Retarded Green's-Function Calculation of Magnetic Resonance Relaxation Time T_1 for Rotating Molecules or Atomic Groups in Solids

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The two-times Green's-function formalism is applied to the calculation of the NMR relaxation time T_1 for systems of hindered-rotating molecules or atomic groups in solids or solid surfaces at very low temperature. The rotation of the molecules is quantum-mechanically considered as one-phonon induced transitions between the hindered-rotator levels. The nuclear spin system is assumed to be coupled to the bath of thermal phonons through the phonon–rotation interaction. The longitudinal relaxation rate is determined by taking the lowest order approximation for the pole structure of the retarded Green's function; in this way a multiexponential behavior due to the different nuclear spin species present in the molecule or atomic group is obtained. © 1992 Academic Press, Inc.

The purpose of this paper is to present a formal derivation, based on the two-times Green's-function formalism, of the NMR relaxation rates for a relatively simple nuclear spin system coupled to a more complex one, acting as a thermal reservoir within the linear response regime. The determination of these relaxation rates is usually carried out by calculating some spectral densities, related through the fluctuation–dissipation theorem with the relaxation rates. As a common practice this is done semiclassically, i.e., the variables associated with the lattice are considered classical entities (*1–4*), and in many cases some parameters, such as correlation times and their specific temperature dependencies, are added without rigorous calculation. Another approach to the problem is given by the solution of coupled master equations for the populations of the different nuclear spin species (*5–9*), where the transition probabilities are calculated quantum mechanically, limiting the treatment to low temperatures.

The formalism that we present in this work offers the possibility of a first-principle calculation for the relaxation rates in such systems where it is possible to write down an effective Hamiltonian that describes the thermal bath over the whole temperature range considered and allows for the direct microscopic modeling of the system, since various model Hamiltonians can be easily introduced in an attempt to reproduce the experimental results. There is no need to introduce in addition any phenomenological parameters or some very strong assumptions like the existence of a common spin temperature, since all this information is included in the dynamics given by the Hamiltonian and in the formalism itself; i.e., the generalized susceptibilities given by the Green's functions satisfy Kramers–Kronig relations, fluctuation–dissipation theorems, symmetry properties, sum rules, and so on.

In the calculation presented here, we shall consider spin-carrying molecules or atomic groups in a solid or solid surface, subjected to an external strong magnetic field and a small perpendicular RF magnetic field. The spin-carrying molecules are assumed to undergo hindered rotations due to the scattering of phonons. In this sense, the rotational degrees of freedom are modeled by a Hamiltonian whose potential-energy term is taken as the interaction energy of the molecule with all the other atoms and molecules in the solid fixed at their equilibrium positions. The existence of collective vibrational modes in the crystal modulates this potential energy and gives rise to an interaction between the rotational degrees of freedom and the lattice vibrations or phonons. For simplicity, we shall consider the effect of the phonon–rotation interaction up to terms linear in the displacements of the atoms and molecules from their equilibrium positions, allowing in this way only one-phonon processes. This means that our calculation is limited to relaxation phenomena at very low temperatures. In regard to the magnetic interaction involved, the nuclear spins are taken to interact among themselves through magnetic dipolar forces of intramolecular type; intermolecular spin interactions are not included.

In order to calculate the longitudinal relaxation rate, it is first necessary to set up the equations for the Green's function, which in general consist of a system of hierarchical equations, usually infinite in number, and next to impose some physical approximations in order to decouple and further reduce the system of equations to a workable level. Finally, with these approximations, a solution with physical meaning is obtained. By this, we mean a solution which is consistent with general symmetry properties of the Green's function and general sum rules. The approximations we shall impose include, to its lowest order, the rotation–phonon interaction, which means one-phonon processes, and the validity of the random-phase approximation, which in this context is related to the absence of correlation between different components of nuclear spin operators and those which correspond to the thermal bath, in this particular case, phonon operators.

GREEN'S FUNCTIONS AND THE RELAXATION RATE

We will consider a system which can be modeled by the total Hamiltonian

$$\mathcal{H} = \mathcal{H}_S + \mathcal{H}_{SL} + \mathcal{H}_L, \tag{1}$$

where $\mathcal{H}_S$ represents the nuclear spin Hamiltonian, $\mathcal{H}_L$ is the Hamiltonian for the heat bath, and $\mathcal{H}_{SL}$ represents the coupling between both systems, usually under the condition $\mathcal{H}_L > \mathcal{H}_S > \mathcal{H}_{SL}$, which occurs commonly in NMR experiments. In order to consider the evolution of the system toward thermal equilibrium, it is necessary to prepare the system in an initial nonequilibrium state. This can be achieved by the adiabatic switching on of a perturbation, which in our case is a magnetic field along a particular direction, and suddenly, at a time $t = 0$, this perturbation is switched off, letting the system evolve freely according to the Hamiltonian $\mathcal{H}$. The perturbation can be written

