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Microscopic theory of electron spin relaxation in N@C$_{60}$

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Endohedral N@C$_{60}$ exhibits an extremely long electron spin relaxation time and offers a great potential in storing and processing quantum information. Here, we present a microscopic theory of electron spin relaxation in N@C$_{60}$. The theory combines (1) the spin-orbit interaction of N $2p$ electrons, which mixes the ground-state ^4S with excited ^2P and ^2D states, and (2) the coupling between the N $2p$ electrons and C$_{60}$ H_g vibrations, which facilitates transitions between ^2P and ^2D states. The spin relaxation occurs via a two-phonon (Raman) process by absorbing a H_g phonon and emitting another at the (approximately) same frequency. The theory consistently explains measured spin relaxation time T_1 and its temperature dependence, and predicts two independent spin decoherence T_2 constants for $\pm 3/2 \rightarrow \pm 1/2$ transitions.

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I. INTRODUCTION

Electron spin relaxation in nanostructures plays a central role in designing spintronic devices[1] and quantum computing schemes.[2,3] Endohedral N@C$_{60}$ (Ref. 4) is particularly promising for these applications because of its long spin relaxation time.[5–8] This system is unique, wherein the N atom and its spins, shielded by the C$_{60}$ cage, are largely immune from environmental influences.[4,9,10] Consequently, existing theories of spin relaxation for conventional liquids and solids are not directly applicable. Recent temperature-dependent measurements reveal the central role of C$_{60}$ vibrations in electron spin relaxation in N@C$_{60}$.[7,8] The observed identical T_1 constants for different nuclear spin states of N rule out relaxation mechanisms from the hyperfine interaction. The exponential temperature dependence of T_1 is inconsistent with a weak temperature dependence expected from the phenomenological fluctuating zero-field splitting model,[5,7] but resembles that from an Orbach[11] process, which involves resonant transitions between the ground state and excited states. In addition, a constant ratio of 2/3 is observed between outer- and inner-transition T_2 constants.

In this paper, we present a microscopic theory that derives an effective fluctuating Hamiltonian among the ground-state quartet and elucidates spin relaxation in N@C$_{60}$ assisted by C$_{60}$ phonons. The Hamiltonian describes effects of *virtual* excitations of the N electrons via absorbing a H_g phonon and emitting another on spin dynamics, which is not an Orbach process.[12] The theory, which is also valid for P@C$_{60}$ (Ref. 9) and can be readily extended to other endohedral fullerenes,[13] suggests a universal importance of the two-phonon process in determining electron spin relaxation in nanostructures.

The paper is organized as follows. First, we describe in Sec. II the relevant electronic states in N@C$_{60}$ with emphasis on the spin-orbit (SO) interaction. In Sec. III, we examine the coupling between the N $2p$ electrons and C$_{60}$ vibrations and evaluate the coupling strength. Then, in Sec. IV, we derive an effective Hamiltonian among N spin quartets for spin relaxation and calculate spin relaxation time T_1. We continue to study spin decoherence in Sec. V by applying the Redfield theory to the obtained spin Hamiltonian. Finally, we summarize our results in Sec. VI.

II. ELECTRONIC CONFIGURATIONS

Both experimental observations[4,10] and first-principles calculations[9] indicate that the electronic configuration of N in N@C$_{60}$ retains its atomic form and that no chemical bonding between the N and the C$_{60}$ cage takes place. In the ground state of a free N atom, three $2p$ electrons align their spins in parallel according to Hund's rule, forming a degenerate quartet ^4S with total spin $S=3/2$ and total orbital angular momentum $L=0$. Its orbital wave function, in terms of single-electron $2p$ orbitals, is

$$^4S = -\frac{1}{\sqrt{6}}\begin{vmatrix} \phi_{-1}(1) & \phi_0(1) & \phi_1(1) \\ \phi_{-1}(2) & \phi_0(2) & \phi_1(2) \\ \phi_{-1}(3) & \phi_0(3) & \phi_1(3) \end{vmatrix}, \tag{1}$$

where $\phi_1=-\frac{1}{\sqrt{2}}(p_x+ip_y)$, $\phi_0=p_z$, and $\phi_{-1}=\frac{1}{\sqrt{2}}(p_x-ip_y)$. Because of its zero orbital angular momentum, the SO interaction does not have any effect within the quartet.

