On Nuclear Magnetic Relaxation in Dilute Gases of Symmetric and Spherical Top Molecules

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Nuclear magnetic relaxation in dilute gases of spherical and symmetric top molecules is considered from the point of view of the kinetic theory of transport and relaxation equations based on the Waldmann-Snider equation. The derivation of the form of the spin-rotation Hamiltonian in the absence of centrifugal distortion is reexamined and an expression for the "spin-lattice" relaxation time is given for this case.

This note is concerned with the kinetic theory of the nuclear magnetic relaxation in dilute polyatomic gases. The relaxation[1] of nuclear spins $\frac{1}{2}$ is considered for the case in which the decay of the nuclear magnetization is associated with the spin-rotation interaction. Two cases are distinguished:

(i) symmetric top molecules containing a single nucleus of spin $\frac{1}{2}$, e. g., CHD_3, and

(ii) spherical top molecules with four or six equivalent nuclei of spin $\frac{1}{2}$, e. g., CH_4, CF_4 or SF_6.

In particular, it is discussed under which conditions the theoretical expressions for the nuclear relaxation times are the same for both cases (i) and (ii). Such an assumption had previously been used successfully by Bloom and co-workers[2] in an analysis of their experimental data. Moreover, it is pointed out that in this approximation the theoretical expressions for the nuclear spin relaxation are the same for both tetrahedral (CH_4, CF_4) and octahedral molecules (SF_6). This is in contrast to an earlier claim by McCourt and Hess[3] which, however, resulted from an incorrect treatment[4] of the "anisotropic" part of the spin-rotation interaction Hamiltonian.

This work is restricted to dilute gases (pressures below 30 atm. at room temperature) where the condition

$$\omega_{\text{coll}} \ll E_{\text{rot}}/\hbar \qquad (1)$$

is satisfied. Here ω_{coll} is a typical collision frequency for a change of the rotational angular momentum and E_{rot} is a typical rotational energy splitting. Condition (1) implies that only that part of the spin-rotation coupling Hamiltonian diagonal with respect to the rotational energy need be considered.

Symmetric Top Molecules

The spin-rotation interaction Hamiltonian $\mathcal{H}_{\text{SR}}$ governing the relaxation of a nuclear spin $\frac{1}{2}$ in a symmetric top molecule such as CHD_3 can be written as

$$(1/\hbar)\, \mathcal{H}_{\text{SR}} = C\, \boldsymbol{I}\cdot\boldsymbol{J} + \Delta c\, \boldsymbol{I}\cdot\overline{\boldsymbol{e}\,\boldsymbol{e}}\cdot J\,. \qquad (2)$$

Here $\boldsymbol{I}$ and $\boldsymbol{J}$ are the nuclear spin and rotational angular momentum vector operators in units of $\hbar$ ($I^2 = \frac{3}{4}$, J^2 has eigenvalues $j^2 + j$). The unit vector parallel to the figure axis of the molecule has been denoted by $\boldsymbol{e}$, the sign $\overline{\ldots}$ refers to the symmetric traceless part of a tensor. The strength of the spin-rotation coupling is determined by the isotropic and the anisotropic coupling coefficients C and Δc. Due to the coupling described by (2), $\boldsymbol{I}$ precesses about the total angular momentum $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$; $\Delta c \neq 0$ implies that the precession frequency is different for $\boldsymbol{J} \parallel \boldsymbol{e}$ ($\overline{\boldsymbol{e}\,\boldsymbol{e}}\cdot\boldsymbol{J} = \frac{2}{3}\boldsymbol{J}$) and for $\boldsymbol{J} \perp \boldsymbol{e}$ ($\overline{\boldsymbol{e}\,\boldsymbol{e}}\cdot\boldsymbol{J} = -\frac{1}{3}\boldsymbol{J}$).

