Sulfur-33 Relaxation and Nuclear Quadrupole Coupling Constant in Dimethylsulfoxide

Helena Kovacs, Jozef Kowalewski and Arnold Maliniak

Division of Physical Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

Kovacs, H., Kowalewski, J. and Maliniak, A., 1987. Sulfur-33 Relaxation and Nuclear Quadrupole Coupling Constant in Dimethylsulfoxide. – Acta Chem. Scand., Ser. A 41: 471–479.

^{33}S nuclear spin relaxation rates for deuterated dimethylsulfoxide (DMSO-d_6) were determined for the neat compound at different temperatures and for mixtures with D_2O. A value for the ^{33}S quadrupole coupling constant of −31 MHz was obtained by SCF LCAO MO calculations on the model system, dihydrogen-sulfoxide (H_2SO). The measured relaxation rates and the calculated quadrupole coupling constant were used to obtain the rotational correlation times. The results were compared with previously published data on ^{17}O relaxation in the same molecule.

Measurements of the linewidth for quadrupolar nuclei at low symmetry sites in molecules are of interest as they provide good estimates of the spin-spin relaxation rate. The relaxation rate is essentially a product of a dynamic property (the rotational correlation time) and a static property (the square of the quadrupole coupling constant) of the molecules in solution. If one of the properties is known from an independent source, the other one can be estimated.

In this communication we report linewidth measurements for sulfur-33 in dimethylsulfoxide, both as the neat liquid and in mixtures with D_2O. The sulfur-33 nucleus is quite insensitive to NMR detection. Its receptivity is only about one-tenth of that of carbon-13 due to low natural abundance and low magnetogyric ratio.[1] In addition, sulfur-33 is a quadrupolar nucleus (spin quantum number of 3/2), the signals of which tend to be broad despite the moderate size of the nuclear quadrupole moment.[2] Furthermore, accurate measurements of ^{33}S linewidths are often aggravated by acoustic ringing of the NMR probes.[3,4]

The quadrupole coupling constants of sulfur-33 nuclei have so far been determined for only a handful of molecules. Most often this has been done using microwave spectroscopy[5] or methods involving NMR techniques, such as linewidth measurements[6–8] or measurements on a dielectrically aligned liquid.[9] *Ab initio* quantum chemical calculations have been reported for some small molecules.[10,11] Here, we report *ab initio* calculations of the sulfur-33 quadrupole coupling parameters for a model system, dihydrogen sulfoxide (H_2SO). From the NMR linewidths together with the calculated quadrupole coupling constant, we obtain the rotational correlation times and compare them with the data obtained by oxygen-17 NMR spectroscopy.[12]

Theory

Under the extreme narrowing conditions, the spin-spin relaxation time of a quadrupolar nucleus is equal to the spin-lattice relaxation time. The relaxation rate for a nucleus located at a site of low symmetry under these conditions is given by eqn. (1),[13] where q is the numerically largest component of the field gradient tensor in its principal axis system (q_{zz}), Q the nuclear quadrupole moment and η the asymmetry parameter of the field gradient tensor, $(q_{xx}-q_{yy})/q_{zz}$. The maximum value η can attain is unity, and its contribution to the relaxation rate can often be neglected.

$$T_2^{-1} = T_1^{-1} = \frac{3\pi^2}{10}\left(\frac{2I+3}{I^2(2I-1)}\right)\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{h}\right)^2 \tau_c \qquad (1)$$

(e^2qQ/h) is called the nuclear quadrupole coupling constant (NQCC). τ_c is the effective rotational correlation time, a measure of the rate of the tumbling of the principal axis of the field gradient tensor.

The components of the electric field gradient tensor can be expressed as the sum of the nuclear contribution and an expectation value taken over the electron distribution of the tensor operator

$$\hat{q}_{ab} = (3r_a r_b - \delta_{ab} r^2)/r^5 \qquad (2)$$

[eqn. (2)], where $a,b = x,y,z$ and the radius vector is expressed relative to the site where the field gradient is required. It is computationally convenient to express the expectation value in terms of the density matrix P and the integrals over the atomic orbitals s and t [eqn. (3)]. The principal

$$q_{ab} = \sum_{s,t} P_{st} < s|\hat{q}_{ab}|t > + \text{nucl. contr.} \qquad (3)$$

components of the field gradient tensor are obtained by diagonalizing q_{ab}. Combining the calculated principal field gradient components with the known sulfur-33 quadrupole moment and with the measured ^{33}S relaxation rate, we can use eqn. (1) to obtain the rotational correlation time for the reorientation of the principal axis of the field gradient tensor at the site of the sulfur atom. This correlation time can be compared with correlation times for other axes in the molecule and it becomes possible to assess whether the molecular motion is isotropic.