To account for spin relaxation, one must consider the SO interaction between the ground state and excited states. The lowest excited states are doublets ($S=1/2$), ^2P ($L=1$), and ^2D ($L=2$). For doublets ^2P and ^2D, without loss of generality, we assume electron 2 and 3 are spin up and electron 1 is spin down, and their orbital wave functions ^2L_m ($m=-L$, $-L+1,\ldots,L$) can be written as

$$^2D_2 = \frac{1}{\sqrt{2}}\phi_1(1)\begin{vmatrix} \phi_0(2) & \phi_1(2) \\ \phi_0(3) & \phi_1(3) \end{vmatrix}, \tag{2}$$

$$^2P_1 = \frac{1}{2}\phi_1(1)\begin{vmatrix} \phi_{-1}(2) & \phi_1(2) \\ \phi_{-1}(3) & \phi_1(3) \end{vmatrix} - \frac{1}{2}\phi_0(1)\begin{vmatrix} \phi_0(2) & \phi_1(2) \\ \phi_0(3) & \phi_1(3) \end{vmatrix}. \tag{3}$$

The orbital wave functions of other ^2D_m and ^2P_m can be obtained by applying the operator $\hat{L}_-=(\hat{L}_x-i\hat{L}_y)$ to $^2D_2$ and $^2P_1$.

Since N has a rather weak SO coupling, the SO interaction is aptly described by the *LS* scheme,[14] where states are denoted as $^{2S+1}L_J^M$, where $J=|L-S|,\ldots,L+S$ and $M=-J,\ldots,J$. Hence, through the SO coupling, S^4 forms $^4S_{3/2}$, ^2P forms $^2P_{3/2}$ and $^2P_{1/2}$, and ^2D forms $^2D_{5/2}$ and $^2D_{3/2}$,

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$$
{}^2P^M_{1/2(3/2)} = \sqrt{\frac{3/2-(+)M}{3}}\,{}^2P^+_{M-1/2} -(+)\sqrt{\frac{3/2+(-)M}{3}}\,{}^2P^-_{M+1/2}, \tag{4}
$$

$$
{}^2D^M_{3/2(5/2)} = \sqrt{\frac{5/2-(+)M}{5}}\,{}^2D^+_{M-1/2} -(+)\sqrt{\frac{5/2+(-)M}{5}}\,{}^2D^-_{M+1/2}, \tag{5}
$$

where ${}^2L^{+(-)}_m$ denotes the up spin (down spin) state with an orbital ${}^2L_m$.

The electronic Hamiltonian for the N $2p$ electrons is $H=U^+(H^0+H_{SO})U$, where the basis set $U=({}^4S_{3/2},{}^2D_{3/2},{}^2P_{3/2},{}^2D_{5/2},{}^2P_{1/2})^T$. H^0 describes the term energies of the ${}^4S$, ${}^2D$, and ${}^2P$,

$$
H^0 = \begin{pmatrix} E_1 & 0 & 0 & 0 & 0 \\ 0 & E_2 & 0 & 0 & 0 \\ 0 & 0 & E_3 & 0 & 0 \\ 0 & 0 & 0 & E_2 & 0 \\ 0 & 0 & 0 & 0 & E_3 \end{pmatrix}, \tag{6}
$$

where $E_1=E_S$, $E_2=E_D$, $E_3=E_P$, and the SO interaction is[14]

$$
H_{SO} = \frac{1}{2}\zeta_p \begin{pmatrix} 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & \sqrt{5} & 0 & 0 \\ 2 & \sqrt{5} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \tag{7}
$$

where ζ_p is the SO coupling strength for a single $2p$ electron. In the LS scheme, ${}^2P_{1/2}$ and ${}^2D_{5/2}$ are not mixed with states with $J=3/2$. By diagonalizing the Hamiltonian, we obtain in the $J=3/2$ manifold the three eigenenergies $\tilde{E}_i$ and eigenstates, denoted by ${}^{2S+1}\tilde{L}_J$, which is related to ${}^{2S+1}L_J$ through a transformation matrix K. In particular, the ground state is

$$
{}^4\tilde{S}^M_{3/2} = K_{11}\,{}^4S^M_{3/2} + K_{12}\,{}^2D^M_{3/2} + K_{13}\,{}^2P^M_{3/2}. \tag{8}
$$

Hence, these eigenstates ${}^{2S+1}\tilde{L}_J$ are not pure spin states and transitions between them will cause spin relaxation. Using the experimental values $E_D-E_S=2.38$ eV, $E_P-E_S=3.58$ eV, and $\zeta_p=76$ cm^{-1} for a free N atom,[15–17] we obtain $K_{11}=1.0$, $K_{12}=1.2\times10^{-5}$, $K_{13}=2.6\times10^{-3}$, and $\tilde{E}_i\simeq E_i$.

