration interaction is treated.[6−12] More of the calculations favor a singlet ground state[6−10] than a triplet.[11,12] Calculations that assign a singlet ground state have found a triplet excited state to be only 650[9] or 1500 cm^{-1} [6,10] higher in energy. For the calculations that assign a triplet ground state, the first singlet excited state is estimated to be only 300[11] or 800 cm^{-1} [12] above the ground state. Since many of these calculations assume that I_h symmetry is retained, the small energy separations could be modified substantially by Jahn−Teller distortions. Jahn−Teller stabilization energies for fulleride anions have been estimated to be 440,[13] 460,[14] or 700 cm^{-1},[15] which is the same order of magnitude as the electron spin correlation terms[16] and the calculated singlet−triplet splittings.[6−12] The difficulty of molecular orbital calculations for these systems makes experimental determination of ground spin states and ground−excited state separations especially important.

The observation of EPR signals in samples of C_{60}^{2-} initially was interpreted as evidence for a triplet ground state,[17−19] although the EPR signal intensity was not quantitated. Two studies have reported that reduction of C_{60} to C_{60}^{-} and then to C_{60}^{2-} led to an increase and then a decrease in EPR signal intensity, consistent with $S = {}^1/_2$ for C_{60}^{-} and $S = 0$ for C_{60}^{2-}.[20,21] Based on the low intensity of the EPR signal for TDAE−C_{60}^{2-} (TDAE is tetrakis(dimethylamino)ethylene) it was proposed that the ground state is a singlet and that the sharp signal observed in many C_{60}^{2-} samples is due to a thermally-accessible triplet excited state.[22] The integrated intensity of the

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[⊗] Abstract published in *Advance ACS Abstracts*, June 1, 1995.

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sharp EPR signals in samples of C_{60}^{2-} in toluene:acetonitrile corresponded to a spin concentration that was much smaller than the concentration determined by vis−NIR and square-wave voltammetry so it was proposed that the ground state of C_{60}^{2-} is diamagnetic ($S = 0$) and that the sharp signals in the EPR spectra are due to impurities or reaction products.[23] Based on the solid state magnetic susceptibility of C_{60}^{2-} it was proposed that the dianion has a singlet ground state and a nearly-degenerate excited triplet state with a singlet−triplet splitting of about 1 cm^{-1}.[24] Thus, although there is mounting evidence that the ground state of C_{60}^{2-} is singlet, there is a diversity of opinions concerning possible assignments of EPR signals to excited triplet states and there has been no measurement of the singlet−triplet splitting.

Key to the assignment of EPR signals to thermally-accessible excited states and characterization of the singlet−triplet splitting is quantitative data as a function of temperature with careful attention to possible complications due to changes in microwave power saturation as a function of temperature. These data can then be compared with intensity changes predicted by the Boltzmann equation for proposed signal assignments and ground−excited state energy separations. In the studies reported in this paper C_{60}^{2-} was generated electrochemically in DMSO; formation was monitored *in situ* by vis−NIR spectra. Time-domain EPR was used to monitor the temperature dependence of the intensity of the sharp EPR signal between 4.5 and 50 K. Continuous wave (CW) EPR spectra were used to monitor the intensity of the sharp EPR signal between 106 and 255 K and to observe a previously unreported broad signal that is observed above 135 K and is assigned to a thermally accessible triplet state of C_{60}^{2-}.

Experimental Section

Electrochemistry and vis−NIR spectroscopy were performed at the Seiler Research Laboratory and EPR spectroscopy was performed at the University of Denver.

Electrochemistry and Vis−NIR Spectroscopy. C_{60} (99.5%) was purchased from Strem Chemicals and used without further purification. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (Electronic Grade, Fluka) was dried at 110 °C under a vacuum of $<10^{-3}$ Torr for 72 h. Dimethyl sulfoxide (DMSO) (<0.1% H_2O, Aldrich) was kept over 4 Å molecular sieves (dried for 72 h at 400 °C and $<10^{-3}$ Torr) for several days prior to use. Solvents were filtered with a 0.2-μm PTFE filter (Whatman) to remove molecular sieve particulate prior to use. Solvents were carefully dried as a precaution, although addition of stoichiometric H_2O to the electrochemical cell had no impact on the generation of C_{60}^{2-}.[25]

Electrochemistry, vis−NIR spectroscopy, and EPR sample preparation were performed in a Vacuum Atmospheres drybox with O_2 and H_2O levels less than 1 ppm. Vis−NIR spectra were obtained *in situ* using a reflective fiber optic dip probe as previously described.[23] The total optical path length for the probe is 0.382 cm.

Square-wave voltammetry (SWV) and bulk electrolysis were performed with the same experimental setups as described previously[23] with only minor changes in the electrochemical cell. The working electrode for the square-wave voltammetry was a glassy carbon, GC, disk electrode (3-mm diameter, Bioanalytical Systems), while a coiled Pt wire (0.5-mm diameter) was used as the working electrode in the bulk electrolysis. The counter and reference electrodes were constructed in the double junction arrangement described previously.[23] The counter electrode consisted of a coiled Pt wire (0.5-mm diameter), and the reference electrode was a silver wire immersed in DMSO containing 0.1 M $TBAPF_6$ and 0.01 M $AgNO_3$. The $E_{1/2}$ of the ferrocene/ferrocinium couple in the electrochemical solvent was found to be +0.205 V relative to this reference electrode.

