Continuous Wave EPR of the Reduced Fullerene C_{60}^{3-}

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CW EPR spectroscopy of C_{60}^{3-} has shown that the power saturation of the narrow line (the spike attributed to impurities) is capable of distorting the broad line attributed to C_{60}^{3-} itself. Further distortions of the broad line are caused by the effect of different freezing rates on solute aggregation. These observations cast doubt on the validity of observations of dynamic Jahn-Teller distortions at low temperatures and of the relevance of models based on the icosahedral symmetry of C_{60} to the electronic structure of its anions.

1. Introduction

The interpretation of the continuous wave (CW) EPR spectrum of the fullerene anion C_{60}^{3-} in frozen solution has been the subject of controversy [1]. Most reported spectra show a "broad line" of width between 15 and 35 G upon which is superimposed a narrow line (the "spike") whose width varies between 2 and 5 G. The widths and the relative intensities of the broad line and the spike depend on the purity of the samples and the measurement conditions. It is generally accepted that the broad line arises from C_{60}^{3-} itself [1]. The spike has been shown by Paul et al [2] to arise from the presence in air exposed samples of the difullerene $C_{120}O$ as an ubiquitous and unavoidable impurity. Drew et al. [3], using Electron Spin Transient Nutation (ESTN) spectroscopy, showed that the broad line attributed to C_{60}^{3-} arises from a spin system with S = ½. However, these observations are not in accord with theoretical expectation, which predicts a triply degenerate orbital ground state and hence a spin S = 3/2. Attempts to reconcile theory and experiment invoke the existence of Jahn-Teller (JT) distortions to split the ground state, giving an orbital singlet ground state with a quartet state at some higher energy [4]. Evidence for JT distortions has been claimed by Eaton et al. [5] who interpreted their spectra at 8 K in terms the freezing in of JT distortions to give a spectrum with 3 g-values and highly anisotropic linewidths. This paper examines some of the factors influencing the appearance of the CW spectra and their implications for the existence of low lying excited states and of JT distortions at low temperatures.

2. Experimental and Sample Preparation

Highly purified samples of C_{60} and its anions were prepared as described elsewhere [2]. The EPR measurements reported in this paper were performed at temperatures between 2.5K and 170K with a Bruker ESP380E CW/FT spectrometer at Monash University [3].

3. Results and Discussion

Given the appropriate experimental conditions, the CW spectra of $[Na(dibenzo\text{-}18\text{-}crown\text{-}6)]_3C_{60}$ in a 1:2 mixture of DMSO and THF show the same spectral features as reported previously [1, 2, 5]. In Fig.1 we compare the spectra recorded at 2.5 K and the microwave power levels indicated. These show that the spike is partially resolved at 209 nW but becomes less distinct as the power is increased. The smearing out of the spike resonance is

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due to power saturation and the broad line shows no evidence for saturation below powers of around 3mW at this temperature. These spectra and others recorded at temperatures up to 160 K show that the broad line and the spike are independent species and have a different dependence on the microwave power. Fig. 1 shows that the peak to peak separation of the 1st derivative extrema of the broad line decreases from ~17G to ~14 G as the power is increased.

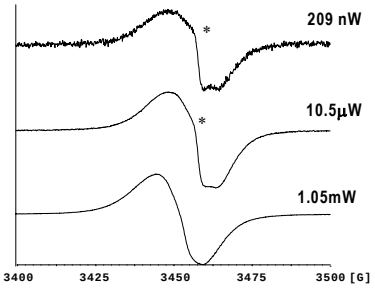

Fig. 1. EPR spectrum of C_{60}^{3-} at 2.5 K. 100 kHz modulation amplitude 0.1 G; microwave frequency 9.692 GHz. Relative intensities not to scale. The presence of the spike is indicated by the * at the steeply descending feature in the top two spectra near 3460 G.