$$H_1' = -\mathbf{M} \cdot \mathbf{H}_1', \tag{2}$$

where

$$H_1' = \theta(-t)e^{\epsilon t}\mathbf{H}_1 \qquad \epsilon \to 0^+. \tag{3}$$

Within the linear response theory, the magnetization for $t > 0$ is given by the expression (10)

$$\langle \mathbf{M}(t) \rangle = \langle \mathbf{M} \rangle_0 - \int_{-\infty}^{+\infty} \langle\langle \mathbf{M}(t); \mathbf{M}(t') \rangle\rangle^{(-)} \cdot \mathbf{H}_1^r dt', \qquad [4]$$

which is written in terms of the two-times-retarded Green's function, $\langle\langle \mathbf{M}(t); \mathbf{M}(t') \rangle\rangle^{(-)}$. By using the causality property (10) of the retarded Green's function, it is possible to write the equation for the displacement of magnetization from the equilibrium situation in the following way,

$$\langle \delta\mathbf{M}(t) \rangle\rangle = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \frac{\langle\langle \mathbf{M}|\mathbf{M} \rangle\rangle_\omega^{(-)} \cdot \mathbf{H}_1}{i(\omega - i\epsilon)} e^{-i\omega t}, \qquad \epsilon \to 0^+, \qquad [5]$$

where $\langle \delta\mathbf{M}(t) \rangle = \langle \mathbf{M}(t) \rangle - \langle \mathbf{M} \rangle_0$.

It can be shown that

$$\langle \delta\mathbf{M}(t = 0) \rangle \rangle = -\langle\langle \mathbf{M}|\mathbf{M} \rangle\rangle_0^{(-)} \cdot \mathbf{H}_1 \qquad [6]$$

so that by taking the Laplace transform of Eq. [5], one can write

$$\langle \delta\mathbf{M}(z) \rangle = \mathbf{f}(z) \cdot \langle \delta\mathbf{M}(t = 0) \rangle, \qquad [7]$$

where

$$\mathbf{f}(z) = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \frac{\langle\langle \mathbf{M}|\mathbf{M} \rangle\rangle_\omega^{(-)} (\langle\langle \mathbf{M}|\mathbf{M} \rangle\rangle_0^{(-)})^{-1}}{(\omega - i\epsilon)(\omega - iz)}. \qquad [8]$$

We are interested in the asymptotic behavior of $\langle \delta\mathbf{M}(t) \rangle$, since it is that regime in which the relaxation rates are experimentally measured. According to Tauber's theorem ($11, 12$), an asymptotic expansion of $\mathbf{f}(t)$ can be written as

$$\mathbf{f}(t) = \sum_\nu \exp(z_\nu t) \sum_{k=0}^{\infty} C_k^{(\nu)} \{\Gamma(-n_k^{(\nu)})\}^{-1} t^{-(1+n_k^{(\nu)})}, \qquad [9]$$

where z_ν represents the poles of the function $\mathbf{f}(z)$, $n_k^{(\nu)}$ represents the order of the pole, and $C_k^{(\nu)}$ represents the coefficient in a Laurent expansion of $\mathbf{f}(z)$ around the pole z_ν. In the particular case of $\mathbf{f}(z)$ having only first-order poles, Eq. [9] can be written

$$\mathbf{f}(t) = \sum_\nu C^{(\nu)} \exp(z_\nu t). \qquad [10]$$

Let us suppose that the Green's function can be written in the general form

$$\langle\langle M_\alpha | M_{-\alpha} \rangle\rangle_\omega = \frac{\sigma_\alpha(\omega)}{[\omega - \alpha\omega_0 - W_\alpha(\omega)]}, \qquad [11]$$

where σ_α and W_α are complex functions. According to Eq. [8] the poles of the function $\mathbf{f}(z)$ are related to the poles of the Green's function so that only those poles that are located at the upper complex plane must be considered (13). In general it is necessary to make a complete analysis of the pole structure of the Green's function at the upper complex plane in order to describe the total asymptotic behavior of the function $\mathbf{f}(t)$.