The current and vis−NIR spectra were continually monitored during the bulk electrolysis. Integration of the chronoamperometric data provides a measure of the charge passed during electrogeneration of the anions, while the vis−NIR spectra indicate how much charge is actually injected into the C_{60} to produce anions. During the direct reduction of 80 mL of 0.30 mM C_{60} to C_{60}^{2-} at −1.4 V, the current dropped rapidly from 1.8 to 0.2 mA in the first 2 h with an integrated charge of 5.35 C. However, the vis−NIR spectroscopy showed that only 0.083 mM of C_{60}^{-}, and no C_{60}^{2-}, was formed during this time, which indicated that only 0.64 C was injected into the C_{60} and the remainder (5.35 − 0.64 = 4.7 C) probably reduced trace solvent impurities. For the next 23 h, the current slowly decayed from 0.2 mA to 10 μA with an integrated charge of 4.54 C and the vis−NIR spectrum of C_{60}^{2-} increased. Although the spectrum remained constant after the first 25 h, electrolysis was continued for an additional 17.5 h to ensure complete reduction of the C_{60} suspension. During this final time interval the current remained at ca. 10 μA with an integrated charge of 0.69 C. The charge calculated for complete reduction of the C_{60} to C_{60}^{2-} is 4.5 C. Using the charge after 25 h (0.64 C + 4.54 C = 5.18 C), the number of electrons added per C_{60} is 2.3. However, the charge passed during the last 17.5 h indicates a background charge of ca. 0.039 C h^{-1}. Inclusion of this correction (5.18 C − (0.039 C h^{-1} × 25 h) = 4.2 C) gives 1.9 as the number of electrons added per C_{60}. Therefore the experimental number of electrons used to produce C_{60}^{2-} from C_{60} is 1.9−2.3, in agreement with the theoretical value of 2.0.

During preparation of EPR samples, special care was taken to minimize oxygen and water contamination. Prior to use, EPR tubes were attached to a vacuum line using a tip-off manifold (Wilmad) and heated with a torch while under a vacuum of $<10^{-3}$ Torr. The tip-off manifolds were closed and the flamed EPR tubes transferred into the drybox for sample preparation. All EPR samples were prepared immediately after termination of the bulk electrolysis. The anion solution (ca. 3 mL) was withdrawn from the electrochemical cell into a glass syringe fitted with a LUER-LOK cap. A 0.45-μm PTFE filter disk (Whatman) was attached to the end of the syringe, and the solution was mechanically filtered into a small vial. This filtration step ensured removal of any partially-reduced C_{60} particulate that might affect the EPR signal. Two EPR tubes were then filled with the anion solution, while the remaining filtered anion solution was reserved for anion stability studies. The filled EPR tubes were attached to the tip-off manifold and immediately transferred from the drybox to a dewar of liquid nitrogen. The frozen EPR samples were then attached to a vacuum line where they were evacuated and sealed with a torch. The samples were stored in liquid nitrogen until EPR spectra were recorded. Vis−NIR spectra taken over the course of 2.5 weeks showed that the C_{60}^{2-} in the sample vial was stable in the drybox at room temperature.

EPR Spectroscopy. In the discussion of EPR data "integration" or "integral" implies double integration of the first-derivative CW EPR spectrum to obtain the area under the corresponding absorption curve.

During all manipulations subsequent to removal from the drybox, the C_{60}^{2-} samples were maintained at liquid nitrogen temperatures to maximize stability of the dianion. Repeat measurements on the same frozen solutions showed no time dependence of the EPR spectra over several months. However, if a sample was warmed to near the solvent melting point or thawed, an irreversible loss of the broad signal that is assigned to the excited triplet state of C_{60}^{2-} was observed. When the sample was thawed there was rapid loss of the characteristic red color of C_{60}^{2-}. These observations indicate that the dianion is less stable under the conditions in the sealed EPR tube than in the drybox. During the process of sealing the tubes with a torch there was some charring of solvent and/or supporting electrolyte in the vicinity of the seal. Pyrolysis products may react with the C_{60}^{2-} when the DMSO matrix becomes soft enough to permit facile diffusion from the vapor space above the sample. Despite careful precautions we cannot rule out the possibility that a trace of oxygen enters the sample during the tube sealing process.

Two-pulse electron spin echoes (ESE) and free induction decays

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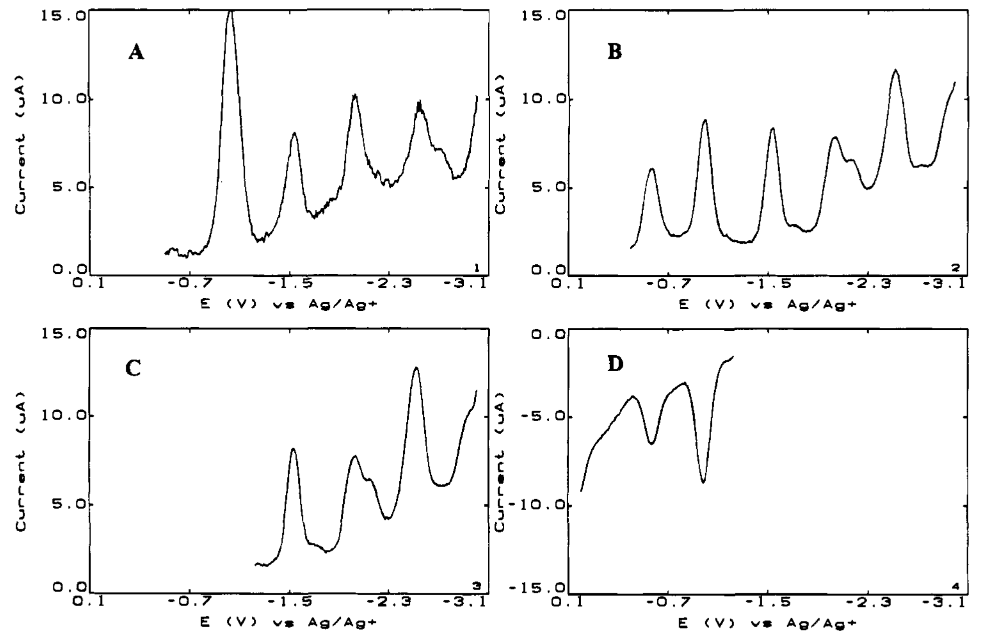

Figure 1. SWV at a GC electrode in DMSO containing 0.1 M $TBAPF_6$ for (A) the reduction of the 0.30 mM C_{60} suspension and for the electrogenerated C_{60}^{2-} after (B) a 60-s hold at −0.4 V, (C) a negative scan from the open-circuit potential, and (D) a positive scan from the open-circuit potential. Step increment = 10 mV, SW amplitude = 50 mV, frequency = 10 Hz.

