

SLOW MOTIONAL NMR LINESHAPES FOR VERY ANISOTROPIC DIFFUSION: $I = 1$ NUCLEI*

EVA MEIROVITCH** and Jack H. FREED

*Department of Chemistry, Cornell University,
Ithaca, New York 14853, USA*

Received 8 January 1979; in final form 15 February 1979

A general method to analyze NMR slow motional lineshapes is extended to $I = 1$ nuclei and illustrated on ^2H NMR lineshapes of a clathrate hydrate of tetrahydrofuran (THF- d_8). It is shown that "ring puckering" could be the dominant mode of motion for the enclathrated THF- d_8 molecule, whereas several other models are inconsistent with experiment

The development of techniques for obtaining high resolution NMR spectra of magnetically diluted spins in crystalline and related types of samples [1] stimulated a considerable number of studies on static probe nuclei, focusing mainly on information of a structural nature [2]. The dynamical aspects, in particular the study of slow motions occurring on time scales defined by the various magnetic interactions, have also been considered in several cases, usually by using the technique of broad line proton NMR [3,4]. However, lineshape analyses of isolated nuclear spins have only been performed in a few special cases[‡].

We have recently developed [6] a general method to analyze slow motional lineshapes of $I = 1/2$ nuclei, where the main anisotropic term in the hamiltonian is due to the secular part of an asymmetric chemical shift tensor. That work generalized the slow motional ESR analysis of Freed et al. [7] to generate lineshapes for "very anisotropic" reorientation [8], i.e. relatively more rapid rotation about a particular axis in a rigid molecule or a particular axis (or axes) of internal rotation in a non-rigid molecule which is, in general, tilted relative to the principal magnetic axes. The various motions may be treated by brownian and/or by

jump diffusion and include a variety of possible combinations of models [6]. In the present note we extend this lineshape analysis to the case of $I = 1$ nuclei, where the main anisotropic term in the hamiltonian is the secular part of an asymmetric quadrupole interaction. This work may also be considered as a generalization of the earlier treatment by Freed et al. [9] of slow-tumbling triplet ESR spectra, which they point out is equivalent to the $I = 1$ NMR case with a quadrupole tensor (except in the present case non-secular terms are negligible) [10].

These methods of spectral analysis provide, we believe, an indispensable tool for the study of such phenomena as: molecular reorientation in low-temperature uniaxial and biaxial smectic liquid crystals [11–13], chain reptation and kink diffusion in polymers [3,4], dynamic characteristics of particular functional side groups in biological macromolecules [14], anisotropic reorientation of guest molecules in organic clathrates [15] and the relationship between the dynamic behavior of the guest and its selective reactivity with the host [16], various problems related to the dynamic state of molecules in colloid and interface science [17], etc.

By using the formal equivalence between the quadrupole interaction in NMR for $I = 1$ and the ESR $S = 1$ zero field splitting [9] it follows from a comparison of refs. [6,7,9] that the results of ref. [6] may be used for $I = 1$ nuclei, provided the definitions used for $I = 1/2$ nuclei:

* Supported by NSF Grant = CHE77-26996 and NIH Grant = GM25862-01.

** Chaim Weizmann Postdoctoral Fellow.

‡ Pines et al. [5] studied modulation of the ^{13}C chemical shift tensor in hexamethylbenzene by jumps about the six-fold symmetry axis.

$$\mathcal{F}_0 = \frac{2}{3}\gamma_N [\sigma_{zz} - \frac{1}{2}(\sigma_{xx} - \sigma_{yy})],$$

$$\mathcal{F}_2 = 6^{-1/2}(\sigma_{xx} - \sigma_{yy})\gamma_N$$

are replaced by $\mathcal{F}_0 = \mp D$ and $\mathcal{F}_2 = \mp(\frac{2}{3})^{1/2}E$, corresponding to the two allowed transitions for $l = 1$ (or $S = 1$). (Here $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$ are the principal components of the shielding tensor with $D = \frac{2}{3}D_z$ and $E = \frac{1}{2}(D_x - D_y)$, with D_x, D_y and D_z denoting the principal components of the quadrupole tensor. (In usual notation $\frac{4}{3}D = e^2qQ$.)