NMR experiments

The samples of DMSO-d_6 and D_2O used in this study were the same as in the previous work on oxygen and deuteron relaxation.[12] The ^{33}S NMR experiments were performed on a JEOL GX400 NMR spectrometer operating at 9.4 Tesla without the field/frequency lock. The field drift is less than 0.5 Hz h^{-1}, which is negligible. The temperature was controlled using the standard JEOL variable temperature accessory. The spectral width in all experiments was 160 kHz (dwell time 6.2 μs) and the acquisition time was 6 ms. 90° pulses of 45 μs were used and a pulse delay of 4 ms was inserted between consecutive acquisitions. The number of acquisitions varied between 500 000 and 5 000 000, corresponding to the experiment times of 1.5 to 15 h. Each linewidth was measured in at least two separate experiments.

No particular measures were taken to suppress probe ringing, except for inserting a 17.5 μs delay between the end of the pulse and the beginning of the acquisition (we have tested some acoustic ringing elimination procedures[3,14] but found that they did not work satisfactorily with our equipment for the very broad signals involved). Instead, the following procedures were applied for evaluating the linewidth. The FID's were transferred to a VAX 11/750 computer. Two methods of evaluation were applied: In the first method, it was assumed that there is only one NMR signal, i.e. that both the real and the imaginary part of the signal can be described by a single exponentially damped oscillation of arbitrary frequency and phase plus a small constant term (dc offset). The real and imaginary parts of the FID were thus fitted to the following expressions:

$$f_{\text{real}}(t) = p_1 \cos(2\pi p_2 t + p_3) \exp\left(-\frac{t}{p_4}\right) + p_5 \qquad (4)$$

$$f_{\text{imag}}(t) = p_1 \sin(2\pi p_2 t + p_3) \exp\left(-\frac{t}{p_4}\right) + p_5 \qquad (5)$$

The fitted parameters are: amplitude (p_1), frequency (p_2), phase (p_3), T_2 (p_4) and dc offset (p_5). In order to eliminate the acoustic ringing, a number of points at the beginning of each FID were discarded. The final fits were performed using about 50 points in the approximate range of 3 to 6 times the final T_2. The least-squares fits performed using the GENLSS program[15] for the real and imaginary parts of the FID, respectively, agreed very well in all cases. The standard deviations of the fitted T_2 value were typically of the order of 5%. In the second approach, we obtained the linewidths by least-squares fitting of a single Lorentzian to the frequency domain spectrum using the NMR1 program.[16] In this case also, it was necessary to discard a number of initial points in the FID prior to the Fourier transformation. The results of the frequency domain fits were in good agreement with fits in the time domain. The quality of the experimental data and the effect of discarding initial points in the FID are illustrated in Figs. 1–4.