(FID) were obtained between 4.5 and 50 K on a Bruker ESP380E pulsed EPR spectrometer operating at 9.71 GHz with a dielectric resonator and an Oxford CF935 liquid helium cryostat. Sample temperatures were calibrated with a Lakeshore 820 readout and a TG-120PL GaAlAs diode immersed in silicone oil in a 4-mm OD quartz EPR tube that replaced the sample tube. The diode and readout had been calibrated recently. Continuous wave (CW) EPR spectra were obtained on a Varian E9 with a TE_{102} rectangular resonator operating at 9.166 GHz. Temperatures between 100 and 280 K were obtained with a Varian flow-through dewar and temperature controller and nitrogen gas cooled with liquid nitrogen. The sample temperature was monitored continuously with a thermocouple positioned above the sample. The thermocouple was calibrated at liquid nitrogen and room temperature. The estimated uncertainty in sample temperature is ±1 K.

Results

Electrochemical Generation, Vis–NIR, and Square-Wave Voltammetry of C_{60}^{2-} in DMSO. C_{60} is essentially insoluble in DMSO; however, the anions of C_{60} are expected to be soluble in this polar solvent.[26] Consequently, the electrochemical generation of C_{60}^{2-} was performed in a manner similar to that reported for other polar solvents in which electrolysis of the heterogeneous C_{60} electrolyte mixtures yielded homogeneous C_{60} anion solutions.[26] To accomplish this, a quantity of C_{60} solid sufficient to give a 0.30 mM solution was added to ca. 100 mL of DMSO containing 0.1 M $TBAPF_6$ in a Qorpak glass jar. The C_{60}/electrolyte mixture was sonicated outside the drybox inside the sealed helium-filled jar for 2 h at 60 °C, giving a liquid with a fine brown suspension. This suspension was transferred back to the drybox and used as the analyte solution in the electrochemical cell.

The square-wave voltammetry of the C_{60} suspension is shown in Figure 1A. This voltammogram was obtained immediately after buffing the GC working electrode on a Microcloth polish cloth (Buehler) wetted with acetonitrile. Although the first reduction wave at −1.03 V was seen regardless of electrode treatment, the following reduction steps at −1.54, −2.03, and −2.54 V could only be clearly observed immediately after the above buffing procedure. Based on its reduction potential and the C_{60}^{2-} SWV discussed below, the electrochemical process at −1.03 V corresponds to a direct two-electron conversion of C_{60} to C_{60}^{2-}. This assignment also is consistent with the height of this wave compared to the heights of the following sequential one-electron reduction steps. The mechanism of the two-electron conversion almost certainly involves adsorption of neutral C_{60} at the GC surface. This adsorption phenomena and the voltammetric behavior seen in Figure 1A are reminiscent of that reported for the formation and electrochemistry of C_{60} films.[27,28]

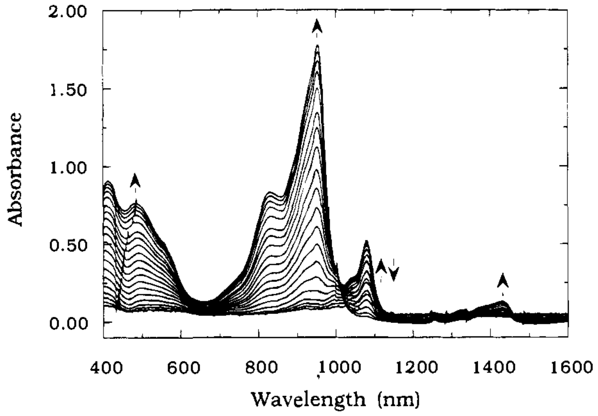

Figure 2. Progression of the *in situ* vis–NIR spectra during electrogeneration of C_{60}^{2-} (peak at 950 nm) from a suspension of C_{60} in DMSO containing 0.1 M $TBAPF_6$. Arrows indicate the direction of intensity change during the electrolysis. The C_{60}^{-} absorptions at 1075 nm increase initially, and then decrease near the end of the electrolysis.

Based on the SWV behavior, bulk electrolysis to C_{60}^{2-} was performed at −1.4 V using a coiled Pt wire electrode. Although the potential is negative of the −1/−2 couple, *in situ* vis–NIR revealed the initial appearance of C_{60}^{-} (absorption at 1075 nm), followed immediately by spectra indicating the simultaneous formation of C_{60}^{-} and C_{60}^{2-} (absorption at 950 nm) (Figure 2). The C_{60}^{2-} absorption increased with continued electrolysis and became constant after 25 h. The absorptions due to C_{60}^{-} gradually decreased. The C_{60}^{-} probably is produced in the bulk

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solution by the homogeneous comproportionation reaction

$$C_{60}{}^{0} + C_{60}{}^{2-} \leftrightarrow 2C_{60}{}^{-} \qquad (1)$$

The broad absorption at 1400 nm reported previously[23] is here assigned to an O−H first overtone vibration resulting from SiOH groups in the fiber optic glass;[29] this was confirmed by the absence of this absorption in $C_{60}{}^{n-}$ spectra collected using a different fiber optic cable designed for minimal absorption in this region.[30] Because C_{60} anions have been observed to weakly adsorb onto the polished fibers ends,[30] the increase in this O−H overtone band with increasing $C_{60}{}^{2-}$ concentration may result from a specific adsorptive interaction of $C_{60}{}^{2-}$ with the glass fiber.

The absorbance at 950 nm was used to quantitate the $C_{60}{}^{2-}$ generated by the electrolysis. Quantitation is especially important for these experiments because some of the solid C_{60} could have been lost due to adsorption onto the glass jar surface and glass components of the electrochemical cell. The molar absorptivity reported for $C_{60}{}^{2-}$ at 950 nm is 16 000 (DMSO),[31] 18 750 (CH_2Cl_2, −60 °C),[32] 18 000 (THF),[20] and 20 900 (CH_2Cl_2)[33] $dm^3\ mol^{-1}\ cm^{-1}$. Since it is difficult to separate solvent effects from uncertainty due to sample preparation and handling, the average literature value of ϵ ($((18\pm2) \times 10^3\ dm^3\ mol^{-1}\ cm^{-1})$) was used to convert absorbance to concentration. The uncertainty in concentration is estimated from the range in literature values of ϵ. Based on the final spectrum in Figure 2 (absorbance at 950 nm = 1.78), the $C_{60}{}^{2-}$ concentration is 0.26 ± 0.03 mM, corresponding to 87 ± 10% conversion. As detailed in the Experimental Section, the charge consumed in the electroreduction process also is consistent with formation of the −2 anion.