As a simplifying assumption, we consider the following zeroth-order approximation to the pole structure. We first assume that the function σ_ω does not contribute with any pole. This assumption must be analyzed in every particular case with some care. Second, we assume that the function W_α can be approximated by its value at the frequency $\alpha\omega_0$. This second assumption usually is a very strong one since the whole pole structure is sometimes collapsed to a single first-order pole, but nevertheless, in many cases, this approximation gives the right relaxation behavior, correlating quite well with the experimental results (14). The relaxation rates obtained with these assumptions can be written in terms of the imaginary part of the function W_α evaluated at the frequency $\alpha\omega_0$, that is,

$$\frac{1}{T_1} = -\mathrm{Im}\ W_0(0) \tag{12}$$

and

$$\frac{1}{T_2} = -\mathrm{Im}\ W_+(+\omega_0) = -\mathrm{Im}\ W_-(-\omega_0) \tag{13}$$

HAMILTONIAN OF THE SYSTEM

In this work we are interested in the calculation of the NMR longitudinal relaxation rates of nuclei in symmetric molecules or molecular ionic groups in solids. With neglect of internal vibration modes of the molecules, the Hamiltonian of a molecular crystal placed in an external magnetic field is written as

$$\mathscr{H} = \mathscr{H}_Z + \mathscr{H}_R + \mathscr{H}_{Ph} + \mathscr{H}_{D\text{-}D} + \mathscr{H}_{R\text{-}Ph}, \tag{14}$$

where $\mathscr{H}_Z$ is the nuclear Zeeman Hamiltonian in the external magnetic field, and $\mathscr{H}_{D\text{-}D}$ represents the intramolecular magnetic dipolar interaction Hamiltonian between the nuclei. We assume that the intermolecular interaction is negligible as in most cases of practical interest. $\mathscr{H}_{Ph}$ is the phonon Hamiltonian given by

$$\mathscr{H}_{Ph} = \sum_{ks} \epsilon_{ks}(b_{ks}^+ b_{ks} + 1/2), \tag{15}$$

where b_{ks}^+ and b_{ks} are phonon creation and annihilation operators, s denotes the branch and polarization of the phonons, and k is its wave vector.

Finally, the terms $\mathscr{H}_R$ and $\mathscr{H}_{R\text{-}Ph}$ represent the molecular rotation Hamiltonian and the rotation–phonon interaction Hamiltonian, respectively. In general, the rotational Hamiltonian for a symmetric top molecule can be written as (15–17)

$$\mathscr{H}_R' = \frac{J^2}{2I} + V(\Omega, r_M, \{r_i\}), \tag{16}$$

where J is the molecular angular momentum operator, I is the moment of inertia, and V represents the intermolecular interaction potential, which depends on the set of Eulerian angles Ω, describing the molecular orientation with respect to the lattice axes, the position r_M of the molecule or ionic group in the lattice, and the set $\{r_i\}$ of positions of all other molecules and atoms in the lattice. This interaction potential $V(\Omega, r_M, \{r_i\})$ must be at least invariant with respect to the point symmetry group of the molecule or ionic group (18, 19) and it can be expanded as

$$V(\Omega, \mathbf{r}_M, \{\mathbf{r}_i\}) = \sum_\alpha C_\alpha(\mathbf{r}_M, \{\mathbf{r}_i\}) V_\alpha(\Omega), \qquad [17]$$

where $V_\alpha(\Omega)$ is some linear combination of Wigner matrices $\mathbf{D}^J_{KM}(\Omega)$ with the appropriate molecular symmetry invariance properties (18). The molecular positions in the crystal are not fixed but rather are undergoing displacements around the lattice equilibrium sites due to the presence of collective vibrational modes, i.e., phonons. Assuming that the displacements are very small, Eq. [17] can be expanded in a Taylor series around the molecular equilibrium positions, to obtain

$$V(\Omega, \mathbf{r}_M, \{\mathbf{r}_i\}) = \sum_\alpha C_\alpha(\mathbf{r}_{0M}, \{\mathbf{r}_{0i}\}) V_\alpha(\Omega)$$

$$+ \sum_\alpha (\mathbf{C}^M_\alpha \cdot \mathbf{U}_M) V_\alpha(\Omega) + \sum_\alpha \sum_i (\mathbf{C}^i_\alpha \cdot \mathbf{U}_i) V_\alpha(\Omega), \quad [18]$$

where

$$\mathbf{C}^M_\alpha = \nabla_M C_\alpha(\mathbf{r}_{0M}, \{\mathbf{r}_{0i}\}) \qquad \text{and} \qquad \mathbf{C}^i_\alpha = \nabla_i C_\alpha\{\mathbf{r}_{0M}, \{\mathbf{r}_{0i}\}). \qquad [19]$$

The second and third terms on the right-hand side of Eq. [18] represent the phonon–rotation interaction, which can be written in terms of phonon creation and annihilation operators as

$$\mathcal{H}_{\text{R-Ph}} = \sum_{ks} \sum_\alpha \frac{\hbar}{(2M\epsilon_{ks})^{1/2}} [(\mathbf{C}^M_\alpha \cdot \mathbf{e}_s) e^{i\mathbf{k}\cdot\mathbf{r}_{0M}} b_{ks}$$

$$+ (\mathbf{C}^M_\alpha \cdot \mathbf{e}^*_s) e^{-i\mathbf{k}\cdot\mathbf{r}_{0M}} b^+_{ks}) V_\alpha(\Omega). \quad [20]$$

