The spin lattice relaxation rates of deuterated methyl groups are calculated for threefold and sixfold potentials. It is shown that it should be possible to determine the symmetry of the potential hindering the methyl groups from deuteron spin lattice relaxation experiments. The temperature dependence of the spin lattice relaxation rates is discussed using a simple model. The similarities and the differences between proton NMR and deuteron NMR are pointed out. The main difference is that $E_a \leftrightarrow E_b$ transitions are forbidden by spin selection rules in case of CH$_3$, but not for CD$_3$. Therefore, and due to the fact that the quadrupolar interaction is a single particle interaction, deuteron NMR allows the study of the rotational dynamics of single methyl groups.

1. Introduction

The rotational dynamics of light molecules like methane or molecular groups like methyl groups in molecular crystals has been under extensive study, both theoretically and experimentally during the last two decades. A field of considerable interest is the temperature dependence of rotational tunnelling and several theoretical approaches have been given [1-5]. In all of the proposed theories it is supposed that the coupling of the methyl rotors to lattice modes is responsible for the temperature dependence of both the tunnel splitting and the line width.

Besides incoherent neutron scattering [6, 7] proton NMR has proved a powerful tool in the investigation of the dynamics of methyl groups [8, 9].

In a typical neutron scattering experiment the widths of the inelastic ($A \leftrightarrow E$) and the quasielastic ($E_a \leftrightarrow E_b$) line as well as the shift of the inelastic line are studied as a function of temperature. Both quantities are often found to exhibit an Arrhenius like temperature dependence with activation energies of the order of the energy difference between the torsional ground state and the first exited state. At elevated temperatures the two lines coalesce and a single quasielastic line is observed. The temperature dependence of the broadening of this line usually also follows an Arrhenius law with an activation energy of the order of the difference between the potential barrier height and the torsional ground state energy.

From proton NMR spin lattice relaxation experiments the temperature dependence of the 'reorientation rates' (line broadenings) are extracted, which usually exhibit analogous Arrhenius laws as observed by incoherent neutron scattering [10]. For low potential barriers two minima in a $\ln(T)$ versus $T^{-1}$ plot occur which allow the determination of the tunnel splitting from the high temperature minimum. Furthermore, a strong correlation between the temperature of the $T$-minimum and the tunnel splitting has been found [11].

In order to study the shape and the height of the hindering potential not only the temperature dependence, but also the pressure dependence and the isotope effect are of interest [12, 13]. The simplest modification is achieved by deuteration, which results in a reduction of the rotational constant $B = \hbar/2I$ by a factor of two leading to tunnel splittings which are much smaller than for protons (typical factors of reduction are of the order of 20...50 [13]).

Deuteron NMR seems to be a promising technique to complement the investigation of the rotational dynamics of methyl groups due to the fact that the strongest interaction is the quadrupolar interaction, which is a single particle interaction. Therefore, $^2$H-NMR allows the study of the dynamics of single CD$_3$ rotors. Small tunnel splittings up to 2 MHz (~0.01 µeV) may be extracted directly from $^2$H-NMR spectra as has been shown by Lalowicz et al. [14]. In this paper we shall calculate the spin lattice relaxation rates of CD$_3$ groups experiencing potentials of three- and sixfold symmetry.

In Sect. II we shall construct symmetry adapted wave functions obeying the Pauli principle for bosons and calculate the quadrupolar matrix elements by making use of
all selection rules. Section III is devoted to the calculation of the spin lattice relaxation rates and the differences between three- and sixfold potentials will be pointed out. Furthermore, the temperature dependence of $T_1$ is discussed using some of the aforementioned models. Finally, we compare our results to those obtainable by incoherent neutron scattering and proton NMR.

II. The quadrupolar matrix elements

1. The Hamiltonian

In the following, we consider a methyl group embedded in a crystalline (or amorphous) matrix. Since we are interested in the rotational dynamics of the methyl group in the solid state, we shall assume the molecule to which the methyl group is attached to be in the vibrational ground state and treat the CD$_3$ groups as rigid plane rotors [6].

The Hamiltonian for a CD$_3$ group under the influence of a large magnetic field reads as:

$$H = H_R + H_Z + H_Q + H_{RF}$$ (1)

Here, $H_R$ denotes the Mathieu operator

$$H_R = -B\partial^2_z + V(\alpha)$$ (2)

where $B = \hbar/2I$ is the rotational constant of a CD$_3$ group ($B = 323.7$ μeV) and $V(\alpha)$ is the so-called hindering potential or crystalline field [15]. It is well known [6], that the symmetry group of $V(\alpha)$, denoted as $G_o$ hereafter, is given by the direct product group of the molecular and the site symmetry. In contrast to the usual treatment of CH$_3$ (see, however, [16]) we use $C'_{3o}$, which is isomorphic to the permutation group $S_3$, as the molecular symmetry of a CD$_3$ group. The bar indicates that the molecular symmetry is an internal symmetry. The irreducible representations of which are denoted as $\hat{F}$. The symmetry operators $F_R$, $\hat{R}e C_{3\alpha}$ [17] are defined so as to rotate about molecule fixed axes. The molecule fixed frame (MFF) is defined such that the symmetry axis of the methyl group coincides with the $z$-axes and the positions in our considerations means we treat both right- and left-handed methyl groups (lefthanded methyl groups are obtained e.g. by interchanging the particles 2 and 3 in Fig. 1) in the same manner [19]. Since the potential $V(\alpha)$ is not able to induce transitions between these, we have to forbid any overlap between wave functions of different parity. The reason for using $C_{3\alpha}$ instead of $C_3$ is only to be able to use the Pauli principle in a stricter sense than usual and to take into account all selection rules, as will be discussed in more detail in the next section.

The Zeeman Hamiltonian $H_Z$ is given by:

$$H_Z = -\omega_0 I_z; \quad I_z = \sum_{s=1}^{3} I_z^{(s)}$$ (3)

where $\omega_0$ is the Larmor precession frequency (typically, $\omega_0$ is of the order of $50$ MHz ($\sim 0.2 \mu$eV) in high field NMR). The sum is over the three deuterons of a CD$_3$ group.

$H_{RF}$ represents the rotor phonon interaction and is responsible for the temperature dependence of rotational tunnelling. It is usually decomposed into a product of operators acting on rotor and phonon states, respectively [2, 20]. It has only matrix elements between rotational states of the same symmetry, i.e. $H_{RF}$ is totally symmetric with respect to $G_o$. We shall not go into detail concerning $H_{RF}$ and we assume that only the rotational states are affected by this.

The quadrupolar Hamiltonian $H_Q$ consists of products of spin operators and position operators of the second rank acting on the rotational states. Since $H_Q$ commutes neither with $H_Z$ nor with $H_R$ or $H_{RF}$, we make the assumption that the ground state tunnel splitting (the smallest frequency in the spectrum of $H_R$) is large compared to the strength of the quadrupolar interaction, measured in units of $\omega_0$, the quadrupolar beating frequency (for methyl deuterons, the efg tensor is axially symmetric to a very good approximation and $\omega_0$ is of the order of $120$ kHz ($\sim 0.5$ neV)). If this condition is fulfilled, we can treat $H_Q$ in perturbation theory, restricting ourselves to high field NMR ($\omega_0 \gg \omega_Q$). The appropriate states are linear combinations of products of spin states and rotational states, to be constructed in the next section.