ROTATIONAL MOBILITY OF Sc$_2$@C$_{80}$CH$_2$Ph STUDIED BY EPR SPECTROSCOPY

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Abstract

This work summarizes the mobility properties of the scandium bimetal encapsulated in a fullerene cage studied in detail in our previous works over a wide temperature range. It was shown that in the liquid phase, the lines of the electron paramagnetic resonance (EPR) spectrum differ in the amplitude and width, while low-temperature (20–120 K) pulse EPR measurements revealed that the phase relaxation depends on the state of the total spin of scandium nuclei. The observed properties are in good agreement with the mobility of both the fullerene and encapsulated bimetal inside.

Introduction

The motion of molecules and their fragments fundamentally changes the physical and chemical properties of matter, and controlling molecular dynamics has the potential to advance a wide range of scientific fields and technologies, including nanotechnology and quantum information. Endofullerenes have an encapsulated fragment that enables the core mobility within host fullerenes. Thus, two types of motions can be studied in such molecules: the motion of the molecule as a whole and the rotation of its core. In particular, it was shown that in some fullerenes the endohedral fragment rotates inside the fullerene even when the carbon cage is frozen [1, 2].

Molecular mobility can have a significant effect on spin dynamics and relaxation. EPR spectroscopy is one of the most powerful methods for studying molecular dynamics. It is known that the shape and width of an EPR line depend on the molecular mobility. In addition, changes in the position and orientation affect spin coherence and relaxation times [3–5]. In the case of endofullerenes, the spin system is sensitive to the mobility of both the carbon cage and encapsulated fragment.

Herein, we summarized our EPR studies on scandium bimetallofullerene Sc$_2$@C$_{80}$CH$_2$Ph [4, 5]. The encapsulated fragment consists of two scandium ions sharing a single delocalized electron ($S = 1/2$) [6]. This electron strongly interacts (509 MHz) with two equivalent scandium ^{45}Sc nuclei ($I_{Sc} = 7/2$). As a result, the spin state of the scandium nuclei is characterized by a total spin, which has one of the possible values I = 0–7 and a magnetic quantum number m. The strong hyperfine interaction (HFI) splits all spin sublevels, and all 64 lines of the EPR spectrum are resolved. The spin structure of Sc$_2$@C$_{80}$CH$_2$Ph is well known [3, 4], so that, despite the large number of resonance lines, each of them can be unambiguously

assigned to a specific state of the nuclear spin (I, m).

The study of the bimetallofullerene in a wide temperature range by both steady-state and pulse EPR allowed for observing different regimes of molecular motion. It was shown that the rotational motion of the bimetallic unit significantly affects the EPR line broadening and phase relaxation time. The variation of these properties, which are specific to the nuclear spin (I, m), indicates that the motion of the bimetallic unit within the fullerene cage persists down to 100 K [5].

Molecular mobility of the bimetallofullerene

The high-temperature spectra of Sc$_2$@C$_{80}$CH$_2$Ph were studied by continuous wave EPR spectroscopy. The resonance positions of the EPR lines at temperatures 230–300 K are determined by the isotropic Zeeman (ω) and hyperfine (a) interactions. Due to the large HFI, the flip-flop terms of the HFI Hamiltonian affect the resonance conditions. Thus, the higher order terms in the expansion of resonance fields over the factor (ma/ω) are significant. Due to this property, the bimetallofullerenes with the same m-value but differing in the I-values have different resonance positions. All 64 EPR lines are resolved and have a Lorentzian shape. The lines are broadened by incomplete averaging of the anisotropic part of the HFI ($\Delta a = 61.4\ MHz$) and their widths are specific to the spin state (I, m). The EPR spectra below the melting point of the solvent (178 K) remain well resolved, although significant changes in the shape of the EPR lines are observed. In this region, the carbon cage of the fullerene is frozen and the shape of the EPR spectra is determined by the motion of the bimetallic unit. This motion partially reduces the anisotropic part of the HFI (Δa), which is manifested by a change in the inhomogeneous line broadening and in the resonance conditions (the maxima of the
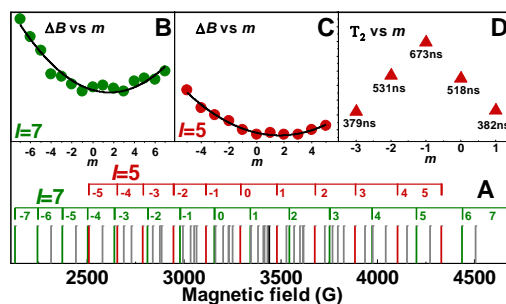
EPR lines) [4].