The first term on the right-hand-side of Eq. [18] represents the static rotation Hamiltonian. In the representation of spin–rotation states, the rotation–phonon Hamiltonian can be written

$$\mathcal{H}_{\text{R-Ph}} = \sum_{\substack{\mu\mu' \\ ks}} \{ F^*_{\mu\mu'}(ks) |\mu'\rangle\langle\mu| b^+_{ks} + F_{\mu\mu'}(ks) |\mu\rangle\langle\mu'| b_{ks} \}, \qquad [21]$$

where

$$F_{\mu\mu'}(ks) = \sum_\alpha \frac{\langle\mu| V_\alpha(\Omega) |\mu'\rangle \hbar}{(2M\epsilon_{ks})^{1/2}} (\mathbf{C}^M_\alpha \cdot \mathbf{e}_s) e^{i\mathbf{k}\cdot\mathbf{r}_{0M}}, \qquad [22]$$

where we have included molecular displacements only.

CALCULATION OF THE GREEN'S FUNCTION $\langle\langle I^0 | I^0 \rangle\rangle_\omega$

It was shown in (19) and (20) that a convenient representation basis for the operators occurring in the system Hamiltonian is the set of eigenstates of the Zeeman and rotation Hamiltonians

$$(\mathcal{H}_Z + \mathcal{H}_R) |\mu\rangle = (E^Z_\mu + E^R_\mu) |\mu\rangle. \qquad [23]$$

The states $|\mu\rangle$ are linear combinations of products of spin and rotational wave functions (14) so that the label μ represents a set of quantum numbers which, in general, can be chosen as ($Im_I; Jm_J; \Gamma_I\Gamma_J\Gamma_0 t$), where I is the total nuclear spin, m_I its projection on the z axis, J the angular momentum, and m_J its projection on the

laboratory-frame z axis. For the most frequently studied hindered rotators of the type XY_3 and XY_4 with molecular point groups C_{3v} and T_d, respectively, it is safe to assume that the "feasible" operations of the full molecular symmetry group $P_N X S_2$ (P_N is the symmetric group of N elements) form a subgroup which is isomorphic to the molecular point group. In this case the Γ_S denotes irreducible representations of the molecular point group. Γ_I is the irreducible representation associated with a particular spin species of total nuclear spin I. Γ_J is the irreducible representation according to which the rotational wave function transforms and Γ_0 must be of symmetry A_1 or A_2 depending on our choice of the state $|\mu\rangle$ as a symmetric or antisymmetric state with respect to the exchange of two identical nuclei. Finally the label t distinguishes between the different states, where all the other quantum numbers are the same. In most cases t can be left out since there are no such other states. In what follows and for the sake of simplicity in our notation we will denote these Zeeman–rotation states only by the label μ.

In this representation the Green's function $\langle\langle I^0 | I^0 \rangle\rangle$ can be represented by

$$\langle\langle I^0 | I^0 \rangle\rangle_\omega = \sum_\mu \langle\langle |\mu\rangle\langle\mu| | I^0 \rangle\rangle_\omega I_\mu^0, \qquad [24]$$

where $I_\mu^0 = \langle\mu| I^0 |\mu\rangle$. In this form the Green's function $\langle\langle I^0 | I^0 \rangle\rangle_\omega$ is decomposed into a combination of new Green's functions $\langle\langle |\mu\rangle\langle\mu| | I^0 \rangle\rangle_\omega$ that can be considered as its components in the given representation. The equation of motion for any of the components of [24] is given by

$$\hbar\omega\langle\langle |\mu\rangle\langle\mu| | I^0 \rangle\rangle_\omega = \langle[|\mu\rangle\langle\mu|, I^0]\rangle_0$$

$$+ \sum_{\mu_1 \neq \mu} h_{\mu\mu_1}\langle\langle |\mu\rangle\langle\mu_1| | I^0 \rangle\rangle_\omega - \sum_{\mu_1 \neq \mu} h_{\mu_1\mu}\langle\langle |\mu_1\rangle\langle\mu| | I^0 \rangle\rangle_\omega$$

$$+ \sum_{\mu_1 ks} \{ F_{\mu\mu_1}(ks)\langle\langle |\mu\rangle\langle\mu_1| b_{ks} | I^0 \rangle\rangle_\omega - F_{\mu_1\mu}(ks)\langle\langle |\mu_1\rangle\langle\mu| b_{ks} | I^0 \rangle\rangle_\omega \}$$

$$+ \sum_{\mu_1 ks} \{ F^*_{\mu_1\mu}(ks)\langle\langle |\mu\rangle\langle\mu_1| b^+_{ks} | I^0 \rangle\rangle_\omega - F^*_{\mu\mu_1}(ks)\langle\langle |\mu_1\rangle\langle\mu| b^+_{ks} | I^0 \rangle\rangle_\omega \}. \qquad [25]$$