III. ELECTRON-VIBRATION COUPLING AND COUPLING STRENGTH

Vibrations can directly couple to electron orbitals but not to spins. The three $2p$ electron orbitals of a N atom at the center of C$_{60}$ transform like t_{1u} in the icosahedral group I_h. According to the Jahn–Teller theorem $t_{1u}\otimes t_{1u}=A_g\oplus T_{1g}\oplus H_g$, they can couple only to vibrations with these three representations. Among them, the total symmetric A_g and antisymmetric T_{1g} are ineffectual because the former cannot break the degeneracy of $2p$ orbitals[18] and the latter cannot couple. C$_{60}$ has eight $H_g(k)$ branches ($k=1,\cdots,8$) and each branch is fivefold degenerate in energy. We focus only on the lowest branch $k=1$ since other H_g modes have much higher energies and are not much excited at room temperature.

The orbital-vibration coupling between the p_q orbital and the five H_g modes Q_i ($i=1,\ldots,5$) is[19,20]

$$
H_{\mathrm{OV}} = \frac{1}{2}g\begin{pmatrix} Q_5-\sqrt{3}Q_4 & -\sqrt{3}Q_1 & -\sqrt{3}Q_2 \\ -\sqrt{3}Q_1 & Q_5+\sqrt{3}Q_4 & -\sqrt{3}Q_3 \\ -\sqrt{3}Q_2 & -\sqrt{3}Q_3 & -2Q_5 \end{pmatrix}, \tag{9}
$$

where g is the coupling strength. Using the wave functions in Eqs. (1)–(3), we find that the matrix elements between ${}^4S$, ${}^2P$, and ${}^2D$ are

$$
\langle {}^2P_1|H_{\mathrm{OV}}|{}^2D_1\rangle = \langle {}^2P_{-1}|H_{\mathrm{OV}}|{}^2D_{-2}\rangle^* = -\frac{\sqrt{3}}{2}g(Q_2+iQ_3), \tag{10}
$$

$$
\langle {}^2P_1|H_{\mathrm{OV}}|{}^2D_1\rangle = -\langle {}^2P_{-1}|H_{\mathrm{OV}}|{}^2D_{-1}\rangle = \frac{3g}{2}Q_5, \tag{11}
$$

$$
\langle {}^2P_1|H_{\mathrm{OV}}|{}^2D_0\rangle = \langle {}^2P_{-1}|H_{\mathrm{OV}}|{}^2D_0\rangle^* = \frac{3}{2\sqrt{2}}g(Q_2-iQ_3), \tag{12}
$$

$$
\langle {}^2P_1|H_{\mathrm{OV}}|{}^2D_{-1}\rangle = -\langle {}^2P_{-1}|H_{\mathrm{OV}}|{}^2D_1\rangle^* = \frac{\sqrt{3}}{2}g(Q_4-iQ_1), \tag{13}
$$

$$
\langle {}^2P_0|H_{\mathrm{OV}}|{}^2D_2\rangle = -\langle {}^2P_0|H_{\mathrm{OV}}|{}^2D_{-2}\rangle^* = -\sqrt{\frac{3}{2}}g(Q_4+iQ_1), \tag{14}
$$

$$
\langle {}^2P_0|H_{\mathrm{OV}}|{}^2D_1\rangle = \langle {}^2P_0|H_{\mathrm{OV}}|{}^2D_{-1}\rangle^* = -\frac{\sqrt{3}}{2\sqrt{2}}g(Q_2+iQ_3), \tag{15}
$$

and all other elements $\langle {}^2P_m|H_{\mathrm{OV}}|{}^2D_{m'}\rangle$ are zero. With the wave functions ${}^{2S+1}L^M_J$ in Eqs. (4) and (5), the matrix elements of orbital-vibration interaction between all possible ${}^{2S+1}L^M_J$ and ${}^{2S'+1}L'^{M'}_{J'}$ states can be obtained.

We estimate the coupling strength g by setting $Q_i=0$ for $i=1-4$ and a nonzero $Q_5=\delta Q(3\cos^2\theta-1)$, with θ being the polar angle, and evaluating the energy change of a N $2p$ electron. The $2p$ electron wave functions in a free N atom are[14]

$$
|2p_z\rangle = \frac{1}{\sqrt{\pi}}\alpha_0^{5/2}re^{-\alpha_0 r}\cos\theta, \tag{16}
$$

$$|2p_x\rangle = \frac{1}{\sqrt{\pi}}\alpha_0^{5/2} r e^{-\alpha_0 r} \sin\theta \cos\phi, \tag{17}$$