That part of $\mathcal{H}_{\text{SR}}$ which is diagonal with respect to the rotational energy is given by

$$(1/\hbar)\, \mathcal{H}_{\text{SR}}^{\text{diag}} = c\, \boldsymbol{I}\cdot\boldsymbol{J} + \Delta c\, \boldsymbol{I}\cdot\alpha\, \boldsymbol{J}\,, \qquad (3)$$

$$c = C + \langle\beta\rangle_0\, \Delta c\,,$$
$$\alpha = \beta - \langle\beta\rangle_0\,, \qquad \beta = J^{-2}\, \boldsymbol{J}\cdot\overline{\boldsymbol{e}\,\boldsymbol{e}}\cdot\boldsymbol{J}\,. \qquad (4)$$

Given the coupling Hamiltonian (3), expressions can be derived for the nuclear spin relaxation times T_1, T_2, by application of the kinetic equation approach

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[1] In dealing with relaxation phenomena in gases it should be kept in mind that the collision frequency ω_{coll} rather than the precession frequency ω_{H} plays a very significant rôle in determining which parts of the intramolecular Hamiltonian are of importance. Notice, that even for $\omega_{\text{H}} = 0$ there is a nuclear spin relaxation, the relevant relaxation time being that obtained in the limit of extreme narrowing if, as usual, the direct effect of the magnetic field on molecular collisions is neglected.

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[4] The existence of an error has been pointed out by I. Ozier in the preceeding note[5]. No corrected result has been given there, however: indeed, most of the remarks made there are not relevant to the method of calculation employed here or in Ref.[3]. In particular, the remarks made by Ozier[5] in his second paragraph apply only at very low pressures where not only the characteristic frequencies of rigid rotation but also those of centrifugal distortion are very large compared with the collision frequency. This condition is satisfied in molecular beam magnetic resonance but not in the standard nuclear magnetic relaxation experiment in dilute gases.

[5] I. Ozier, Z. Naturforsch. **26 a**, 1232 [1971], the preceeding note.

(based on the Waldmann-Snider equation [6, 7]) as used in Ref. [3]. For the extreme narrowing limit where $T_1 = T_2 \equiv T$, the resulting expression reads

$$\frac{1}{T} = \frac{2}{3}\, c^2 \langle J^2\rangle_0 \left\{ \frac{1}{\omega_{\mathrm{coll}}} + \left(\frac{\Delta c}{c}\right)^2 \frac{\langle \alpha^2 J^2\rangle_0}{\langle J^2\rangle_0} \frac{1}{\omega'_{\mathrm{coll}}} \right\}. \tag{5}$$

The bracket $\langle \dots \rangle_0$ refers to an average evaluated with an equilibrium distribution function. Eq. (5) is equivalent to an expression derived by BLOOM, BRIDGES and HARDY [2] and also by BLICHARSKI [8] using a correlation function approach. Here, however, the correlation times $\omega_{\mathrm{coll}}^{-1}$ and $\omega'^{-1}_{\mathrm{coll}}$ can be related to the linearized Waldmann-Snider collision term [3, 6, 9, 10] $\omega(\dots)$ through

$$\omega_{\mathrm{coll}} = \langle J^2\rangle_0^{-1} \langle \boldsymbol{J}\cdot\omega(\boldsymbol{J})\rangle_0 , \tag{6}$$

$$\omega'_{\mathrm{coll}} = \langle \alpha^2 J^2\rangle_0^{-1} \langle \alpha \boldsymbol{J}\cdot\omega(\alpha \boldsymbol{J})\rangle_0 . \tag{7}$$

It has been assumed in these expressions that the nuclear spin is not affected by collisions. In the frequently used "equal correlation time approximation" [2], ω'_{coll} is put equal to ω_{coll}.