The new higher order Green's functions that appear and which contain phonon creation and annihilation operators obey the equations of motion

$$\{\hbar\omega - \Delta E^{(1)}_{\mu_2\mu_1} + \epsilon_{ks}\}\langle\langle |\mu_1\rangle\langle\mu_2| b^+_{ks} | I^0 \rangle\rangle_\omega = \langle[|\mu_1\rangle\langle\mu_2| b^+_{ks}, I^0]\rangle_0$$

$$+ \sum_{\mu_3 \neq \mu_2} h_{\mu_2\mu_3}\langle\langle |\mu_1\rangle\langle\mu_3| b^+_{ks} | I^0 \rangle\rangle_\omega - \sum_{\mu_3 \neq \mu_1} h_{\mu_3\mu_1}\langle\langle |\mu_3\rangle\langle\mu_2| b^+_{ks} | I^0 \rangle\rangle_\omega$$

$$+ \sum_{\mu_3 k's'} \{ F_{\mu_2\mu_3}(k's')\langle\langle |\mu_1\rangle\langle\mu_3| b^+_{ks} b_{k's'} | I^0 \rangle\rangle_\omega$$

$$- F_{\mu_3\mu_1}(k's')\langle\langle |\mu_3\rangle\langle\mu_2| b^+_{ks} b_{k's'} | I^0 \rangle\rangle_\omega \}$$

$$+ \sum_{\mu_3 k's'} \{ F^*_{\mu_3\mu_2}(k's')\langle\langle |\mu_1\rangle\langle\mu_3| b^+_{ks} b^+_{k's'} | I^0 \rangle\rangle_\omega$$

$$- F^*_{\mu_1\mu_3}(k's')\langle\langle |\mu_3\rangle\langle\mu_2| b^+_{ks} b^+_{k's'} | I^0 \rangle\rangle_\omega \}$$

$$- \sum_{\mu_3} F_{\mu_3\mu_1}(ks)\langle\langle |\mu_3\rangle\langle\mu_2| | I^0 \rangle\rangle_\omega \qquad [26]$$

and

$$\{\hbar\omega - \Delta E^{(1)}_{\mu_2\mu_1} - \epsilon_{ks}\}\langle\langle|\mu_1\rangle\langle\mu_2|b_{ks}|I^0\rangle\rangle_\omega = \langle[|\mu_1\rangle\langle\mu_2|b_{ks}, I^0]\rangle_0$$

$$+ \sum_{\mu_3\neq\mu_2} h_{\mu_2\mu_3}\langle\langle|\mu_1\rangle\langle\mu_3|b_{ks}|I^0\rangle\rangle_\omega - \sum_{\mu_3\neq\mu_1} h_{\mu_3\mu_1}\langle\langle|\mu_3\rangle\langle\mu_2|b_{ks}|I^0\rangle\rangle_\omega$$

$$+ \sum_{\mu_3 k's'} \{F_{\mu_2\mu_3}(k's')\langle\langle|\mu_1\rangle\langle\mu_3|b_{ks}b_{k's'}|I^0\rangle\rangle_\omega$$

$$- F_{\mu_3\mu_1}(k's')\langle\langle|\mu_3\rangle\langle\mu_2|b_{ks}b_{k's'}|I^0\rangle\rangle_\omega\}$$

$$+ \sum_{\mu_3 k's'} \{F^*_{\mu_3\mu_2}(k's')\langle\langle|\mu_1\rangle\langle\mu_3|b^+_{ks}b_{k's'}|I^0\rangle\rangle_\omega$$

$$- F^*_{\mu_1\mu_3}(k's')\langle\langle|\mu_3\rangle\langle\mu_2|b^+_{ks}b_{k's'}|I^0\rangle\rangle_\omega\}$$

$$+ \sum_{\mu_3} F^*_{\mu_3\mu_2}(ks)\langle\langle|\mu_1\rangle\langle\mu_3||I^0\rangle\rangle_\omega, \quad [27]$$

and

$$\Delta E^{(1)}_{\mu_2\mu_1} = (E^Z_{\mu_2} - E^Z_{\mu_1}) + (E^R_{\mu_2} - E^R_{\mu_1}) + (h_{\mu_2\mu_2} - h_{\mu_1\mu_1}). \quad [28]$$