In the case where neutral C_{60} is insoluble in the desired electrolyte, it has been demonstrated that the anions generated by electrolysis often show clean electrochemical behavior.[26] Therefore, SWV was performed on the electrogenerated $C_{60}{}^{2-}$ starting at the open-circuit potential of −1.228 V for the electrolyzed solution (Figures 1C and 1D) and at −0.4 V, a potential positive of the 0/−1 couple (Figure 1B). The open-circuit potential was measured at a Pt-wire sensing electrode because the open-circuit at GC was found to quickly drift to more positive potentials when inserted into the $C_{60}{}^{2-}$ solution. When the GC was removed, buffed, and reinserted, its potential returned to the Pt electrode value, but again drifted to positive potentials. This phenomenon is explained by the fact that the GC electrode surface possesses organic-like functional groups that can undergo redox reactions;[34] therefore, the reducing −2 anion appears to react with the functionalized surface of the GC electrode. The SWV behaviors shown in Figures 1B−D are essentially the same as that seen for $C_{60}{}^{2-}$ in 4:1 toluene: acetonitrile where all C_{60} species are soluble; therefore, the electrochemistry of $C_{60}{}^{2-}$ in DMSO appears to behave as a fully soluble species. The one-electron reductions at −0.57, −0.99, −1.53, −2.03, and −2.52 V are assigned to the 0/−1, −1/−2, −2/−3, −3/−4, and −4/−5 couples, respectively. No attempt was made to use the SWV data to quantitate the $C_{60}{}^{2-}$ concentration because the electrochemistry of the neutral molecule does not provide an accurate measure of the SWV peak heights for an unreduced solution, a requirement for this quantitation technique.[23]

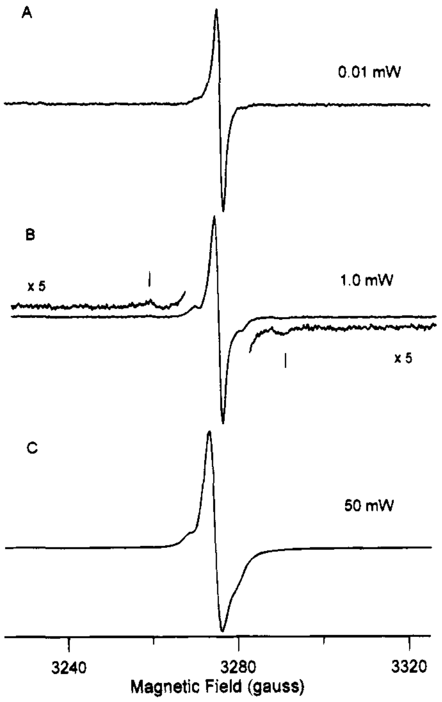

Figure 3. CW EPR spectra (9.17 GHz, 100 G scans) at 106 K of the sharp signals observed for samples containing $C_{60}{}^{2-}$ in DMSO at the following experimental conditions: (A) 0.01 mW microwave power, 1.0-G modulation amplitude, (B) 1.0 mW microwave power, 1.0-G modulation amplitude, (C) 50 mW microwave power, 4.0-G modulation amplitude.

CW EPR Spectra of Solutions Containing $C_{60}{}^{2-}$ at 106 K. CW spectra of the solutions containing $C_{60}{}^{2-}$ in DMSO at 106 K are shown in Figure 3. These spectra are similar to ones that have been reported in the literature.[17−19,23,24] Since the spectra are so dependent upon microwave power (Figure 3), and many of the literature reports do not indicate the power at which spectra were obtained, it is difficult to make detailed comparisons of line shapes. However, it appears that similar spectra have been obtained for a variety of preparations of $C_{60}{}^{2-}$.

The central sharp signal (Figure 3) saturates readily with increasing microwave power at 106 K. In the absence of power saturation the double integral (after correcting for changes in spectrometer gain) should increase linearly with the square root of microwave power. However, the double integral of the spectrum at 1.0 mW after correcting for spectrometer gain was only about 8 times as large as for the spectrum at 0.01 mW which indicates saturation at 1.0 mW. The intensity of the sharp signal obtained at 0.01 mW microwave power was quantitated by comparison of the double integral with that for a sample of the stable nitroxyl radical 4-oxo-2,2,6,6-tetramethylpiperidin-1-oxyl (tempone, Aldrich) at the same temperature. The comparison indicated that the sharp signal accounted for 2 to 3% of the total C_{60} if it is assumed to have $S = {}^1/_2$ or less than 1% if it has $S = 1$, because of the factor of $S(S + 1)$ in the EPR transition probability.

It has been proposed that sharp signals in EPR spectra of $C_{60}{}^{-}$ and $C_{60}{}^{3-}$ are due to thermally-accessible excited states.[17,24] It has also been proposed that the sharp signal in spectra of $C_{60}{}^{2-}$ is due to a thermally-accessible triplet.[22] If the sharp signals in spectra of $C_{60}{}^{2-}$ are due to a thermally accessible excited state and the population is only a few percent at 106 K, the singlet−triplet splitting must be larger than kT at 106 K and the signal intensity should be strongly temperature dependent at temperatures above and below 106 K. Therefore, the

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temperature dependence of the intensity of the sharp signal was measured between 4.5 and 50 K by time-domain measurements and between 100 and 270 K by CW measurements,

Time Domain EPR of Solutions Containing C_{60}^{2-} at 4.5−50 K. For the sharp signal at 4.5 K the intensity of a 2-pulse echo was measured as a function of the pulse sequence repetition time, i.e. the time between the pulse sequences during which the spins are permitted to return to equilibrium. The value of T_1 estimated from these data was 0.6 s. An analogous series of measurements at 30 K gave $T_1 = 30$ ms. These values of T_1 are so long that it is not possible to record unsaturated CW spectra at the lowest microwave power available on the ESP380E (0.2 μW). In addition, these values of T_1 are so long that the lowest available magnetic field modulation frequency on the ESP380 (1.56 kHz) is too fast to record undistorted spectra. These constraints are likely to be a problem for CW measurements of these sharp signals on any commercially available CW EPR spectrometer. Since T_1 is strongly temperature dependent, attempts to run CW spectra as a function of temperature under saturating conditions are likely to be dominated by changes in the extent of power saturation rather than by the temperature dependence of spin concentration, Therefore time domain measurements were used instead of CW measurements to determine the temperature dependence of the spin concentration.