Spherical Top Molecules

For spherical top molecules [11] such as CH_4 or SF_6, the spin-rotation interaction Hamiltonian can be written as [12]

$$(1/\hbar)\, \mathcal{H}_{\mathrm{SR}} = c\, \boldsymbol{I}\cdot\boldsymbol{J} + \Delta c \sum_i \boldsymbol{s}_i \cdot \overline{\boldsymbol{e}_i \boldsymbol{e}_i} \cdot \boldsymbol{J} , \tag{8}$$

with the total nuclear spin [13]

$$\boldsymbol{I} = \sum_i \boldsymbol{s}_i . \tag{9}$$

Here the nuclear spin operator of nucleus "i" is denoted by $\boldsymbol{s}_i$ ($s_i^2 = \frac{3}{4}$) and $\boldsymbol{e}_i$ is a unit vector pointing from the center of the spherical molecule to nucleus "i". The summation over i runs from 1 to 4 and from 1 to 6 for tetrahedral, respectively, octahedral molecules. That part of $\mathcal{H}_{\mathrm{SR}}$ which is diagonal with respect to the rotational energy is, in this case, given by

$$(1/\hbar)\, \mathcal{H}_{\mathrm{SR}}^{\mathrm{diag}} = c\, \boldsymbol{I}\cdot\boldsymbol{J} + \Delta c\, \tilde{\boldsymbol{I}}\cdot\boldsymbol{J} , \tag{10}$$

with

$$\tilde{\boldsymbol{I}} \equiv \sum_i \alpha_i \boldsymbol{s}_i \tag{11}$$

where α_i is given by Eq. (4) with $\boldsymbol{e}_i$ instead of $\boldsymbol{e}$.

In Ref. [3], some terms had been incorrectly omitted in the "Δc" part of $\mathcal{H}_{\mathrm{SR}}^{\mathrm{diag}}$. Hence, both Eqs. (2.12) and (2.17) of Ref. [3] should be replaced by Eq. (10) [14]. This has the consequence that the quantity $q/45$ occurring in Eqs. (4.6) – (4.10) of Ref. [3] has to be replaced by $\langle \tilde{I}^2 J^2\rangle_0 (\langle J^2\rangle_0 \langle I^2\rangle_0)^{-1}$. In the extreme narrowing limit the resulting nuclear relaxation time T is now given by

$$\frac{1}{T} = \frac{2}{3}\, c^2 \langle J^2\rangle_0 \left\{ \frac{\langle I^2 J^2\rangle_0}{\langle I^2\rangle_0 \langle J^2\rangle_0} \frac{1}{\omega_{\mathrm{coll}}} + \left(\frac{\Delta c}{c}\right)^2 \frac{\langle \tilde{I}^2 J^2\rangle_0}{\langle J^2\rangle_0 \langle I^2\rangle_0} \frac{1}{\tilde{\omega}_{\mathrm{coll}}} \right\} \tag{12}$$

with

$$\tilde{\omega}_{\mathrm{coll}} = \langle \tilde{I}^2 J^2\rangle_0^{-1} \langle \boldsymbol{J}\tilde{\boldsymbol{I}} : \omega(\tilde{\boldsymbol{I}}\boldsymbol{J})\rangle . \tag{13}$$

For ω_{coll}, see Eq. (6).

If any symmetry-imposed correlation between the magnitudes of the total nuclear spin and of the rotational angular momentum is ignored, the result for the averages occurring in Eq. (12) is [15]

$$\langle I^2 J^2\rangle_0 = \langle I^2\rangle_0 \langle J^2\rangle_0 \quad \text{and} \quad \langle \tilde{I}^2 J^2\rangle_0 = \frac{4}{45} \langle I^2\rangle_0 \langle J^2\rangle_0 . \tag{14}$$

With this Eq. (12) reduces to [2]

$$\frac{1}{T} = \frac{2}{3}\, c^2 \langle J^2\rangle_0 \left\{ \frac{1}{\omega_{\mathrm{coll}}} + \frac{4}{45} \left(\frac{\Delta c}{c}\right)^2 \frac{1}{\tilde{\omega}_{\mathrm{coll}}} \right\} . \tag{15}$$

The same result is obtained if Eq. (5) with $\omega'_{\mathrm{coll}} = \tilde{\omega}_{\mathrm{coll}}$ is applied to the case of a spherical top where

$$\langle \alpha^2 J^2\rangle_0 = (4/45) \langle J^2\rangle_0 .$$

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[7] For a review of those effects which can be treated using the Waldmann-Snider equation, see J. J. M. BEENAKKER and F. R. MCCOURT, Ann. Rev. Phys. Chem. **21**, 47 [1970].