Green's functions are also present in the dipolar coupling terms

$$\{\hbar\omega - \Delta E^{(1)}_{\mu_2\mu_1}\}\langle\langle|\mu_1\rangle\langle\mu_2||I^0\rangle\rangle_\omega = \langle[|\mu_1\rangle\langle\mu_2|, I^0]\rangle_0$$

$$+ \sum_{\mu_3\neq\mu_2} h_{\mu_2\mu_3}\langle\langle|\mu_1\rangle\langle\mu_3||I^0\rangle\rangle_\omega - \sum_{\mu_3\neq\mu_1} h_{\mu_3\mu_1}\langle\langle|\mu_3\rangle\langle\mu_2||I^0\rangle\rangle_\omega$$

$$+ \sum_{\mu_3 ks} \{F_{\mu_2\mu_3}(ks)\langle\langle|\mu_1\rangle\langle\mu_3|b_{ks}|I^0\rangle\rangle_\omega - F_{\mu_3\mu_1}(ks)\langle\langle|\mu_3\rangle\langle\mu_2|b_{ks}|I^0\rangle\rangle_\omega\}$$

$$+ \sum_{\mu_3 ks} \{F^*_{\mu_3\mu_2}(ks)\langle\langle|\mu_1\rangle\langle\mu_3|b^+_{ks}|I^0\rangle\rangle_\omega$$

$$- F^*_{\mu_1\mu_3}(ks)\langle\langle|\mu_3\rangle\langle\mu_2|b^+_{ks}|I^0\rangle\rangle_\omega\}. \quad [29]$$

Considering that we are interested in the evaluation of the longitudinal relaxation rate, as was mentioned before, we must only look for terms that will contribute to poles in the neighborhood of the frequency $\omega = 0$. On the other hand in order to decouple the chain of equations, we will make the following approximation for the higher order two-phonon Green's functions appearing in Eqs. [26] and [27],

$$\langle\langle|\mu_3\rangle\langle\mu_2|b^+_{ks}b^+_{k's'}|I^0\rangle\rangle_\omega = \langle\langle|\mu_3\rangle\langle\mu_2|b_{ks}b_{k's'}|I^0\rangle\rangle_\omega = 0,$$

$$\langle\langle|\mu_1\rangle\langle\mu_2|b^+_{ks}b_{k's'}|I^0\rangle\rangle_\omega = \langle n(ks)\rangle_0\delta_{kk'}\delta_{ss'}\langle\langle|\mu_1\rangle\langle\mu_2||I^0\rangle\rangle_\omega, \quad [30]$$

where $\langle n(ks)\rangle_0 = \langle b^+_{ks}b_{ks}\rangle_0 = \bar{n}(ks)$.

The approximations are justified since they only take into account one-phonon processes in the rotation–phonon interaction, and at the same time there is the assumption of a lack of correlation between the number of phonon operators in the state ks, $\bar{n}_{ks}$, and the operator I^0. By keeping terms up to second order in the inter-

actions together with this set of approximations, the chain of equatios is effectively decoupled, to obtain the solution for the component Green's function

$$\langle\langle |\mu\rangle\langle\mu| \,|\, I^0\rangle\rangle_\omega = \frac{F_\mu(\omega) + S_\mu(\omega)}{\{\hbar\omega - M_\mu(\omega)\}} . \tag{31}$$

The complex functions $F_\mu(\omega)$ and $S_\mu(\omega)$ are sums of matrix elements of the interaction Hamiltonians over the spin–rotation and phonon states and usually these sums do not contribute with poles to the total Green's function. Nevertheless these functions contribute to the intensity with which every component contributes to the time evolution of the longitudinal magnetization. Since, in order to get the relaxation rates, we are interested in the singular points of the Green's function, it is important to study only the denominator of Eq. [31], which can be written for the total Green's function as

$$\langle\langle I^0 | I^0\rangle\rangle_\omega = \sum_\mu \frac{I_\mu^0 N_\mu(\omega)}{\hbar\omega - M_\mu(\omega)} , \tag{32}$$

where now $N_\mu(\omega) = F_\mu(\omega) + S_\mu(\omega)$ and

$$M_\mu(\omega) = \sum_{\mu_1 \neq \mu} |h_{\mu\mu_1}|^2 \left\{ \frac{1}{\Delta_{\mu_1\mu}} + \frac{1}{\Delta_{\mu\mu_1}} \right\} + \sum_{\substack{\mu_1 \\ \mathbf{k}s}} \left\{ |F_{\mu\mu_1}(\mathbf{k}s)|^2 \frac{(\bar{n}_{\mathbf{k}s} + 1)}{\Delta_{\mu_1\mu}^-} \right.$$

$$\left. + |F_{\mu_1\mu}(\mathbf{k}s)|^2 \frac{\bar{n}_{\mathbf{k}s}}{\Delta_{\mu\mu_1}^-} + |F_{\mu\mu_1}(\mathbf{k}s)|^2 \frac{(\bar{n}_{\mathbf{k}s} + 1)}{\Delta_{\mu\mu_1}^+} + |F_{\mu_1\mu}(\mathbf{k}s)|^2 \frac{\bar{n}_{\mathbf{k}s}}{\Delta_{\mu_1\mu}^+} \right\} \tag{33}$$

with $\Delta_{\mu_2\mu_1}^\pm = \hbar\omega - \Delta E_{\mu_2\mu_1}^{(1)} \pm \epsilon_{\mathbf{k}s}$.