In this analysis, the reorientation of the entire molecule is represented by the diffusive eigenvalues [6,18]:

$$B_L [R_{\parallel} L(L+1) + (R_{\parallel} - R_{\perp})K^2],$$

where R_{\parallel} and R_{\perp} are the parallel (relatively fast) and perpendicular components of the rotational diffusion tensor, while B_L is the "model parameter" ranging from $B_L = 1$ for brownian motion to $B_L = [L(L+1)]^{-1}$ for $L > 0$ for strong jump diffusion. The eigenvalues for internal rotational diffusion are: $R_1 K^2 / (1 + R_1 \tau_1 K^2)$, where R_1 is the diffusion coefficient for the internal rotation and τ_1 is the mean time between diffusion jumps ($R_1 \tau_1$ is then proportional to the size of a mean diffusive step).

To illustrate the use of the method, we considered recently published experimental ^2H spectra of the structure II clathrate hydrate of perdeuterated tetrahydrofuran (THF- d_8) as a function of temperature [15]. These lineshapes were interpreted (without the aid of any simulation) in terms of the onset of motion at about 20 K, assuming rapid "very anisotropic" reorientation about the preferred diffusion axis; however, the qualitative features of the spectra could only be understood assuming a relatively wide static distribution of diffusion axes, implying a distribution in cage configurations of the clathrate structure. In general, the assumption of a broad distribution of reorientational correlation times has often been used in previous studies on clathrate structures (see ref. [15] and references cited therein) to interpret results of physical measurements on guest molecules.

We wish to suggest an alternative interpretation: the guest molecule reorients about a unique axis, determined by the molecular symmetry and by the symmetry of a well-defined cage configuration; however, instead of assuming that the motion about the diffusion axis has attained the limit of fast "very aniso-

tropic" reorientation (i.e. rapid motion about the main diffusion axis and very slow reorientation perpendicular to it) we allow for both of these dynamic rates to assume arbitrary values.

Although the structure of the structure II clathrate hydrate of THF has been solved by X-rays [19], no direct information regarding the configuration of the guest THF molecule could be obtained since the oxygen atom just gave rise to a diffuse electron density, which has been related to dynamic disorder rather than to a static distribution of orientations. By analogy with other derivatives of cyclopentane [20], it was assumed [19,20] that THF assumes a C_2 half-chair configuration, rather than a C_s envelope configuration.

To generate a series of dynamic ^2H NMR lineshapes, one has to specify the orientation of the main diffusion axis relative to the local frame of the deuterium quadrupole tensor. Should the molecule contain more than one deuterium atom, the overall spectrum will be given by the superimposed spectra of the various deuterons in the molecule. The lineshapes will differ from site to site, according to the relative orientation θ of the main diffusion axis and the various C-D bonds which lie along the principal axis of the axially symmetric quadrupole tensor [21]; from rigid limit simulations the quadrupole tensor in THF- d_8 was found to be axially symmetric with $\frac{4}{3}D \approx 178$ kHz. Thus, in order to simulate theoretically the overall ^2H NMR lineshape, one has to assume a particular molecular conformation so as to be able to associate particular angles θ with the various deuterons. As mentioned above, our method is general in imposing no restrictions on the orientation of the main diffusion axis; it will be shown shortly that the lineshapes are very sensitive to this orientation which, for an axially symmetric quadrupole tensor is defined by one angle θ . Thus, although the spectral resolution might be lowered by having different angles θ for the various deuterons (i.e. several superimposed lineshapes), our method enables one to differentiate between various possible conformations. This unique feature, i.e. the possibility of determining molecular geometry from lineshape analysis is of considerable importance in the example considered here, since, as we have already noted, X-ray studies in the THF- d_8 hydrate inclusion compound could not provide information regarding the molecular geometry of the guest molecule.