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[9] S. HESS, Z. Naturforsch. **22 a**, 1871 [1967].

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[11] The Hamiltonian for internal states for such molecules has been discussed extensively in connection with molecular beam magnetic resonance work by C. H. ANDERSON and N. F. RAMSEY, Phys. Rev. **149**, 14 [1966]; P.-Y. YI, I. OZIER, and C. H. ANDERSON, Phys. Rev. **165**, 92 [1968]; I. OZIER, L. M. CRAPO, and S. S. LEE, Phys. Rev. **172**, 63 [1968]. For comparison with the results given in these papers, note that $c_{\mathrm{d}} = \Delta c$ and $c_{\mathrm{a}} = -c$.

[12] Section 2 of Ref. [3] is correct up to and including Eq. (2.9). The paragraph immediately following Eq. (2.9) is not only misleading but also incorrect. The results (2.10), (2.13) and (2.17, 18) are incorrect because the complete degeneracy of the "K" levels in spherical tops was not correctly taken into account. Thus, Section 2 from Eq. (2.9) to the end can be completely dispensed with and is superceded by the present treatment.

[13] The total nuclear spin vector is treated as an operator also with respect to its magnitude and this implies that I^2 has the eigenvalues 0, 2, 6. Hence if some operator has nonvanishing matrix elements only within a given I-manifold, this is automatically taken into account by the formalism employed.

[14] This new definition of $\tilde{\boldsymbol{I}}$ has certain consequences in Section 3 of Ref. [3]. (i) The third term in Eq. (3.8) should now be just $J\tilde{I} : \tilde{\boldsymbol{b}}$ with the consequence that in Eq. (3.9), $\tilde{\boldsymbol{b}}$ should now be given by $\tilde{\boldsymbol{b}} = 9(\langle \tilde{\boldsymbol{I}} \boldsymbol{J}\rangle - \langle \tilde{\boldsymbol{I}} \boldsymbol{J}\rangle_{\mathrm{eq}}) / \langle \tilde{I}^2 J^2\rangle_0$. (ii) Eqs. (3.10) should be modified as follows: in the first equation, $\frac{1}{2} \Delta c \langle \tilde{I}^2 \alpha^2 J^2\rangle_0 / (3\langle I^2\rangle_0)$ should be replaced by $-\frac{1}{3} \Delta c \langle J^2 \tilde{I}^2\rangle_0 / \langle I^2\rangle_0$; in the third equation, $-\frac{1}{2}\Delta c$ should be replaced by $+\Delta c$. (iii) The definition of $\tilde{\omega}_{\mathrm{coll}}$, Eq. (3.12), is replaced by Eq. (13) of this note.

[15] In evaluating the traces occurring in these averages, the trace over the nuclear magnetic quantum numbers has been taken over each nuclear spin independently.

Notice that Eq. (15) applies equally to tetrahedral and octahedral molecules. Eq. (15) should replace Eq. (4.11) of Ref. [3]. With this result, the conclusion of DONG and BLOOM [2] that the best value for $|\Delta c|$ in the "equal correlation time approximation" is 18.2 kHz [16] rather than 21.0 kHz [11] is reconfirmed.

In the treatment presented here, the effect of centrifugal distortion on the relaxation of the nuclear magnetization has been completely disregarded. This can be done as long as the associated energy splitting $E_{\text{c.d.}}$ is collisionally quenched, i. e., if the condition

$$(1/\hbar)\, E_{\text{c.d.}} \ll \omega_{\text{coll}} \tag{16}$$

is satisfied. Condition (16) imposes a lower limit on the pressures for which Eqs. (12) or (15) can be applied. Since $\omega_{\text{coll}} \approx 10^9$ Hz at 1 atm., and [11] $E_{\text{c.d.}}/\hbar \approx 10^7$ to 10^8 Hz for molecules such as CH_4, SiH_4, this lower pressure limit is of the order of 0.1 to 1.0 atm. (at room temperature). Certainly, then, the rôle of centrifugal distortion on NMR needs further theoretical clarification. Recent experiments [17] in CH_4 indicate that the influence of centrifugal distortion shows up below 0.5 atm. On the other hand, recent measurements [18] in CF_4, SiF_4, GeF_4, and SF_6 show that centrifugal distortion does not affect the nuclear spin relaxation down to about 0.01 atm.