The imaginary part of the function $M_\mu(\omega)$, which is related to the relaxation rates, can be written

$$\text{Im } M_\mu(\omega) = -\pi \sum_{\mu_1 \neq \mu} |h_{\mu\mu_1}|^2 \{\delta(\hbar\omega - \Delta E_{\mu_1\mu}^{(1)}) + \delta(\hbar\omega - \Delta E_{\mu\mu_1}^{(1)})\}$$

$$-\pi \sum_{\substack{\mu_1 \\ \mathbf{k}s}} \{|F_{\mu\mu_1}(\mathbf{k}s)|^2(\bar{n}_{\mathbf{k}s} + 1)[\delta(\hbar\omega - \Delta E_{\mu_1\mu}^{(1)} - \epsilon_{\mathbf{k}s})$$

$$+ \delta(\hbar\omega - \Delta E_{\mu\mu_1}^{(1)} + \epsilon_{\mathbf{k}s})] + |F_{\mu_1\mu}(\mathbf{k}s)|^2 \bar{n}_{\mathbf{k}s} [\delta(\hbar\omega - \Delta E_{\mu\mu_1}^{(1)} - \epsilon_{\mathbf{k}s})$$

$$+ \delta(\hbar\omega - \Delta E_{\mu_1\mu}^{(1)} + \epsilon_{\mathbf{k}s})]\} . \tag{34}$$

DISCUSSION

According to Eqs. [12] and [34], each spin–rotation level presents a single nuclear-spin longitudinal relaxation rate, given by

$$\frac{1}{T_{1\mu}} = \frac{2\pi}{\hbar} \sum_{\mu_1 \neq \mu} |h_{\mu\mu_1}|^2 \delta(\Delta E_{\mu\mu_1}^{(1)}) + \frac{2\pi}{\hbar} \sum_{\substack{\mu_1 \\ \mathbf{k}s}} \{|F_{\mu\mu_1}(\mathbf{k}s)|^2(\bar{n}_{\mathbf{k}s} + 1)\delta(\Delta E_{\mu\mu_1}^{(1)} - \epsilon_{\mathbf{k}s})$$

$$+ |F_{\mu_1\mu}(\mathbf{k}s)|^2 \bar{n}_{\mathbf{k}s} \delta(\Delta E_{\mu\mu_1}^{(1)} + \epsilon_{\mathbf{k}s})\} \tag{35}$$

and the total relaxation function $f(t)$ can be written

$$f(t) = C^{-1} \sum_\mu K_\mu \exp\left[-\frac{t}{T_{1\mu}}\right],$$ [36]

where

$$K_\mu = \frac{1}{\hbar} T_{1\mu} I_\mu^0 \text{Im}\{F_\mu(0)\}$$ [37]

and the normalization constant C is given by

$$C = \frac{1}{\hbar} \sum_\mu T_{1\mu} I_\mu^0 \text{Im}\{F_\mu(0)\}.$$ [38]

Equation [35] can be separated into two contributions, one coming from the relaxation induced by the rotational motion, characterized by the transition matrix elements $h_{\mu\mu}$, of the dipolar interaction between the nuclear spins, which, because of the δ function in [35], represents the first relaxation channel between spin–rotation levels with nearly the same energy. This contribution has a temperature dependence due to the presence of the rotation–phonon interaction which is at least third order in the perturbations of the rotation–Zeeman Hamiltonian (see the Appendix) and that can be physically explained by the induced time dependence of the dipolar interaction due to the phonon reservoir.

The second contribution comes from the instability of the rotational levels due to the rotation–phonon coupling, introducing a width for each rotational level which increases the total transition probability between the Zeeman energy levels in the nucleus, therefore increasing the total longitudinal relaxation rate. This represents the second relaxation channel: the phonons induce transitions between different sets of spin–rotation levels, thereby increasing the probability that a transition between Zeeman levels will take place. The relaxation function given by Eq. [36] shows a multiexponential behavior with a different relaxation rate for each spin–rotational level. Since the spin–rotational states are classified according to the irreducible representations of the symmetry group of the molecule, and since the matrix elements given by Eq. [22] contain matrix elements of the molecule–surface interaction, which is, at least, invariant according to the same symmetry group, it is possible that for those states belonging to the same irreducible representation, the relaxation rate could be nearly of the same value, giving us a further simplification of the total relaxation function containing only terms corresponding to the different irreducible representations of the molecular symmetry group. This behavior is consistent with experimental evidence and other theoretical approaches (9).