where $\alpha_0 = Z^*/2a_0$, a_0 is the Bohr radius, and $Z^* = 3$ is the valence charge. These wave functions are the eigenstates of a Schrödinger equation with a Coulomb potential $(-e)V_0 = -Z^* e^2/r$ in a free space. In the presence of C_{60}, the boundary condition and the potential will change. We consider a C_{60} cage in equilibrium as a spherical shell with inner and outer radii r_0 and R_0 and a dielectric constant $\epsilon = 4-5$. From the van der Waals radius of C, $r_0 = 1.74$ Å and $R_0 = 5.09$ Å. Since the radius of $2p$ electrons is $1/\alpha_0 \simeq 0.3$ Å$\ll R_0$, it is safe to assume $R_0 \to \infty$ here. Thus, to the $2p$ electrons, the C_{60} cage is a cavity with radius r_0 in a dielectric medium. The surface of the cavity is assumed to be conducting, mimicking the free π electrons sticking out toward the center, which also maintains a constant potential on the surface. The nonzero Q_5 makes the C_{60} sphere shrink along one direction but elongate along the other two normal directions, resulting in an ellipsoid described by the equation $\rho^2/a^2 + z^2/c^2 = 1$, where $\rho^2 = x^2 + y^2$, $c = r_0 - 2\delta Q$, and $a = r_0 + \delta Q$.

The potential created by a point charge $Z^* e$ at the center of such an ellipsoidal cavity is

$$V_1 = \begin{cases} \dfrac{Z^* e}{\sqrt{a^2 - c^2}} \tan^{-1}\sqrt{\dfrac{a^2 - c^2}{\xi + c^2}}: & a^2 - c^2 < \xi < 0 \\ \dfrac{Z^* e}{\epsilon\sqrt{a^2 - c^2}} \tan^{-1}\sqrt{\dfrac{a^2 - c^2}{\xi + c^2}}: & \xi > 0, \end{cases} \tag{18}$$

where ξ and η are ellipsoidal coordinates, which are related to the Cartesian coordinates through $x = \sqrt{\frac{(\xi + a^2)(\eta + a^2)}{a^2 - c^2}} \cos\phi$, $y = \sqrt{\frac{(\xi + a^2)(\eta + a^2)}{a^2 - c^2}} \sin\phi$, $z = \pm\sqrt{\frac{(\xi + c^2)(\eta + c^2)}{c^2 - a^2}}$, and ϕ is the azimuthal angle.

The energy changes of the $2p$ electrons due to $\delta V \equiv V_1 - V_0$ are $\delta E_q = \langle 2p_q | -e\delta V | 2p_q \rangle$ and the coupling strength is $g = \frac{1}{2}\frac{\delta E_z - 2\delta E_x}{\delta Q}$. We obtain $g = 1.4$ eV/Å for $\epsilon = 5$ and $g = 1.37$ eV/Å for $\epsilon = 4.5$. It is noted that this value is considerably larger than the coupling between a C π electron and the vibrations in C_{60},[20] but similar to the displacement derivative of electrostatic energy of an electron centered in a C_{60} cage $\simeq 1$ eV/Å from *ab initio* calculations.[9] Interactions between the C_{60} vibrations and the N nucleus and core electrons are not considered here because they do not contribute to electron spin relaxation.

IV. SPIN RELAXATION TIME T_1

For spin relaxation, the energy loss due to spin flip must be dissipated into a local environment. Since the energy involved in spin flips is $\sim 10^{-5}$ eV with a Larmor frequency at 9.7 GHz, whereas, the lowest energy of C_{60} vibrations is about 30 meV, it is impossible to flip a spin by absorbing or emitting a single C_{60} vibration quanta (one-phonon process). One must consider a higher-order "Raman" process,[21–23] namely, a C_{60} phonon is inelastically scattered by flipping a spin (two-phonon process). Using the second-order perturbation of H_{OV}, we derive an effective Hamiltonian between the ground-state quartets ${}^4\tilde{S}^i_{3/2}$,

$$\langle {}^4\tilde{S}^i_{3/2} | H_{\mathrm{eff}} | {}^4\tilde{S}^j_{3/2} \rangle = \sum_{\mu\nu} \left(\sum_{LJM} \frac{\langle {}^4\tilde{S}^i_{3/2}, n^-_\mu n^+_\nu | H_{\mathrm{OV}} | LJM, n^-_\mu n_\nu \rangle \langle LJM, n^-_\mu n_\nu | H_{\mathrm{OV}} | {}^4\tilde{S}^j_{3/2}, n_\mu n_\nu \rangle}{E_S - E_{LJ} - \hbar\omega_\mu} \right.$$
$$\left. + \sum_{LJM} \frac{\langle {}^4\tilde{S}^i_{3/2}, n^-_\mu n^+_\nu | H_{\mathrm{OV}} | LJM, n_\mu n^+_\nu \rangle \langle LJM, n_\mu n^+_\nu | H_{\mathrm{OV}} | {}^4\tilde{S}^j_{3/2}, n_\mu n_\nu \rangle}{E_S - E_{LJ} + \hbar\omega_\nu} \right), \tag{19}$$