The average values of the measured sulfur-33

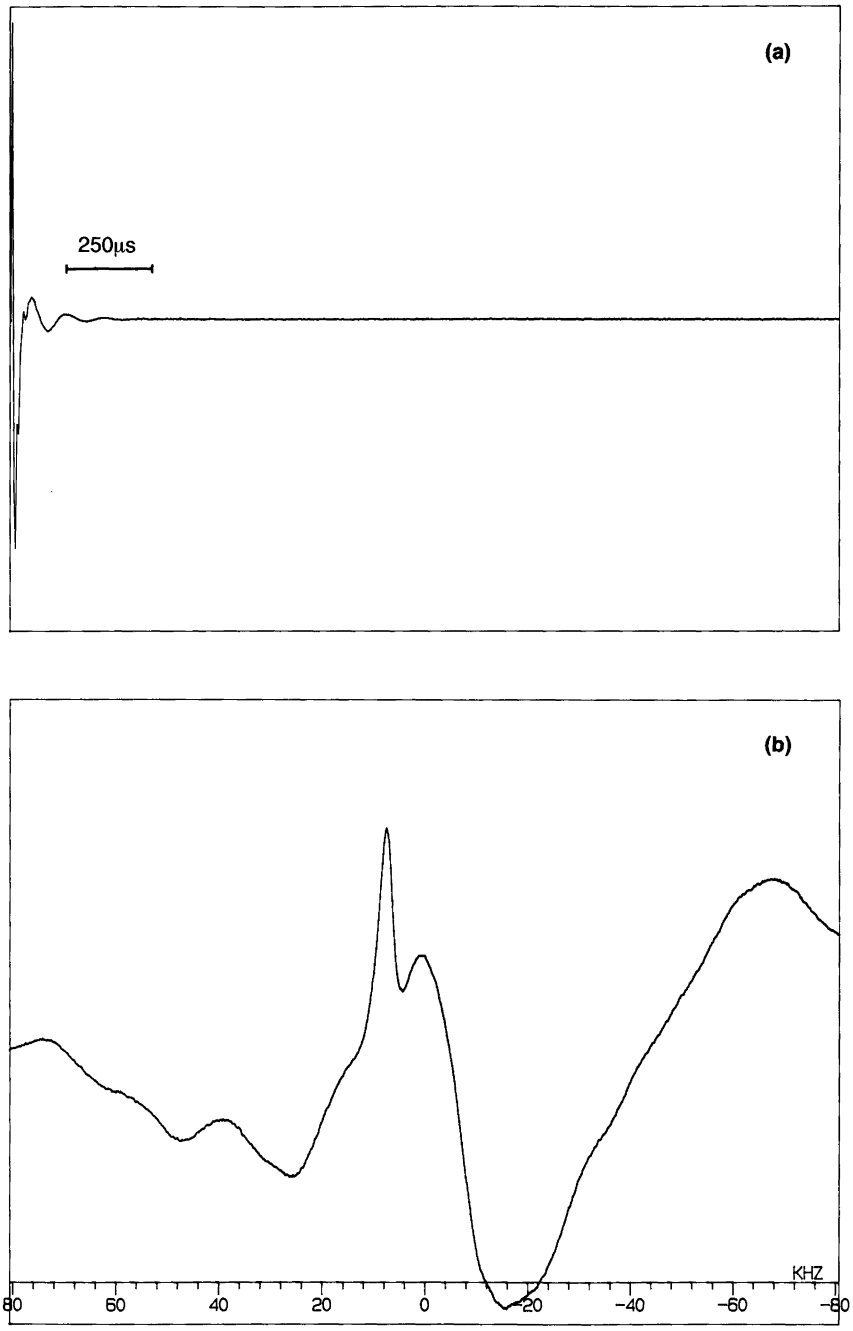

Fig. 1. (a) The first 512 points of the real part of the time domain spectrum, FID, from one of the experiments on 60 mole % DMSO-d_6 at 73 °C; $2.2 \cdot 10^6$ scans. (b) The corresponding frequency domain spectrum obtained after 200 Hz exponential line broadening. The data were processed and plotted using the spectrometer computer.