The magnetic field was set to the value that gave the strongest spin echo, which was approximately the center of the sharp signal (the crossover point in the first derivative signal). At each temperature, the amplitude of the echo for a $90°-\tau-180°-\tau$−echo sequence at $\tau = 200$ ns was measured as a function of the pulse repetition time, which was increased until there was no further increase in echo intensity. The echo intensity in that limit is proportional to the number of spins that contribute to the echo. The echo intensity for the sharp signal decreased by more than an order of magnitude between 4.5 and 50 K. Over this temperature interval the echo decay time constant, T_m, decreased only from 1.34 to 1,25 μs, which has a very small impact on echo intensity at $\tau = 200$ ns. The intensity of a ground-state EPR signal is determined by the relative populations of the $m_s = \pm 1/2$ levels for a doublet or of the $m_s = -1$, 0, 1 levels for a triplet. These population differences decrease with increasing temperature. The energy separation between pairs of levels with $\Delta m_s = \pm 1$ is the EPR quantum which is approximately 0.3 cm^{-1} at X-band. Since this separation is small relative to kT even at 4,5 K, the intensity of the ground state EPR signal varies approximately as $1/T$, which can be compensated by multiplying the observed intensity by temperature, The observed echo intensity (in arbitrary units) for the sharp signal in the C_{60}^{2-} sample multiplied by temperature is plotted as a function of temperature in Figure 4. The product of intensity times temperature decreases slightly with increasing temperature (Figure 4).

An analogous set of experiments was performed monitoring the intensity of the FID following a 90° pulse. The real and imaginary components of the FID were digitized and a phase correction was applied to maximize the amplitude of the real component, The time between pulses was increased until the FID intensity showed no further increase. The amplitude of the phase-adjusted real component of the FID decreased by more than an order of magnitude between 4.5 and 50 K. This value (in arbitrary units) multiplied by temperature also is plotted in Figure 4.

In the CF935 cryostat used in these experiments the resonator is cooled along with the sample, so the intensity of a detected signal depends upon the temperature-dependent characteristics of the resonator, A crucial parameter is the resonator quality factor, Q. The Bruker ESP380E software includes a semiquantitative measure of resonator Q that decreased from 17 000 to 13 000 between 4 and 60 K. To more precisely check the impact of the temperature dependence of resonator Q for a known $S = 1/2$ system, data were obtained for a spin-labeled low-spin methemoglobin,[35] The interaction between the low-spin iron(III) and the nitroxyl radical increases the nitroxyl relaxation rate[35] sufficiently that it is possible to measure unsaturated CW spectra at temperatures above 25 K. The double integrals of the CW spectra (in arbitrary units) multiplied by temperature are plotted in Figure 4.

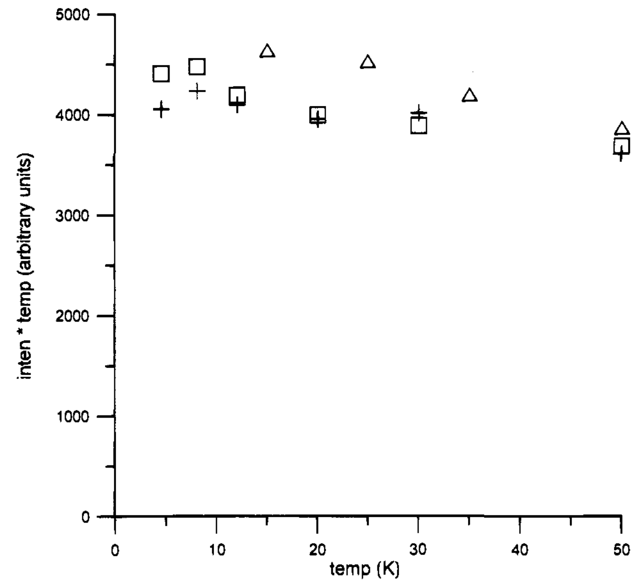

Figure 4. Time domain EPR signal intensity as a function of temperature for the sharp signal in C_{60}^{2-} samples: (□) FID; (+) ESE at $\tau = 200$ ns. The temperature dependence is compared with that for the integrated CW signal intensity in spin-labeled hemoglobin (△).

If the sharp signal in the EPR spectra of solutions containing C_{60}^{2-} is due to a ground state, the product of intensity times temperature is expected to be constant. The small deviation from a constant value (Figure 4) is similar to that observed for a nitroxyl radical and is attributed to the temperature dependence of resonator Q. Thus the temperature dependence of the intensity of the sharp signal in the C_{60}^{2-} sample is consistent with a doublet or triplet ground state and not with a thermally-accessible excited state with singlet−triplet splitting greater than kT.

The microwave power required to produce a 90° pulse depends on S for the species that gives the signal,[23,36] The power required for the sharp signal was the same as that required for the nitroxyl sample within experimental uncertainty (about 0,5 dB), which demonstrates that the sharp signal behaves like an $S = 1/2$ species, analogous to what was observed previously in 4:1 toluene:acetonitrile solution.[23]

Intensity of Sharp Signal between 100 and 200 K. The line width of the sharp signal is approximately constant between 100 and 200 K so peak height is a useful monitor of spin concentration. Spectra were recorded with 0.01 mW microwave power, which does not saturate the signal at 100 K and therefore will not saturate it at higher temperatures. The peak height was