where n_μ is the phonon number of the μth mode, ω_μ is its frequency, and $n^\pm_\mu = n_\mu \pm 1$. The intermediate states $|LJM\rangle$ include all $\tilde{D}^M_{3/2}$, $\tilde{P}^M_{3/2}$, $D^M_{5/2}$, and $P^M_{1/2}$. Since $|E_S - E_{LJ}| > 2$ eV$\gg \hbar\omega_\mu \equiv \hbar\omega \simeq 30$ meV, the energy of the H_g modes, we can safely neglect $\hbar\omega_\mu$ in the denominators in Eq. (19). After a lengthy calculation, we find that the fluctuating Hamiltonian $H_I(t) = H_{\mathrm{eff}} - \overline{H_{\mathrm{eff}}}$ ($\bar{A}$ is the time average of A) due to C_{60} H_g vibrations can be summarized in terms of spin operators

$$H_I(t) = \gamma\left[(\lambda_1 - \bar{\lambda}_1)\left(\hat{S}_z^2 - \frac{5}{4}\right) + (\lambda_2 - \bar{\lambda}_2)(\hat{S}_+\hat{S}_z + \hat{S}_z\hat{S}_+ + \hat{S}_-\hat{S}_z \right.$$
$$\left. + \hat{S}_z\hat{S}_-) + (\lambda_3 - \bar{\lambda}_3)(\hat{S}_+^2 + \hat{S}_-^2) \right],$$

$$\gamma = \frac{K_{12}^2}{E_S - E_P} - \frac{5}{3}\frac{K_{13}^2}{E_S - E_D},$$

$$\lambda_1 = \frac{9g^2}{40}(4Q_1^2 - Q_2^2 - Q_3^2 + 4Q_4^2 - 4Q_5^2),$$

$$\lambda_2 = -\frac{3g^2}{40}[3(Q_2 + iQ_3)(Q_4 - iQ_1) + \sqrt{3}Q_5(Q_2 - iQ_3)],$$

$$\lambda_3 = \frac{3g^2}{80}[4\sqrt{3}Q_5(Q_4 - iQ_1) - 3(Q_2 - iQ_3)(Q_2 - iQ_3)], \tag{20}$$

where $Q_\mu = (\frac{f\hbar}{M\omega})^{1/2}(a_\mu + a_\mu^\dagger)$, $M = 60M_C$ with M_C being the mass of the C atom, $a_\mu^\dagger$ is the phonon creation operator for the μth mode, and $f = \sqrt{5}/2$ is the normalization factor for H_g modes.

In a system with a definable spin temperature,[24,25] the spin relaxation time T_1 can be calculated from

$$T_1^{-1} = \sum_{\xi\eta} W_{\xi\eta}(E_\xi - E_\eta)^2 / 2\sum_\eta E_\eta^2, \tag{21}$$

where E_ξ is the energy of state ξ in the presence of an applied magnetic field and $W_{\xi\eta}$ is the transition rate from ξ to η,

$$W_{\xi\eta} = \frac{2\pi}{\hbar}\overline{|\langle\eta|H_I(t)|\xi\rangle|^2}\rho(E), \tag{22}$$

with $\rho(E)$ being the density of final states in energy. For the vibrational excitations with a line width Γ,

$$\rho(E) = \frac{\hbar\Gamma}{2\pi}[E^2 + (\hbar\Gamma/2)^2]^{-1}. \tag{23}$$

The transition rate in Eq. (22) can be equivalently expressed in terms of temporal correlation functions,

$$W_{\xi\eta} = \int_{-\infty}^{+\infty} \frac{e^{i\omega_{\xi\eta}\tau}}{\hbar^2}\overline{\langle\xi|H_I(t)|\eta\rangle\langle\eta|H_I(t-\tau)|\xi\rangle}d\tau, \tag{24}$$