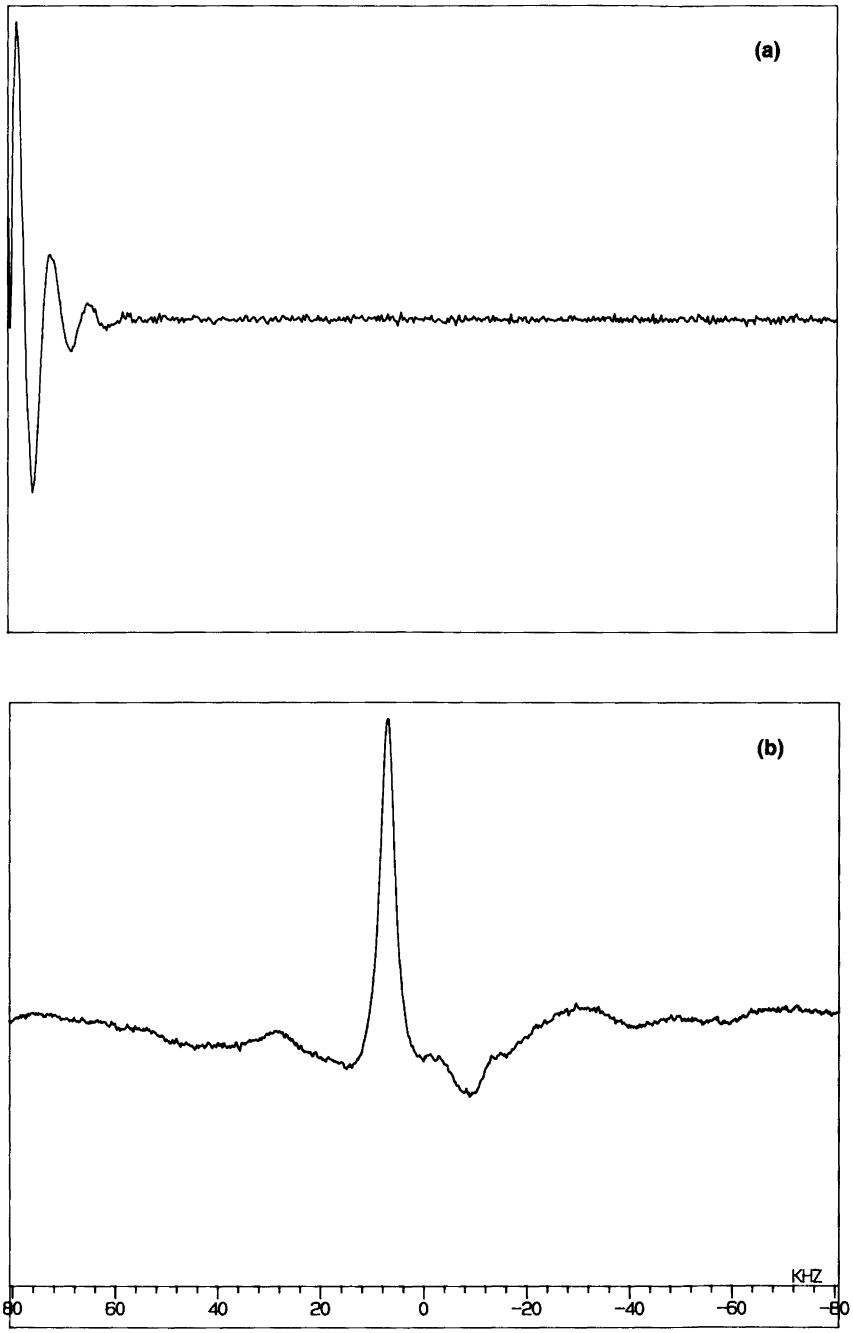

Fig. 2. As in Fig. 1, but after discarding 8 initial points in the real and imaginary parts of the FID.