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[18] J. A. COURTNEY and R. L. ARMSTRONG, private communication.

Defects in Neutron-irradiated ZnO (I)

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After irradiation with fast neutrons, several paramagnetic centers have been observed in ZnO by ESR. They result from electrons trapped at oxygen vacancies and from holes trapped at more complex defect associates.

After exposure to fast particle irradiation (e^-, n), various types of paramagnetic defect centers have been observed in ZnO single crystals by electron spin resonance (ESR). One prominent defect is the F^+-center, i. e. an electron trapped at an oxygen vacancy. An unambiguous identification of this center was made possible by the observation of hyperfine structure arising from the four Zn^{67}-ligands [1]. As in ZnS [2], we found that the F^+-center in ZnO can also be created by grinding single crystals. In contrast, heating in zinc vapour does not lead to a noticeable formation of F^+-centers, but to the incorporation of interstitial zinc into the ZnO lattice. ESR of trapped-hole centers has also been observed in ZnO crystals exposed to 3 MeV electrons [3] or to fast neutrons [4]. The paramagnetic centers were ascribed to holes trapped at zinc vacancies.

It is the purpose of this note to report additional investigations on these trapped-hole centers which make it appear rather unlikely that they arise from *isolated* zinc vacancies: Nominally pure ZnO single crystals, obtained from the 3M-Company, were irradiated to a dosage of 10^{17} fast neutrons/cm², at about 150 °C. To suppress activation, the samples were shielded by 1 mm Cd. Typical X-band ESR-spectra observed for such samples at 77 °K, and under $H \parallel c$ are shown in Fig. 1 a, b.

We first consider the signal labeled P in Fig. 1 b. It arises from a $S = 1/2$ center having C_s-symmetry. The principal components of its $\boldsymbol{g}$-tensor are $g_1 = 2.0038(3)$, $g_2 = 2.0180(3)$ and $g_3 = 2.0191(3)$. The g_1-axis forms an angle of 69.3° with the c-axis. The g_3-axis is perpendicular to the center's mirror plane, spanned by the axial and one of the six non-axial bond directions in the ZnO lattice. Thus, the P-center might arise from holes trapped at one of the three non-axial oxygen ligands around a zinc vacancy, as already postulated before [3, 4].

However, no ESR signal arising from holes trapped at the axial oxygen ligand could be detected. This is surprising since previous ESR-studies of the deep acceptor center formed by substitutional Li^+ in ZnO and BeO have shown that this axial site is energetically strongly favoured [5]. This is also true for the isolated Be-vacancy in BeO [6]. Therefore, the P-center might arise from Zn – O divacancies, or even Zn – O – Zn trivacancies, both oriented along the c-axis.

Above 77 °K, motional effects were observed in the ESR-spectrum of the P-center. At room temperature, the spectrum has reached axial symmetry around the

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c-axis, with $g_{\parallel}=2.0149(5)$ and $g_{\perp}=2.0134(3)$. Thermally activated hopping of the hole among equivalent or, within the range of kT, almost equivalent oxygen sites must account for this averaging process. The value observed for $g_{\parallel}$ at 300 °K is definitely smaller than that observed for the *P*-center at 77 °K under $H \parallel c$, where $g_c=2.0162(3)$. This suggests that the hopping process may not be restricted to occur only between the three non-axial oxygen ligands around a zinc vacancy. Additional oxygen sites, within the range of kT, do not exist around an axial divacancy, but possibly around a linear, axial trivacancy. It should again be noted that the *g*-shifts of the thermally averaged *P*-center are not compatible with a hole rapidly hopping among the four oxygen ligands of an *isolated* metal site. In this case, a much smaller anisotropy $g_{\parallel}-g_{\perp}$ should result, as observed for the Li$^+$-center in BeO [5].