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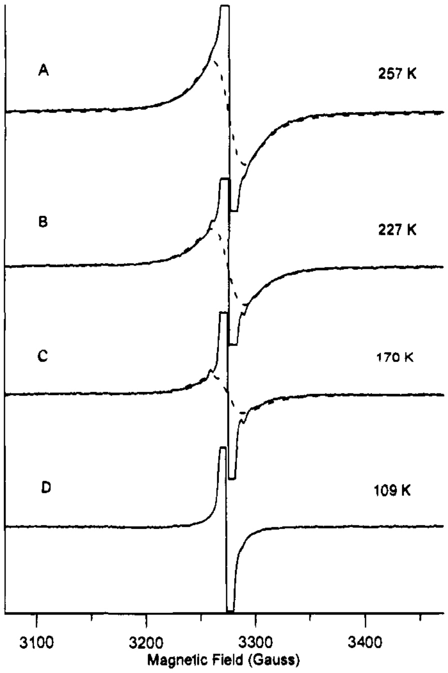

Figure 5. CW spectra (9.17 GHz, 400-G scans) of C_{60}^{2-} generated electrochemically in DMSO as a function of temperature obtained with 50-mW microwave power and 4.0-G modulation amplitude. The *y* axis gain is the same for each of the spectra. The dashed line is a simulation of the broad temperature-dependent spectra calculated for a Lorentzian with a peak-to-peak line width of 30 G.

monitored as a function of temperature between 100 and 200 K using either 1 kHz or 100 kHz magnetic field modulation. In both experiments the peak height decreased with increasing temperature and the product of peak height times temperature was constant within experimental uncertainty (about 10%). The integral of the sharp signal as a function of temperature also was monitored. Analysis of the integrals is subject to additional uncertainty because of the temperature dependence of an underlying signal that is discussed below. However, within experimental uncertainty, the integrals of the sharp signal multiplied by temperature also were constant. For the liquid nitrogen temperature experiments, the dewar is inside of the resonator and the resonator remains at room temperature so the resonator *Q* is approximately independent of temperature.

Broad Signal Observed above 135 K. Above 135 K an additional broad signal was observed in the CW EPR spectra of the C_{60}^{2-} sample in DMSO, which was not detectable at 106 K (Figure 5). To optimize observation of this broad signal in the presence of the superimposed sharp signal, spectra were run at 50 mW with 4 G modulation amplitude. The broad signal is not power saturated at 50 mW. The intensity of this signal increases with increasing temperature. The dashed lines in Figure 5 are simulations of the broad component as a Lorentzian line with a peak-to-peak width of 30 G. To quantitate the intensity of the broad signal, the integral of the sharp signal at 109 K was corrected for its known temperature dependence ($1/T$) and subtracted from the total integral at higher temperatures. The contribution from the sharp signal was about half of the total integral at 136 K, 10% at 199 K, and 4% at 265 K. Although uncertainty in these corrections introduces uncertainty in the calculated intensity for the broad signal, it is clear that the intensity for that signal increases by about an order of magnitude between 136 and 265 K. This temperature dependence is consistent with thermal population of an excited state. The most probable excited state that would be EPR detectable is a triplet, $S = 1$, species. If the temperature was kept below 265 K, the intensity changes were reversible, but at higher temperatures irreversible loss of EPR signal intensity occurred.

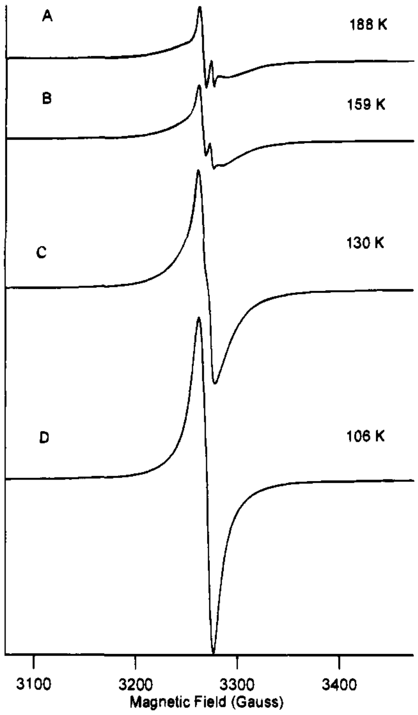

Figure 6. CW spectra (9.17 GHz, 400-G scans) of C_{60}^{3-} generated electrochemically in DMSO as a function of temperature obtained with 50-mW microwave power and 4.0-G modulation amplitude. The *y* axis gain is the same for each of the spectra and approximately $^1/_8$ that shown in Figure 5.

Since broad signals also are observed for C_{60}^- and C_{60}^{3-} in this temperature interval, it is important to examine the characteristics of the broad signal in the C_{60}^{2-} sample that distinguish it from the signals for C_{60}^- and C_{60}^{3-}, namely the temperature dependence (or lack thereof) of the line widths and the dependence of signal intensity on temperature. For C_{60}^- in DMSO the peak-to-peak line width increases from 20 G at 100 K to 40 G at 300 K.[39] For C_{60}^{3-} in DMSO the peak-to-peak line width of the EPR spectrum increases from about 14 G at 106 K to 45 G at 188 K (Figure 6). This increase in line width accounts for much of the decrease in amplitude of the broad signal in Figure 6. A sharp signal is superimposed on the broad signal for C_{60}^{3-}, and because of the line width changes becomes more conspicuous at higher temperatures. The line widths for the C_{60}^- and C_{60}^{3-} signals in other solvents also are strongly temperature dependent.[17,23,39] In contrast, the line widths for the broad signal in Figure 5 are approximately independent of temperature. The double integral of the CW spectra of C_{60}^{3-} (including the spectra shown in Figure 6) multiplied by temperature is approximately constant (within 10%) over the temperature interval from 98 to 188 K, which is the temperature dependence expected for a ground-state signal. This behavior again is in marked contrast to the observations discussed above for the broad signal in the C_{60}^{2-} sample. Thus the temperature dependence of both line widths and integrated intensity clearly distinguish the broad signal in the C_{60}^{2-} sample from the broad signals for C_{60}^- and C_{60}^{3-}.