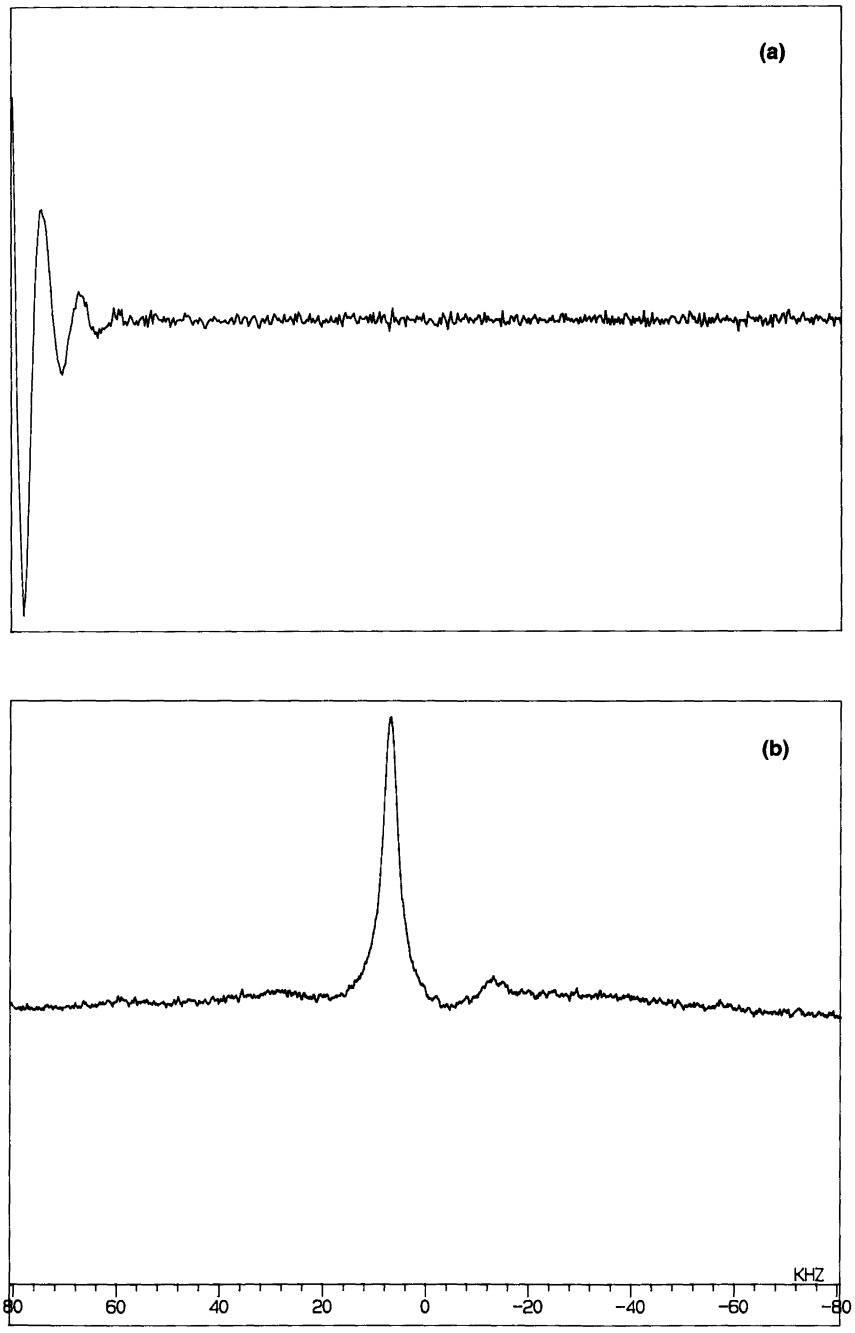

Fig. 3. As in Fig. 1, but after discarding 16 initial points in the real and imaginary parts of the FID.