We refer now to the THF- d_8 molecule which is a five membered ring. By analogy with other cyclopentane derivatives THF- d_8 is expected to assume either a C_2 half-chair conformation or a C_s envelope conformation: Mak and McMullan [19] assume a C_2 conformation although the difference in energy between these two is expected to be relatively small [20]. On this basis the following models shall be considered:

(a) An approximately planar conformation and "very anisotropic" reorientation about one of the symmetry axes $x'y'z'$ of the quasi-planar molecule defined so that x' lies within the molecular plane passing through the oxygen atom, y' is perpendicular to x' within the same plane and z' is perpendicular to both.

(b) Either a C_2 or a C_s stable conformation and very anisotropic motion about an arbitrary axis.

(c) A C_2 or C_s conformation at low temperatures and the onset of "ring puckering" upon increasing the temperature.

(a) We assume that the THF- d_8 molecule is approximately planar and the diffusion axis z''' lies along z' ; in this case all C-D bonds make an angle $\theta = 35^\circ 44'$ with z''' , assuming that DCD is a perfect tetrahedral angle. The only free parameters are now R_{\parallel} , the motional rate along z''' and R_{\perp} the rate perpendicular to z''' . We illustrate in fig. 1a a series of theoretical lineshapes for $R_{\perp} = 1.0 \times 10^3 \text{ s}^{-1}$ and R_{\parallel} varying from 10^3 at low temperatures to 10^8 at high temperatures (further increase in R_{\parallel} does not affect the spectra). The fit between these lineshapes