The spike exhibits a complex dependence on temperature and microwave power. At 77 K and 500 nW microwave power the resonance has a peak-to-peak derivative width of about 2.5 G. The resonance shows evidence for microwave power saturation above about 10 μW and increases in width to approximately 4 G at 1mW. At the lowest power levels and temperatures above about 110 K, the spike appears to consist of more than one resonance. However, at higher power levels the components exhibit saturation behaviour and are broadened to merge into a single line of width ~ 4.5 G. Thus we may conclude that the lineshape of the spike is distorted due to power saturation at 2.5 K even at ~ 200nW and because of its superposition on the broad line, influences the apparent width of the latter.

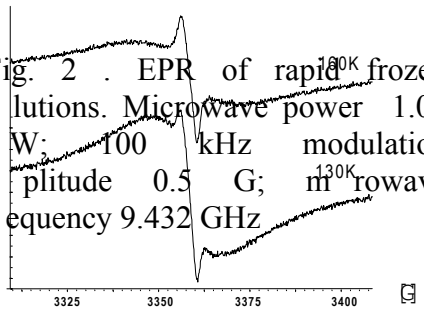

Fig.2. EPR of rapid frozen solutions. Microwave power 1.05 mW; 100kHz modulation amplitude 0.5 G; microwave frequency 9.432 GHz.

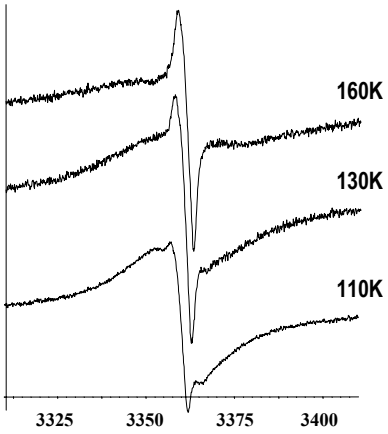

Fig. 3. EPR of solutions slowly cooled from room temperature. Spectrometer settings as for Fig. 2.

The effect of freezing rate is shown in Figs. 2 and 3 where we compare spectra of samples cooled by rapid freezing in liquid nitrogen and then placed in a cold nitrogen gas stream at the desired temperature with those of the same samples when cooled in the gas stream from room temperature. The rapidly frozen samples (Fig. 2), when examined at temperatures above about 120 K, exhibit a smaller peak to peak linewidth, with less intensity

in the wings, than do the slowly cooled samples. The appearance of the spike is also independent of the freezing rate.

The dependence on freezing rate arises from the tendency of many organic solvents to form poor glasses and solute aggregates on freezing. This may result in dipolar broadening of the EPR signals of paramagnetic complexes. When the samples are less rapidly cooled the strains in the glass are more readily annealed and aggregation occurs less readily. Where weak intermolecular exchange interactions are present, exchange narrowing of the dipolar broadened lines occurs and the resonance assumes a more Lorentzian shape. It is unclear whether the increase in peak to peak derivative width of the broad line between 130 K and 160 K is due to a real increase in width or to a reduction of exchange narrowing effects. The latter seems more likely, due to the dispersion of solute aggregates as the solvent approaches its melting point.

4. Conclusions

The interpretation of Eaton et al [5] in terms of the freezing in of Jahn-Teller distortions requires a significant contribution from the spike to the spin system of the broad line. Our EPR results show that the spike is independent of the broad line, consistent with findings of Paul et al.[2]. Further, changes in width of the broad line similar to those observed by Eaton et al [5] have been shown to arise as a result of the power saturation of the spike, to differences in freezing rate and to the dispersion of solute aggregates at higher temperatures. Thus neither our observations nor those of Eaton et al [5] provide convincing evidence for the existence of Jahn-Teller distortions at low temperatures or for the presence of low-lying excited states.
Whilst an elaborate theory of Jahn-Teller effects in icosahedral molecules has been established [4] it is not clear how this relates to the present results. The theory predicts a triply degenerate orbital ground state for C_{60} and a spin S= 3/2 ground state for C_{60}^{3-}. This is not in accord with experiment. The association of the three Na crown ether molecules with the icosahedrally symmetric C_{60} molecule may provide the requisite lowering of symmetry to give an orbital singlet ground state, independent of Jahn-Teller effects, and a quartet state well separated from the ground state.

Acknowledgments

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