where $\hbar\omega_{\xi\eta} = E_\xi - E_\eta$. For a commonly used correlation time assumption $\overline{H_I(t)H_I(t-\tau)} = \overline{|H_I(t)|^2}e^{-|\tau|/\tau_c}$, the two transition rate expressions are identical if $\Gamma = 2/\tau_c$. Equation (24) involves averaged vibrational fluctuations $\overline{(Q_\mu Q_\nu)^2}$ and $\overline{(Q_\mu^2 - \overline{Q_\mu^2})^2}$, which can be expressed in terms of phonon occupations

$$\overline{(Q_\mu Q_\nu)^2} = \left(\frac{f\hbar}{M\omega_\mu}\right)^2\overline{(a_\mu^\dagger a_\nu + a_\nu^\dagger a_\mu)^2} = 2\left(\frac{f\hbar}{M\omega}\right)^2 n(n+1), \tag{25}$$

$$\overline{(Q_\mu^2 - \overline{Q_\mu^2})^2} = 4\left(\frac{f\hbar}{M\omega}\right)^2\overline{(n_\mu - \bar{n}_\mu)^2} = 4\left(\frac{f\hbar}{M\omega}\right)^2 n(n+1), \tag{26}$$

where $n = \bar{n}_\mu \equiv \overline{a_\mu^\dagger a_\mu} = \frac{1}{e^{\beta\hbar\omega}-1}$ and $\beta \equiv 1/k_BT$, with k_B being the Boltzmann constant and T being the temperature. Here, a relation for independent boson $\overline{(n_\mu - \bar{n}_\mu)^2} = \frac{1}{\beta}\frac{\partial\bar{n}_\mu}{\partial\mu_0} = \bar{n}_\mu(\bar{n}_\mu + 1)$ has been used and μ_0 is the chemical potential of the boson system.[26]

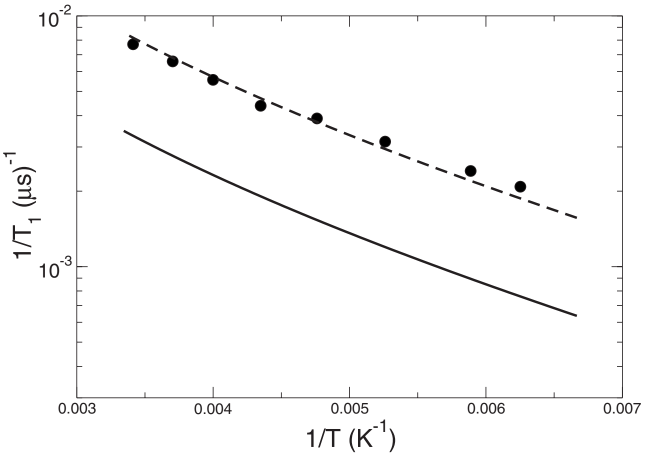

FIG. 1. Logarithm of $1/T_1$ against $1/T$. Circles are the measured data of N@C$_{60}$, adapted from Ref. 7. Solid line is our theoretical results with $\hbar\omega = 30$ meV, $g = 1.4$ eV/Å, and $\hbar\Gamma = 10^{-4}$ meV (corresponding to a lifetime of 10 ps). The dashed line is obtained by multiplying the solid line by a constant 2.46.

Using these relations, we obtain $\overline{|\lambda_2 - \bar{\lambda}_2|^2} = \overline{|\lambda_3 - \bar{\lambda}_3|^2} = \frac{189}{400}g^4 n(n+1)$. If the motional narrowing approximation $\rho(E) \simeq \frac{2}{\pi\hbar\Gamma}$ is adopted, which requires $\hbar\Gamma > 2E$, a condition usually satisfied, for the Larmor frequency, $\Omega_L/2\pi = 9.7$ GHz is slower compared to vibrational relaxation in C$_{60}$, typically $10^{11} - 10^{12}$ Hz,[27] $W_{1/2-1/2} = 0$, $W_{3/2\ 1/2} = W_{3/2-1/2} \equiv w$, and we have

$$\frac{1}{T_1} = 2w = \frac{567}{8}\gamma^2\frac{g^4}{(M\omega)^2\Gamma}\frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}. \tag{27}$$

Figure 1 compares the measured T_1 of N@C$_{60}$ in a nonpolar CS$_2$ solvent with results from Eq. (27). We see an excellent agreement between theory and experiment. The factor of 2.5 difference is considered to be rather small in spin relaxation studies and may be attributed to the fact that the N properties in N@C$_{60}$ may slightly deviate from its free atomic values.