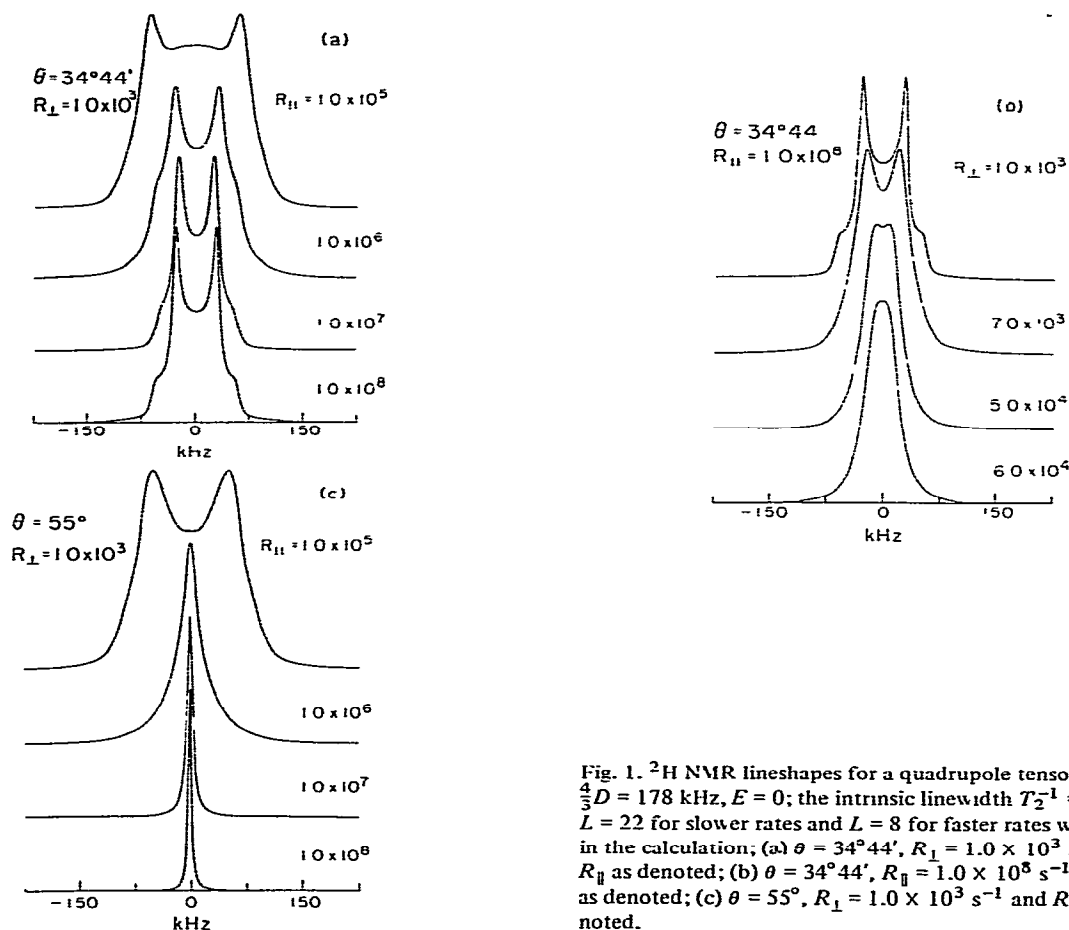


Fig. 1. ^2H NMR lineshapes for a quadrupole tensor with $\frac{4}{3}D = 178 \text{ kHz}$, $E = 0$; the intrinsic linewidth $T_2^{-1} = 2.4 \text{ kHz}$; $L = 22$ for slower rates and $L = 8$ for faster rates were used in the calculation; (a) $\theta = 34^\circ 44'$, $R_{\perp} = 1.0 \times 10^3 \text{ s}^{-1}$ and R_{\parallel} as denoted; (b) $\theta = 34^\circ 44'$, $R_{\parallel} = 1.0 \times 10^8 \text{ s}^{-1}$ and R_{\perp} as denoted; (c) $\theta = 55^\circ$, $R_{\perp} = 1.0 \times 10^3 \text{ s}^{-1}$ and R_{\parallel} as denoted.

and the experimental spectra (cf. fig. 2b) is poor, the main feature present in the simulated spectra and absent in the higher temperature experimental patterns is the doublet splitting persisting up to the limit of fast "very anisotropic" motion about z''' . We then increased R_1 from its value of 10^3 s^{-1} , which is actually close to the rigid limit value for R_1 . The effect of increasing R_1 on the $R_2 = 1.0 \times 10^8 \text{ s}^{-1}$ spectrum

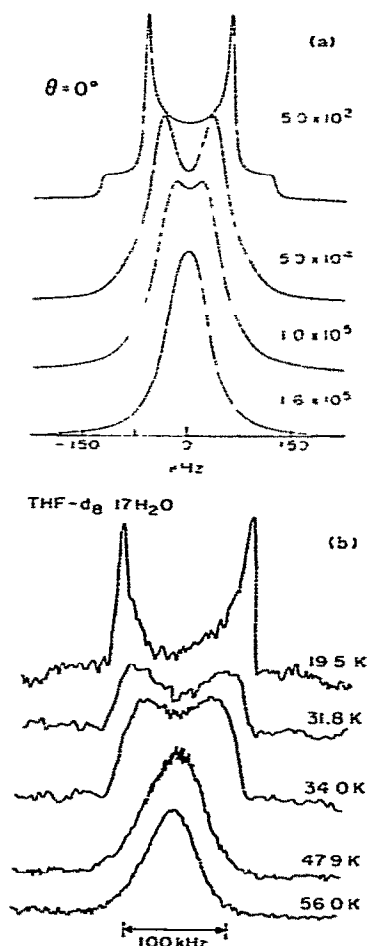


Fig. 2. (a) Same as fig. 1 for $\theta = 0^\circ$ and R_1 as denoted; R_2 can assume any value since for an axially symmetric quadrupole tensor motion about the principal axis does not affect the spectrum. The spectrum at the top is the rigid limit pattern, obtained with $R_1 = 5 \times 10^2 \text{ s}^{-1}$. (b) Deuterium NMR lineshapes of THF- d_8 - $17 \text{H}_2\text{O}$ at various temperatures (reprinted from ref. [15]).

is illustrated in fig. 1b and it can be easily seen that R_1 has to be increased to $6.0 \times 10^4 \text{ s}^{-1}$ to wash out the doublet splitting but at this value of R_1 the line-width is about 30% too narrow as compared to the experimental spectrum in fig. 2b. We could not improve the overall fit by further variations in R_2 and R_1 . (Related arguments easily show that overall isotropic motion is inconsistent with experiment as already pointed out ref. [15].)