In general, the changes of the EPR lines with temperature are much smaller compared to the total width of the spectrum. Therefore, the EPR spectrum of the bimetallofullerene is shown as a stick spectrum in the graphical abstract (panel **A**), which represents the main peculiarities observed by the EPR methods. The properties of the resonance transitions presented in the graphical abstract are highlighted in color. The values belonging to the sub-ensembles with $I = 5$ are marked in red and those with $I = 7$ are marked in green. Panels **B** and **C** show the peak-to-peak linewidths ΔB for the given values of the total nuclear spin ($I = 5$ and $I = 7$). These data correspond to the experimental data recorded at 300 K. The linewidth varies in the range of 1.06–1.55 G for $I = 7$ and 0.77–1.07 G for $I = 5$. Note that the peak-to-peak width (PP) and the full width at half maximum (FWHM) for the Lorentzian lineshape are related as $\Delta B(PP)/\Delta B(FWHM) = \sqrt{3}$. The correlation between the linewidth and the spin state is apparent. The observed linewidths are reproduced well by the Wilson–Kivelson series over the powers of (ma/ω). The linewidths increase monotonically with the total spin I, and there is an obvious dependence on the second order of the m-value. The presence of the higher order terms makes this dependence non-quadratic, as can be clearly seen by comparing the linewidths corresponding to the m-values of opposite sign.

The low-temperature motion broadening is difficult to study by continuous wave EPR due to the poor resolution of spectra in this region. Pulse methods are more sensitive to the slow changes in the local environment of the spin system. Therefore, Hahn's spin-echo method was applied to study the molecular motion by observing the spin decoherence [5]. Panel **D** of the graphical abstract shows the dependence of the phase relaxation time (380–680 ns) obtained for the total nuclear spin $I = 5$ at 120 K. It can be seen that the relaxation time passes through the maximum at $m = -1$. These results were explained by the influence of spectral diffusion. The rotational motion reorients the bimetallic unit in the fullerene cage. This changes the resonance conditions and destroys the spin coherence. As a result, spectral diffusion shortens the phase relaxation time of the transverse magnetization. The inhomogeneous broadening due to the anisotropy of the HFI (Δa) depends almost linearly on the value of the magnetic quantum number m. It was shown that, in the X-band experiment, the anisotropy of the Zeeman interaction is about Δa [5]. As a result, the combined contribution of these interactions is canceled at $m = -1$. This leads to a decrease in the linewidth of the corresponding EPR line, which in turn reduces the spin diffusion effect on the phase relaxation. Changing the value of m in any direction from -1 leads to an increase in the linewidth and consequently to a decrease in the spin decoherence time, as was observed in the experiment.

As the temperature decreases, the difference becomes less significant and practically disappears at 20 K [5]. The mobility of the bimetallic unit was shown to be persistent down to very low temperatures and significantly affects the spin decoherence down to 80–100 K.

Conclusions

The unique properties of endofullerene $Sc_2@C_{80}CH_2Ph$ allowed us to characterize the intra- and intermolecular processes associated with the spin subsystem by EPR spectroscopy. It was shown that the rotational mobility of the endohedral fragment in $Sc_2@C_{80}CH_2Ph$ manifests itself down to very low temperatures, well below the melting temperature of the solvent. This statement is based on both the analysis of EPR spectra and the observation of the dependence of the decay time of the electron spin echo signal envelope on the magnetic quantum number m of the total spin I of two scandium nuclei.

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