V. SPIN DECOHERENCE TIME T_2

Experiments suggest that the system may have more than one T_2 constant. To identify all possible T_2, we start from the Redfield equation in the interaction representation[24,25]

$$d\mathcal{S}_{\xi\xi'}^*/dt = \sum_{\eta\eta'} R_{\xi\xi',\eta\eta'}\mathcal{S}_{\eta\eta'}^*, \tag{28}$$

where $\mathcal{S}_{\xi\xi'}^* \equiv \langle\xi|\hat{S}_x^*|\xi'\rangle$ and $\hat{S}_x^*(t) = e^{-i\frac{\mathcal{H}_0 t}{\hbar}}\hat{S}_x(t)e^{i\frac{\mathcal{H}_0 t}{\hbar}}$. $\mathcal{H}_0$ is the time-independent Zeeman term that determines spin resonance frequency and the Redfield matrix is

$$R_{\xi\xi',\eta\eta'} = \frac{1}{2\hbar^2}\Bigg[J_{\xi\eta\xi'\eta'}(\omega_{\xi'\eta'}) + J_{\xi\eta\xi'\eta'}(\omega_{\xi\eta}) - \delta_{\xi'\eta'}\sum_\zeta J_{\zeta\eta\zeta\xi}(\omega_{\zeta\eta}) - \delta_{\xi\eta}\sum_\zeta J_{\zeta\xi'\zeta\eta'}(\omega_{\zeta\eta'})\Bigg],$$

$$J_{\xi\xi'\eta\eta'}(\omega) = \int_{-\infty}^{+\infty}\overline{\langle\xi|H_I(t)|\xi'\rangle\langle\eta'|_I(t-\tau)|\eta\rangle}e^{-i\omega\tau}d\tau.$$

According to the Redfield theory, the matrix elements are nonzero only for $\eta-\eta'=\xi-\xi'$. Focusing on $\eta-\eta'=1$ and denoting $X_1=\mathcal{S}^*_{3/2\ \ 1/2}$, $X_2=\mathcal{S}^*_{1/2-1/2}$, and $X_3=\mathcal{S}^*_{-1/2-3/2}$, we can rewrite the Redfield equation as

$$dX_i/dt=\mathcal{R}_{ij}X_j. \tag{29}$$

The nonzero elements in matrix $\mathcal{R}$ are

$$\mathcal{R}_{11}=\mathcal{R}_{33}=-\frac{1}{\hbar^2}\int_0^\infty \overline{\varpi(t)\varpi(t-\tau)}d\tau$$

$$-\frac{1}{2}\left(\sum_{\xi\neq 3/2}W_{3/2\xi}+\sum_{\xi\neq 1/2}W_{1/2\xi}\right), \tag{30}$$

$$\mathcal{R}_{22}=-\frac{1}{2}\left(\sum_{\xi\neq 3/2}W_{3/2\xi}+\sum_{\xi\neq 1/2}W_{1/2\xi}\right), \tag{31}$$

$$\mathcal{R}_{13}=\mathcal{R}_{31=}-W_{3/2\ \ 1/2}, \tag{32}$$

where $\varpi(t)=2\gamma(\lambda_1-\bar{\lambda}_1)$. We find $\overline{|\lambda_1-\bar{\lambda}_1|^2}=\frac{567}{200}g^4n(n+1)$ and $\int_0^\infty\overline{\varpi(t)\varpi(t-\tau)}d\tau/\hbar^2=w$. Hence, $\mathcal{R}_{11}=-3w$, $\mathcal{R}_{22}=-2w$, and $\mathcal{R}_{13}=-w$.

The matrix $\mathcal{R}$ indicates that the outer transitions $\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$, which involve X_1 and X_3, are decoupled from the inner transitions $\pm\frac{1}{2}\rightarrow\mp\frac{1}{2}$, which involve only X_2. The general solution of normalized $\mathbf{X}(t)$ is thus

$$\mathbf{X}(t)=C_1\mathbf{U}_1e^{-t/T'_{2o}}+C_2\mathbf{U}_2e^{-t/T''_{2o}}+C_3\mathbf{U}_3e^{-t/T_{2i}}, \tag{33}$$

where $\mathbf{U}_1=(1,0,1)^T/\sqrt{2}$, $\mathbf{U}_2=(1,0,-1)^T/\sqrt{2}$, $\mathbf{U}_3=(0,1,0)^T$, and C_i $(\Sigma_i|C_i|^2=1)$ are coefficients determined by the initial condition. $T'_{2o}=1/4w=T_1/2$ and $T''_{2o}=1/2w=T_1$ are two independent T_2 constants for outer transitions and $T_{2i}=1/2w=T_1$ is the T_2 constant for inner transitions. In the literature, a single T_2 time is always assumed for the outer transitions. Our results suggest that new experiments and data extraction schemes are needed to resolve multiple T_2 constants. The measured T_{2i} is similar to but smaller than T_1 $(T_{2i}\simeq 0.7T_1)$ (Ref. 7) and this discrepancy may be explained by the motional narrowing approximation used in the theory.[28]