For $z''' = x'$, two angles $\theta = 80^\circ$ and $\theta = 26^\circ$ must be considered, since relative to this position of the diffusion axis the two pairs of CD bonds ortho and meta to the oxygen atom assume different orientations. Again, we followed the procedure described for $\theta = 35^\circ 44'$ and found both for $\theta = 80^\circ$ and for $\theta = 26^\circ$ that by the time the doublet splitting vanishes upon increasing R_1 , the line becomes too narrow.

Finally, $z''' = y'$, two values $\theta = 54^\circ$ and $\theta = 56.5^\circ$ must be considered and for these orientations the averaging process is especially efficient since both values are very close to the magic angle of $54^\circ 44'$. Fig. 1c[†] illustrates a series of lineshapes obtained for $\theta = 55^\circ$, $R_1 = 1.0 \times 10^3 \text{ s}^{-1}$ and R_2 ranging from 10^3 to 10^8 s^{-1} .

The doublet splitting vanishes for R_1 in the neighborhood of $5 \times 10^5 \text{ s}^{-1}$. We have not tried to simulate the higher temperature broad structureless lines by varying R_1 by small steps about $5 \times 10^5 \text{ s}^{-1}$, since even if a reasonable fit would have been obtained, there is no physical reason to assume that after having steadily increased the temperature from 19.5 to 56 K, R_1 suddenly assumes a constant value at 56 K and does not increase upon further increasing the temperature (otherwise the lines quickly become extremely narrow). Should a sudden change occur in the structure of the clathrate at 56 K, it would have been detected during the various physical experiments [15] used to study this compound.

We conclude that model (a) can be ruled out.

(b) For stable configurations C_2 or C_5 and an arbitrary axis one has 8 inequivalently oriented CD

[†] It is of interest to emphasize that a single narrow line might be interpreted in a misleading fashion as reflecting isotropic reorientation, although the motion might be anisotropic to some extent (see fig. 1b) or even at the limit of the "very anisotropic" model (see fig. 1c). The main point is that a complete lineshape analysis of an entire series of dynamic spectra is usually necessary for unambiguous interpretation.

bonds; a particular choice of the diffusion axis, related to molecular symmetry could reduce this number to four groups of two.

In any case, although the spectrum is expected to be complex, the features outlined above prevail; the doublet splitting appears as long as the motion is relatively anisotropic (i.e. R_{\parallel}/R_{\perp} is relatively large) and by the time this anisotropy is small enough to wash out that splitting, the lines are already too narrow to fit the experimental spectra. On this basis, we consider model (b) to be inadequate in explaining the experimental results.

(c) The process of "ring puckering" can be visualized as a "rocking" motion of the CD bond at a certain rate R_{\perp} . The exact range of angles θ spanned by this motion is difficult to estimate, although the upper limit of the vertex angle of the cone within which each CD bond is moving would be 36° for the C_5 configuration and 24° for the C_2 configuration (these values were obtained assuming that the angle between the COC plane and the CD bond adjacent to the oxygen is $54^{\circ}16'$ for a perfectly planar structure, 90° and 18° for a C_5 configuration, and 78° and 30° for a C_2 configuration [19]). However, this upper limit might be increased assuming that the "ring puckering" is associated with a swinging motion of the molecule about its center of mass about an axis perpendicular to the planar transition state thus increasing the efficiency in averaging.

We roughly approximated the dynamic model just described by taking the main diffusion axis as lying along the principal axis of the quadrupole tensor for each C-D bond, and let R_{\perp} represent the rate of "ring puckering" which leads to the partial averaging of each C-D bond axis. We did not attempt, in the present analysis, to restrict this averaging (e.g. to $|\theta| \leq 35^{\circ}44'$ for C_5 configurations). Instead we merely limited the range of R_{\perp} to the small values: $5 \times 10^2 \text{ s}^{-1} \leq R_{\perp} \leq 1.6 \times 10^5 \text{ s}^{-1}$, which guaranteed incomplete averaging because of the slow motion.