APPENDIX

In Eq. [29], we have the same type of Green's functions as those in Eqs. [26] and [27], which are given in terms of two-phonon operator Green's functions. If we introduce Eqs. [26] and [27] in [29], we can decouple the system by discarding those Green's functions that represent two-phonon processes, by the same approximation used in Eq. [30]. With this type of decoupling procedure we get an additional temperature-dependent term in the function $M_\mu(\omega)$,

$$R_\mu(\omega; T) = \sum_{\mu_1 \neq \mu} \left[\frac{h_{\mu\mu_1} G^\mu_{\mu_1}(\omega; T)}{\Delta_{\mu_1 \mu}} + \frac{h^*_{\mu\mu_1} G^{\mu *}_{\mu_1}(-\omega; T)}{\Delta_{\mu\mu_1}} \right], \qquad [A1]$$

where

$$G^\mu_{\mu_1}(\omega; T) = \sum_{\substack{\mathbf{k}s \\ \mu_2 \neq \mu}} \left[\frac{F_{\mu_1 \mu_2}(\mathbf{k}s) F^*_{\mu\mu_2}(\mathbf{k}s)(\bar{n}_{\mathbf{k}s} + 1)}{\Delta^-_{\mu_2 \mu}} + \frac{F^*_{\mu_2 \mu_1}(\mathbf{k}s) F_{\mu_2 \mu}(\mathbf{k}s) \bar{n}_{\mathbf{k}s}}{\Delta^+_{\mu_2 \mu}} \right]. \qquad [A2]$$

The additional contribution to the relaxation rate is

$$\left(\frac{1}{T_1} \right)_{\text{add.}} = \frac{2\pi}{\hbar} \sum_{\mu_1 \neq \mu} \text{Re}[h_{\mu\mu_1} G^\mu_{\mu_1}(0; T)] \delta(\Delta E^{(1)}_{\mu\mu_1}) + \frac{2}{\hbar} \mathcal{P} \sum_{\mu_1 \neq \mu} \frac{\text{Im}[h_{\mu\mu_1} G^\mu_{\mu_1}(0; T)]}{\Delta E^{(1)}_{\mu_1 \mu}}, \qquad [A3]$$

where $\mathcal{P}$ represents the principal value of the sum.

REFERENCES

1. A. KUMAR AND C. S. JOHNSON JR., *J. Chem. Phys.* **60**, 137 (1974).
2. C. S. JOHNSON JR., *J. Magn. Reson.* **24**, 63 (1976).
3. J. PETERNELJ AND M. M. PINTAR, *Phys. Rev. B* **15**, 5097 (1977).
4. R. A. WIND, S. EMID, J. F. J. M. POURQUIÉ, AND J. SMIDT, *J. Chem. Phys.* **67**, 2436 (1977).
5. S. CLOUGH, *J. Phys. C Solid State Phys.* **4**, 2180 (1971).
6. M. PUNKKINEN AND S. CLOUGH, *J. Phys. C Solid State Phys.* **7**, 3403 (1974).
7. S. EMID AND R. A. WIND, *Chem. Phys. Lett.* **33**, 269 (1975).
8. J. PETERNELJ, D. W. NICOLL, AND M. M. PINTAR, *Phys. Rev. B* **19**, 474 (1979).
9. J. PETERNELJ AND M. M. PINTAR, *Phys. Rev. B* **28**, 2411 (1983).
10. D. N. ZUBAREV, "Nonequilibrium Statistical Thermodynamics," Consultants Bureau, New York, 1974.
11. L. BERG, "Introduction to the Operational Calculus," Wiley, New York, 1967.
12. M. L. KRASNOV, A. I. KISELEV, AND G. I. MAKARENKO, "Functions of Complex Variable, Operational Calculus and Stability Theory," Mir Publishers, Moskow, 1983.
13. R. E. A. C. PALEY AND W. WIENER, "Fourier Transforms in the Complex Domain," Amer. Math Soc., New York, 1934.
14. M. MARTÍN LANDROVE AND J. A. MORENO, *Philos. Mag. B* **58**, 103 (1988).
15. R. F. CURL, H. P. HOPKINS, AND K. S. PITZER, *J. Chem. Phys.* **48**, 4064 (1968).
16. J. PETERNELJ, *J. Magn. Reson.* **50**, 111 (1982).
17. A. HÜLLER, *Z. Phys. B* **36**, 215 (1980).
18. H. F. KING AND D. F. HORNIG, *J. Chem. Phys.* **58**, 3833 (1973).
19. M. MARTÍN LANDROVE AND J. A. MORENO, *Physica B* **132**, 67 (1985).
20. M. MARTÍN LANDROVE AND J. A. MORENO, *Acta. Cient. Venez.* **33**, 185 (1982).
21. W. M. ITANO, *J. Mol. Spectros.* **71**, 193 (1978).