The signal labeled *Q* in Fig. 1 b also arises from a $S=1/2$ trapped-hole center, with

$$g_1=2.0038(3), \quad g_2=2.0182(3) \quad \text{and} \quad g_3=2.0217(3),$$

at 77 °K. Its symmetry is only C_1. The g_1-axis is tilted by about 10° from a non-axial bond direction. It is tempting to assign the *Q*-signal to centers resulting from non-axial ionic arrangements of a di- or trivacancy in the ZnO lattice.

Apart from the ESR-signal of the F^+-center, seen in Fig. 1 b, the signals labeled *R*, *S* and *U* still await further investigation. The symmetry of the *S*-center is lower than C_{3v}, with $g_c=2.0041(3)$. Its angular dependence occurs in a very narrow range of magnetic fields. The lines labeled *U* in Fig. 1 b arise from a low-symmetry $S=1$ center of unknown structure.

The prominent lines labeled *T* in Fig. 1 a have been investigated more in detail. They arise from a $S=1$ trapped-hole center having C_s-symmetry. The magnetic parameters of this triplet center were reported previously [3] and agree well with our results:

$$g_1=2.0095(5), \quad g_2=2.0141(5), \quad g_3=2.0190(5),$$
$$|D|=1465(5)\ \text{MHz} \quad \text{and} \quad |E|=58(2)\ \text{MHz},$$

at 77 °K. *D* and g_1 are measured along one of the six axes connecting nearest non-axial oxygen sites. The g_3-axis forms an angle of 52° with the *c*-axis. These data are compatible with holes trapped at two non-axial oxygen ligands around a zinc vacancy. However, the lack of corresponding $S=1$ centers formed by holes trapped at one axial and one non-axial oxygen site makes it again appear questionable that the center arises from an isolated zinc vacancy.

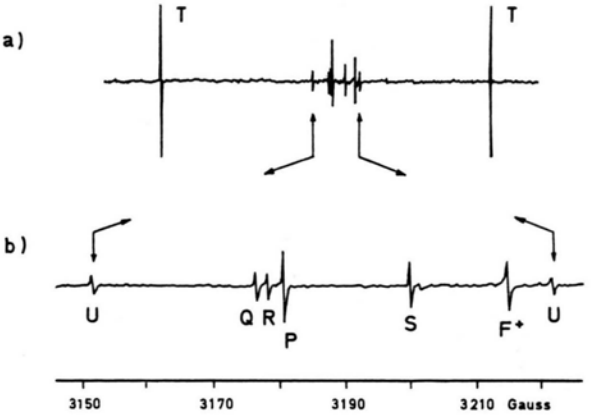

Fig. 1. ESR spectrum of a neutron-irradiated ZnO crystal recorded at 9.1 GHz, 77 °K and under $H \parallel c$. The magnetic field scan of the upper spectrum (a) is 10× that of the lower trace (b).

The ESR-signals of the *T*-center disappear above 100 °K. No motionally averaged ESR-spectra could be detected at elevated temperatures. At 77 °K, both *T*- and *U*-centers were completely quenched by illumination with the green 546 nm Hg-line. A slight increase of the intensity of the *P*- and *Q*-center lines was simultaneously observed. The question remains whether the *T*-center is a different charge state of the *P*-center.

To summarize we can state that fast particle irradiation of ZnO at room temperature and above can lead to the formation of isolated oxygen vacancies in fair concentration, as demonstrated by the ESR-detection of the F^+-center. In contrast, isolated zinc vacancies are probably mobile at room temperature and, consequently, tend to associate with oxygen vacancies — or with impurity ions in ZnO. Association of neutron-induced lattice defects with Fe^{3+} and Cu^{2+} ions will be reported in a forthcoming commmunication. In order to observe ESR of the isolated zinc vacancy in ZnO, fast particle irradiation at low temperature may be advisable.