The fit between the theoretical spectra in fig. 2a and the experimental spectra in fig. 2b is good and significantly better than for the models considered previously. We therefore conclude that while models (a) and (b) are inconsistent with experiment it is possible that the "ring puckering" process (c) is the process which is affecting the ^2H NMR lineshapes and may therefore be the dominant mode of motion for

the enclathrated THF- d_8 molecule[‡].

Of course further theoretical analysis including better modeling of the ring puckering motion would be advisable. A general approach for dealing with restricted internal modes of motion in terms of appropriate potential functions for the motion was briefly outlined in ref. [6] and would be the proper way to proceed. Also, the experimental study of the dynamic behavior of THF- d_8 could be pursued further, e.g. by specific deuteration instead of perdeuteration or by specific ^{13}C enrichment yielding NMR lineshapes to be analyzed as we have outlined. In the present note our main objective has been to illustrate the manner in which the theory can be used in the determination of molecular conformations and motional modes.

We wish to thank Dr. R.F. Campbell for his extensive help with the computer programming.

[‡] It must be pointed out that in principle the intrinsic linewidth $1/T_2$ is an additional free parameter to be varied in the simulation procedure. For all the theoretical spectra we used $1/T_2 = 2.4 \text{ kHz}$ obtained from rigid limit simulations, which is therefore an upper limit for this parameter for all motionally affected spectra. Thus the intrinsic linewidth should probably be even narrower at higher temperatures since the various relaxation processes will become more efficient. Consequently, the doublet resolution would increase, reinforcing our argument in favoring model (c) over both (a) and (b).

References

- [1] A. Pines, M. Gibby and J. Waugh, *J. Chem. Phys.* 59 (1973) 564.
- [2] U. Haeblerlen, *Advan. Magn. Reson.* S1 (1976).
- [3] W.G. Miller, *Ann. Rev. Phys. Chem.* 29 (1978) 519.
- [4] K. Bergmann, *J. Polymer Sci.* 16 (1978) 1611.
- [5] A. Pines, D.J. Ruben and D. Wemmer, private communication.
- [6] R.F. Campbell, E. Meirovitch and J.H. Freed, *J. Phys. Chem.* 83 (1979) 379.
- [7] J.H. Freed, G.V. Bruno and C.F. Polnaszek, *J. Phys. Chem.* 75 (1971) 3385.
- [8] R.P. Mason, C.F. Polnaszek and J.H. Freed, *J. Phys. Chem.* 78 (1974) 1324.
- [9] J.H. Freed, G.V. Bruno and C.F. Polnaszek, *J. Chem. Phys.* 55 (1971) 5270.
- [10] C.F. Polnaszek et al., *Biochemistry* 15 (1976) 954.
- [11] J. Seliger, R. Osredkar, V. Zagar and R. Blinc, *Phys. Rev. Letters* 38 (1977) 411.

- [12] A. de Vries, *Mol. Cryst. Liquid Cryst.* 49 (1978) 19.
[13] A.M. Levelut, *J. Phys. (Paris)* 37 (1976) C3-51.
[14] G. Wagner, A. DeMarco and K. Wuthrich, *Biophys. Struct. Mechanism* 2 (1976) 139.
[15] D.W. Davidson, S.K. Garg and J.A. Ripmeester, *J. Magn. Reson.* 31 (1978) 399.
[16] J.R. Scheffer and A.A. Dzakpasu, *J. Am. Chem. Soc.* 100 (1978) 2163;
J.M. Timko, R.C. Helgeson and D.J. Cram, *J. Am. Chem. Soc.* 100 (1978) 2828.
[17] *Magnetic Resonance in Colloid and Interface Science*, ACS Symposium Series 34, Washington, D.C. (1976).
[18] L.J. Berliner, ed., *Spin labeling, theory and applications* (Academic Press, New York, 1976) p. 63.
[19] T.C.W. Mak and R.K. McMullan, *J. Chem. Phys.* 42 (1965) 2732.
[20] F.V. Brucher Jr., Th. Roberts, S.J. Barrand and N. Pearson, *J. Am. Chem. Soc.* 81 (1959) 4915.
[21] J. Seelig, *Quart. Rev. Biophys.* 10 (1977) 3.