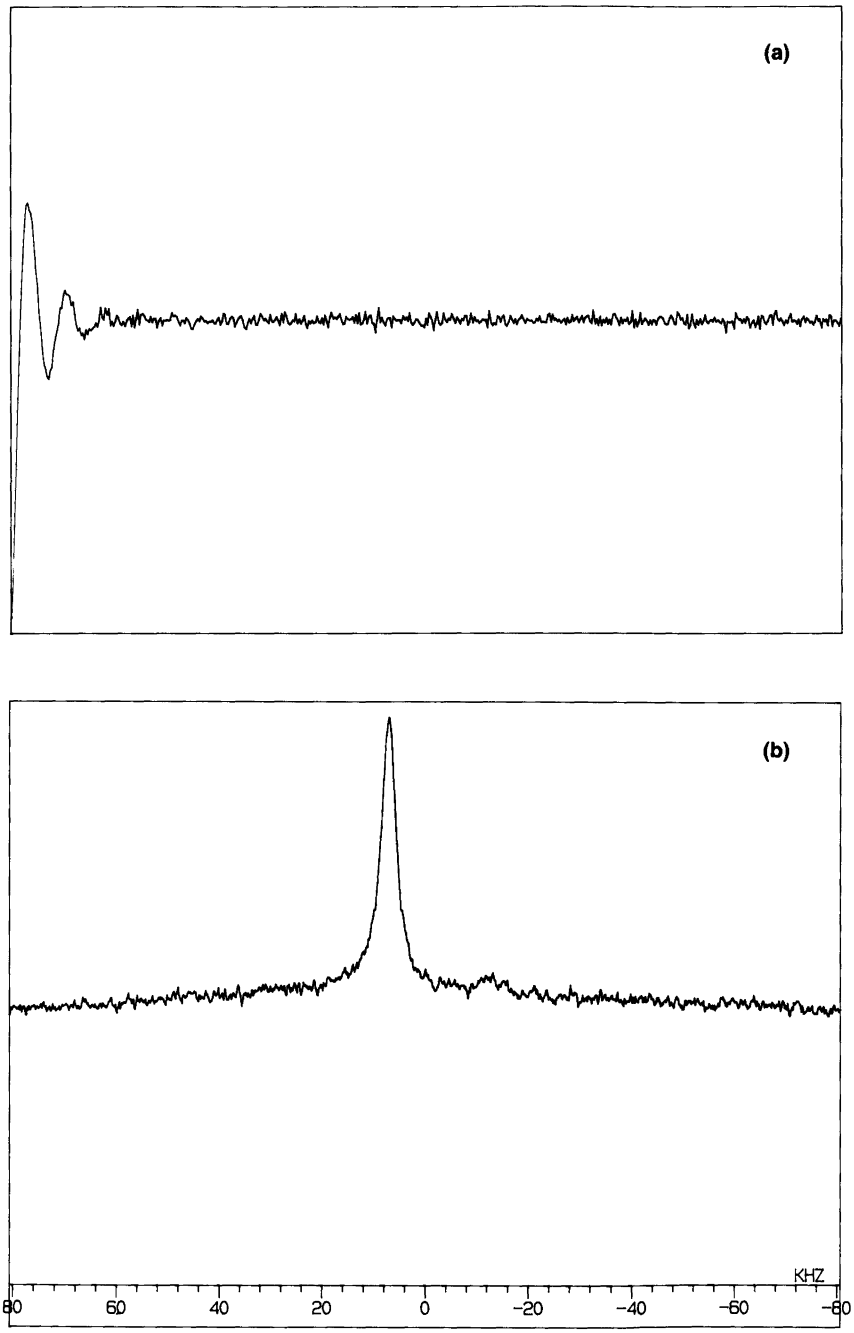

Fig. 4. As in Fig. 1, but after discarding 24 initial points in the real and imaginary parts of the FID.

spin-spin relaxation times are collected in Table 1. At 30 °C, the T_2 for ^{33}S in DMSO-d_6 is 72 μs, which corresponds to a linewidth of 4400 Hz. This compares fairly well with the results of other studies of sulfur-33 relaxation in DMSO; for instance, Belton *et al.*[3] report a linewidth of 4900 Hz at 21 °C, recorded using the RIDE (Ring-Down Elimination) pulse sequence in order to improve the quality of the spectra. Annuziata and Barbarella[17] have measured a linewidth of 5520 ± 230 Hz at 35 °C, whereas Retcofsky and Friedel[18] obtained a linewidth of 2600 Hz in work done in the early seventies.

Quantum chemical calculations

The molecular wavefunction and the field gradient tensors at the sites of both sulfur-33 and oxygen-17 were obtained from extended basis set non-empirical SCFMO calculations for a model system, viz. the H_2SO molecule. The variation in these parameters as a function of the molecular geometry was also examined.

The calculations of the SCF LCAO MO wavefunctions were performed using the program system MOLECULE.[19] Three contracted Gaussian basis sets were used. The smallest basis set was of the double zeta (DZ) quality, with the exponents and contraction coefficients for sulfur taken from Veillard,[20] and for oxygen and hydrogen from Snyder and Basch.[21] The second basis set (DZP) also included polarization functions (exponents 0.54 for *d* on S, 1.33 for *d* on O and 0.8 for *p* on H). The largest basis set (TZP) consisted of the same primitive Gaussian set of Veillard[20] for sulfur, contracted to 6*s* and 5*p* functions, the 5*s* and 3*p* contracted set of Dunning[22] for oxygen, and the 5*s* primitive set of Huzinaga[23] for hydrogen, contracted to 3*s*. Moreover, the same set of polarization functions as in the DZP basis set was included. The calculations of the field gradient tensors were performed using a program by Sadlej.[24] All the calculations were performed on a VAX 11/750 computer.

The SCF calculations were all performed using an S–O distance of 1.485 Å taken from a microwave study on DMSO by Typke,[25] and an S–H distance of 1.360 Å equal to the sum of the van der Waals radii. In the calculations using the DZ basis set, the HSH and HSO angles were varied to a certain extent. The total energies and the principal components of the field gradient tensors are summarized in Table 2. The sensitivity of the calculated field gradient components for ^{33}S to the changes in the valence angles was minor. Therefore, the calculations using the DZP and TZP basis sets were only performed with the HSH and HSO angles equal to the CSC and the CSO angles, respectively, in DMSO.[25] It can also be seen in Table 2 that the basis set variation of

Table 1. The total energies (a.u.) and the three components of the electric field gradient tensor (a.u.) at the sites of the sulfur-33 and oxygen-17 in H_2SO, computed by using three different basis sets [DZ, DZP and TZP (see text)], and as a function of alterations in the HSH and HSO angles (°) for the DZ basis set.