The intensity of the broad signal in the C_{60}^{2-} sample as a function of temperature is shown in Figure 7. Intensities are multiplied by T to correct for the temperature dependence of the relative populations of the m_s sublevels in the $S = 1$

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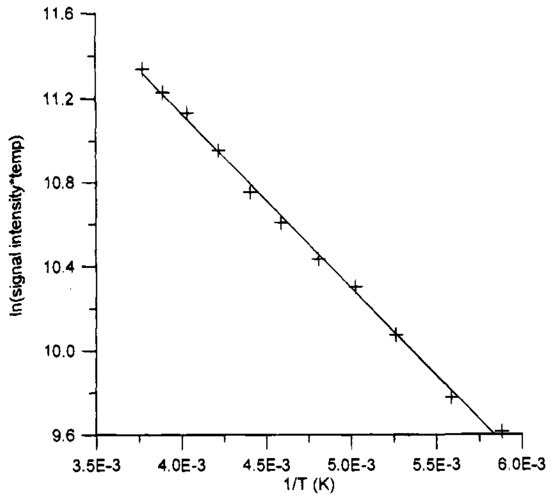

Figure 7. Plot of the temperature dependence of the integrated intensity of the broad signal that is assigned as the thermally-accessible triplet. The slope of the plot corresponds to a singlet–triplet splitting of 600 cm^{-1}.

manifold. The average slope obtained from plots for several data sets gives an energy separation of 600 ± 100 cm^{-1}, which is assigned as the singlet–triplet energy separation. For this magnitude of energy separation the fraction of the molecules in the excited state is 9 ± 4% at 255 K. Comparison of the double integral at 255 K, corrected for the contribution from the sharp signal, with the double integral of the nitroxyl standard indicates 0.043 mM $S = {}^1/_2$ spins or 0.016 mM $S = 1$ spins. Based on the intensity of the NIR spectrum (discussed above) the electrolysis produced 0.26 ± 0.03 mM C_{60}^{2-}. Assuming that the excited state is a triplet, the signal intensity corresponds to 6 ± 1% population of the excited state. This population is in reasonable agreement with that calculated (9 ± 4%) for the observed energy separation and supports the assignment of the broad signal to an excited triplet state in thermal equilibrium with the $S = 0$ ground state of C_{60}^{2-}.

Discussion

The EPR literature concerning C_{60}^{2-} includes proposed assignments of signals to various ground or excited states. In this study we seek to test these assignments by comparison of absolute intensities and temperature dependence of intensities to the behavior predicted by the Boltzmann relationship.

Sharp EPR Signals in Samples Containing C_{60}^{2-}. Several laboratories have reported sharp EPR signals similar to those shown in Figure 3 for samples that contain C_{60}^{2-}.[17–19,23,24] We previously reported that the maximum intensity observed for these sharp signals in 4:1 toluene:acetonitrile solution corresponded to less than 25% of total C_{60} if calculated for $S = {}^1/_2$ and less than 10% if calculated for $S = 1$.[23] In samples where the electrochemistry and NIR spectra indicated the most effective conversion to C_{60}^{2-}, the intensity of the EPR signal corresponded to less than 1% of total C_{60} if calculated for $S = 1$.[25] (Note that the present results show this to be an $S = {}^1/_2$ species.) The present results in DMSO demonstrate that the low intensity of the sharp signals is observed in solvents with quite different properties. The low intensity of the sharp signals is not consistent with assignment to the ground state of C_{60}^{2-} or to an excited triplet state with singlet–triplet splitting substantially less than kT at 106 K (i.e. $\ll$70 cm^{-1}).

To test the possibility that the sharp signals are due to thermally accessible excited states with singlet–triplet splittings greater than kT at 106 K, data were obtained as a function of temperature. Due to the very long relaxation times for the sharp signals at low temperatures, unsaturated CW spectra could not be obtained. Instead, the spin echo intensity and FID intensity were examined. As shown in Figure 4 and described above, the temperature dependence of the signals is consistent with that expected for a ground state, not a thermally-accessible excited state, and the spin properties are those of a doublet, not a triplet. The intensity of the sharp signal varied from preparation to preparation. For example, lower intensities of the sharp signals were observed in DMSO when C_{60}^{2-} was produced directly from neutral C_{60} than when C_{60}^- was first generated followed by generation of C_{60}^{2-}. The low intensity of the signal, the temperature dependence characteristic of a ground state and not of an excited state, and the variability from preparation to preparation argue that the sharp signals in either DMSO or toluene:acetonitrile solutions are not due to either the ground or thermally-accessible excited states of C_{60}^{2-}. The g values near 2.00 and observation of these signals in preparations in a variety of solvents done by several research groups argue that these signals are due to a species derived from C_{60}, but there is no evidence in any of the published papers or in the present work that permits assignment of these signals.

Signals with Splittings of about 11 and 32 G. In the CW EPR spectrum obtained at 1.0-mW microwave power (Figure 3B) additional signals with splittings of 11 and 32 G, respectively, are detectable.[18,24] The increased relative intensities of these signals at higher microwave power indicate that they saturate less readily than the sharp line in the center of the spectrum. The splitting of about 11 G persists as temperature is increased and is superimposed on the broad signal that increases with increasing temperature (Figure 5). These signals are similar to ones shown in ref 24b and in Figure 4 of ref 18 and have been interpreted as a triplet signal from C_{60}^{2-}.[18,24b] The integrated intensities, however, are even less than for the sharp signal, which again is too weak to be due to the ground state of C_{60}^{2-}, although the temperature dependence of intensity is approximately that expected for a ground state signal. It has been proposed that the signal with a splitting of 32 G is due to a thermally-accessible excited triplet state.[24] This signal was so weak at all temperatures examined in this study that it was difficult to quantitate. However, it did not appear to be sufficiently temperature dependent between 100 and 280 K to be consistent with a thermally accessible excited state with a small population at 100 K.

Triplet Signal Observed above 135 K. Above 135 K an additional EPR signal was observed that has not been reported previously. Based on the observed increase in signal intensity with increasing temperature this signal is assigned to a thermally-accessible triplet excited state. Both the temperature independence of the line width and the increasing signal intensity with increasing temperature distinguish this broad signal from the broad signals that have been observed for C_{60}^- and C_{60}^{3-}.