The resonance line shape as a function of frequency Ω can be calculated from $\mathbf{X}$ via $I(\Omega)=\mathrm{Re}[\mathbf{X}^\dagger(0)A^{-1}\mathbf{X}(0)]$, where matrix $A_{mn}\equiv i[\Omega-\Omega_L-(2-m)\Delta]\delta_{mn}+\mathcal{R}_{mn}$. Here, Δ is the frequency shift due to second-order hyperfine-interaction corrections $\Delta\propto M_I^2$ and M_I is the N nuclear spin.[7] For $M_I=\pm 1$, three distinct peaks at $\Omega=\Omega_L-(2-m)\Delta$ $(m=1,2,3)$ were observed, suggesting $\Delta^2>w^2$. In the neighborhood of $\Omega_L\pm\Delta$, i.e., resonance lines corresponding to the outer transitions $I(\Omega)\simeq\frac{3w(|C_1|^2+|C_2|^2)/2}{[\Omega-\Omega_L-(\pm\Delta)]^2+9w^2}$, and the width, or the averaged inverse T_2 constant $T_{2o}^{-1}=3w$, which is independent of values of C_i. Hence, $T_{2i}/T_{2o}=3w/2w=1.5$. Figure 2 compares the measured T_{2o}^{-1} and ratio T_{2i}/T_{2o} (Ref. 7) with the theory and shows good agreements. The excellent agreement on the ratio, which is independent of model parameters, is particularly remarkable. For $M_I=0$, the three resonance peaks coalesce to a single one centered at $\Omega=\Omega_L$ and the resonant line is a superposition of Lorentz curves $I(\Omega)=\frac{4w|C_1|^2}{(\Omega-\Omega_L)^2+16w^2}+\frac{2w(|C_2|^2+|C_3|^2)}{(\Omega-\Omega_L)^2+4w^2}$, with a width of $T_2^{-1}=(2|C_1|^2+|C_2|^2+|C_3|^2)2w$, which, unlike the $M_I=\pm 1$ case, is a function of weights $|C_i|^2$ and ranges from $4w$ to $2w$ for different $|C_i|^2$. Experimentally, it was found that $T_2^{-1}\simeq\frac{3}{2}T_1^{-1}=3w$.[7,8]

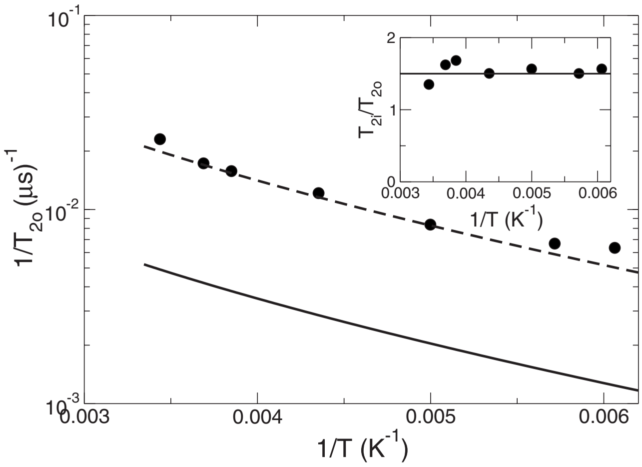

FIG. 2. Logarithm of $1/T_{2o}$ against $1/T$. Circles are the measured values, adapted from Ref. 7, and the solid line is our theoretical results. The dashed line is obtained by multiplying the solid line by a constant 4.0. The inset shows the ratio of T_{2i}/T_{2o} from experiment (circles) and theory (solid line). Other parameters are as in Fig. 1.

VI. SUMMARY

In conclusion, we have developed a microscopic theory of electron spin relaxation in N@C$_{60}$, which combines the SO interaction of N 2p electrons and the coupling between the N 2p electrons and the C$_{60}$ H_g vibrations. The spin relaxation occurs via a two-phonon Raman process by absorbing a H_g phonon and emitting another at the (approximately) same frequency. This microscopic theory consistently explains recently measured T_1 and T_2 and their temperature dependences, and predicts additional T_2 constants in N@C$_{60}$. The two-phonon Raman process, which is overlooked in studying spin relaxation in nanostructures such as quantum dots, is found to be pre-eminent in determining spin relaxation in N@C$_{60}$, suggesting the necessity of including the two-phonon process in other nanostructures.

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