	∠HSH	∠HSO	E_{tot}	S			O		
				q_{xx}	q_{yy}	q_{zz}	q_{xx}	q_{yy}	q_{zz}
DZ									
geom.									
1	96.6	106.6	−473.301664	1.109	1.356	−2.465	3.174	−1.276	−1.899
2	96.6	101.6	−473.298128	1.040	1.298	−2.338	3.190	−1.341	−1.848
3	96.6	111.6	−473.300616	1.176	1.434	−2.610	3.206	−1.228	−1.978
4	101.6	101.6	−473.299766	1.118	1.417	−2.534	3.190	−1.286	−1.904
5	91.6	106.6	−473.301864	1.112	1.281	−2.393	3.161	−1.270	−1.891
DZP									
1			−473.456590	1.140	1.241	−2.381	2.315	−0.818	−1.498
TZP									
1			−473.483984	1.102	1.301	−2.402	2.204	−0.761	−1.443

Table 2. The sulfur-33 transverse relaxation times in neat DMSO-d_6 at four different temperatures, and in three binary mixtures of DMSO-d_6 and D_2O at 346 K.

	Temp./K				Mole % DMSO-d_6		
	303	317	332	346	80	60	40
T_2/μs	72	87	110	130	113	100	86

the field gradient tensor at the experimental geometry of DMSO is small at the site of sulfur but rather large at the site of the oxygen atom.

Adopting the value of the principal component of the electric field gradient tensor computed with the TZP basis set and a nuclear quadrupole moment of −0.055 barn,[26] the ^{33}S NQCC becomes −31 MHz, which is in reasonable agreement with that for other tetravalent sulfur nuclei; e.g. the ^{33}S NQCC in sulfur dioxide is −30 MHz [using $Q(^{33}S)$ = −0.062 barn] according to *ab initio* MO-SCF calculations,[11] and −25.71 MHz according to a microwave study.[27] Similarly, applying a ^{17}O quadrupole moment of −0.026 barn[26] the ^{17}O quadrupole coupling constant was determined to be 13.6 MHz, a somewhat too large value. However, it has become evident in analogous studies that the ^{17}O NQCC tends to be overestimated.[28]

Discussion

Inserting the NQCC and η values together with the relaxation rates into eqn. (1) allows the determination of the rotational correlation times. In Tables 3a and 3b, the rotational correlation times obtained from the sulfur-33 measurements are compared with the data extracted by means of eqn. (1) from oxygen-17 relaxation rates[12] as a function of temperature for neat DMSO-d_6 (Table 3a) and as a function of concentration for some binary mixtures of DMSO-d_6 and D_2O (Table 3b). In the case of oxygen-17, the experimental values of the quadrupolar interaction parameters (NQCC = 9.446 MHz and η = 0.232) reported for diphenyl sulfoxide[29] were used. We can note that the ratio between the two sets of correlation times is constant within the experimental uncertainty (which may be about 15–20 % for the correlation times), and close to unity. This may be taken as an indication that the DMSO molecules reorient isotropically. However, according to our quantum chemical calculations, the angle between the principal *z*-axes of the field gradient tensors at the two sites is not more than 35 °C (the axis at the site of the oxygen atom is almost coincident with the S=O bond). Thus, the two correlation times would not be likely to differ much even if the rotational diffusion of DMSO were moderately anisotropic, and the results of Tables 3a and 3b show primarily that the approach used is internally consistent.

Table 3a. The molecular correlation times of sulfur-33, $\tau_c(^{33}S)$, and oxygen-17, $\tau_c(^{17}O)$, and their ratio in neat DMSO-d_6 given at four different temperatures.