Several characteristics of the DMSO samples made detection and quantitation of the triplet signal possible. (1) In these samples the intensity of the sharp signal was low. If the intensity of the sharp signal were higher it would be difficult to detect the underlying broad signal. (2) The EPR spectrum at 106 K (Figure 3) showed negligible concentrations of either C_{60}^- or C_{60}^{3-}. Both of these species give signals that broaden with increasing temperature,[23] and would overlap extensively with the broad signal shown in Figure 3. Although these signals are distinguishable from the broad signal observed for C_{60}^{2-}, overlap would make quantitation difficult. (3) The melting point of DMSO containing 0.1 M $TBAPF_6$ is higher than 280 K, which permits observation of rigid-lattice spectra at much higher temperatures than in 4:1 toluene:acetonitrile. The higher temperatures are needed to achieve detectable populations of the triplet state.

The temperature dependence of the intensity of the triplet signal (Figure 7) indicates a singlet–triplet splitting of 600 ± 100 cm^{-1}. As discussed above, the absolute intensity of the triplet signal is consistent with that expected for the concentration of ground state $S = 0$ C_{60}^{2-} determined from the NIR spectra and the calculated Boltzmann population for an energy separation of 600 cm^{-1}. Molecular orbital calculations predict low-lying excited states for C_{60}^{2-}.[6–10] These splittings are likely to be strongly dependent upon the environment of the anion. The value of 600 cm^{-1} is consistent with singlet–triplet separations obtained in some calculations (650 cm^{-1} [9] or 1500 cm^{-1} [6,10]).

The broad signal does not exhibit the characteristic zero-field splitting patterns expected for triplets in the slow-motion regime. A tumbling correlation time of 9.1 ps at 283 K was obtained for neutral C_{60} by solid state NMR.[37] For photoexcited $^3C_{60}$ the tumbling correlation time is estimated to be on the order of ps at 213 K in frozen solution.[38] By analogy it is plausible that C_{60}^{2-} also is undergoing sufficiently rapid motion at temperatures above 135 K to average the zero-field splitting. The line shape of the triplet signal was simulated as a Lorentzian with a peak-to-peak line width of 30 G. The Lorentzian line shape indicates that the line width is lifetime determined and a line width of 30 G corresponds to a lifetime of 2 ns. This lifetime could either be the spin lattice relaxation time, T_1, or the lifetime of the triplet state. Although there is uncertainty in the line width due to overlap with the sharp signals, the line width is not measurably temperature dependent.

The line widths of the CW EPR signals for C_{60}^- and C_{60}^{3-} in frozen or glassy solution are strongly temperature dependent.[17,23,39] Measurements of electron spin–lattice and spin–spin relaxation times for these ions at temperatures between 6 and 40 K and extrapolation of the observed temperature dependence of the relaxation times into the temperature range in which the EPR line widths are strongly temperature dependent (above 60 K) suggests that the line widths are determined by electron spin relaxation rates.[23,39] The lack of significant temperature dependence of the line width of the EPR signal for the excited triplet state of C_{60}^{2-} is in sharp contrast to the substantial temperature dependence observed for the signals for the −1 and −3 anions. This difference suggests that the line width of the EPR signal for the triplet excited state may be determined by the lifetime of the excited state rather than by electron spin–lattice relaxation.

For aromatic radicals the lifetime of triplet excited states in solid solutions was found to exhibit weak temperature dependence, with less than a factor of 2 change between 77 and 300 K.[40] Thus the weak temperature dependence of the line width of the EPR signal for the triplet excited state of C_{60}^{2-} is consistent with assignment of the lifetime of the excited state as the process that determines the line width. The non-radiative lifetimes of triplet excited states are strongly dependent upon the singlet–triplet splitting.[40–42] Within a series of closely related compounds an approximately exponential dependence has been observed,[41] which is consistent with a model of relaxation via molecular vibrations.[42] For $^3C_{60}$ the lifetime of the triplet state in fluid solution at room temperature has been reported as 40 μs,[43] 40 to 142 μs depending upon solvent,[44] or 250 μs.[45] $^3C_{60}$ is formed by photoexcitation in the visible energy range with relaxation from the excited singlet to the lower-lying triplet. The energy separation between the ground state singlet and the lowest triplet state for $^3C_{60}$ was initially estimated to be 13 100 cm^{-1} [43] and a more precise measurement gave 12 600 cm^{-1}.[46] This separation is very much larger than the singlet–triplet splitting for C_{60}^{2-} in DMSO (600 cm^{-1}). The much smaller singlet–triplet splitting for C_{60}^{2-} than for $^3C_{60}$ is expected to result in a much shorter lifetime of the triplet state, so 2 ns is a plausible lifetime of the triplet excited state for C_{60}^{2-}. Spin–orbit coupling is a major factor in determining the lifetime of a triplet excited state.[41] The significant deviation of the g value of the triplet excited state (about 2.000) from $g = 2.0023$ also contributes to a short lifetime for the excited state. Group theory arguments show that vibrations with h_g symmetry can couple to the electronic orbitals containing the unpaired electron of C_{60}^{2-} and cause dynamic Jahn–Teller distortion of the anion.[47] Two of the h_g modes occur at 270 and 430 cm^{-1}.[48] The similarity between the energies of these h_g modes and the singlet–triplet splitting may also facilitate radiationless decay. Thus a range of arguments is consistent with a short lifetime for the triplet excited state of C_{60}^{2-}. Although full interpretation must await data in a range of solvents, we propose that the line width of the EPR signal from the triplet excited state of C_{60}^{2-} is determined by the radiationless decay lifetime.

Conclusions

The low intensity of the sharp EPR signals is inconsistent with assignment to the ground state of C_{60}^{2-} or to an excited state with ground–excited state separation less than kT between 4.5 and 200 K. The temperature dependence of the intensity of the sharp signal is that of a ground state and not that of an excited state with ground–excited state energy separation comparable to or greater than kT between 4.5 and 200 K. The response to a microwave pulse is consistent with $S = 1/2$. These observations are inconsistent with assignment of the sharp signals to C_{60}^{2-}. A broad signal that has not been reported previously and increased in intensity with increasing temperature above 135 K is assigned to an excited triplet state with a singlet–triplet splitting of 600 ± 100 cm^{-1}. The absolute intensity of the signal is consistent with the proposed singlet–triplet splitting. The 30-G line width of this signal corresponds to a lifetime of 2 ns, which is tentatively assigned as the lifetime of the triplet excited state.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. An NSF shared instrument grant (CHE-9318714) for purchase of the Bruker ESP380E is gratefully acknowledged.

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