Temp./K	$\tau_c(^{33}S)$/ps	$\tau_c(^{17}O)$/ps	$\tau_c(^{33}S)/\tau_c(^{17}O)$
303	3.7	5.2	0.71
317	3.0	4.0	0.75
332	2.4	3.2	0.75
346	2.0	2.6	0.77

Table 3b. The molecular correlation times of sulfur-33, $\tau_c(^{33}S)$, and oxygen-17, $\tau_c(^{17}O)$, and their ratio given for neat DMSO-d_6 and three binary mixtures of DMSO-d_6 and D_2O at 346 K.

Mole % DMSO-d_6	$\tau_c(^{33}S)$/ps	$\tau_c(^{17}O)$/ps	$\tau_c(^{33}S)/\tau_c(^{17}O)$
100	2.0	2.6	0.77
80	2.3	3.0	0.77
60	2.6	3.6	0.72
40	3.1	4.2	0.74

Acknowledgements. This work has been supported by the Swedish Natural Science Research Council. We are grateful to the N. I. H. Research Resource for Multi-Nuclei NMR and Data Proc-

essing at Syracuse University for providing us with a copy of the NMR1 computer program.

References

1. Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy,* Pitman, London 1983, p. 232.
2. Rodger, C., Sheppard, N., McFarlane, H. C. E. and McFarlane, W. In: Harris, R. K. and Mann, B. E., Eds., *NMR and the Periodic Table,* Academic Press, New York 1978, p. 401.
3. Belton, P. S., Cox, I. J. and Harris, R. K. *J. Chem. Soc., Faraday Trans. 2, 81* (1985) 63.
4. Wasylishen, R. E., Macdonald, J. B. and Friedrich, J. O. *Can J. Chem. 62* (1984) 1181.
5. Lucken, E. A. C. *Nuclear Coupling Constants,* Academic Press, New York 1969, p. 287.
6. Larsson, K. M. and Kowalewski, J. *Acta Chem. Scand., Ser. A 40* (1986) 218.
7. Vold, R. R., Sparks, S. W. and Vold, R. L. *J. Magn. Reson. 30* (1978) 497.
8. Haid, E., Köhnlein, D., Kössler, G., Lutz, O. and Schich, W. *J. Magn. Reson. 55* (1983) 145.
9. Ruessink, B. H., van der Meer, W. J. and MacLean, C. *J. Am. Chem. Soc. 108* (1986) 192.
10. Roos, B. and Siegbahn, P. *Theor. Chim. Acta 27* (1972) 171.
11. Roos, B. and Siegbahn, P. *Theor. Chim. Acta 21* (1971) 368.
12. Kowalewski, J. and Kovacs, H. *Z. Phys. Chem. (Neue Folge) 149* (1986) 49.
13. Abragam, A. *The Principles of Nuclear Magnetism,* Clarendon Press, Oxford 1961, Chap. 8.
14. Gerothanassis, I. P. *Magn. Reson. Chem. 24* (1986) 428.
15. DeTar, D. F. In: *Computer Programs for Chemistry,* Academic Press, New York 1972, Vol. 4, Chap. 3.
16. Levy, G. C. *Curve Fitting Program NMR1.* NMR Laboratory, Syracuse University, Syracuse, NY 1985.
17. Annunziata, R. and Barbarella, G. *Org. Magn. Reson. 22* (1984) 250.
18. Retcofsky, H. L. and Friedel, R. A. *J. Am. Chem. Soc. 94* (1972) 6579.
19. Almlöf, J. *USIP Report 74–29,* University of Stockholm, Stockholm 1974.
20. Veillard, A. *Theor. Chim. Acta 12* (1968) 405.
21. Snyder, L. C. and Basch, H. *Molecular Wave Functions and Properties,* Wiley, New York 1972, pp. 22–24.
22. Dunning, T. H., Jr. *J. Chem. Phys. 55* (1971) 716.
23. Huzinaga, S. *J. Chem. Phys. 42* (1965) 1293.
24. Sadlej, A. *Private communication.*
25. Typke, V. *Z. Naturforsch., A 33* (1978) 842.
26. Fuller, G. *J. Phys. Chem. Ref. Data 5* (1976) 835.
27. Bird, G. R. and Townes, C. H. *Phys. Rev. 94* (1954) 1203.
28. Gready, J. E. *J. Phys. Chem. 88* (1984) 3497.
29. Cheng, C. P. and Brown, T. L. *J. Am. Chem. Soc. 102* (1980) 6418.

Received June 17, 1987.