Sulfur-33 Relaxation and Nuclear Quadrupole Coupling Constant in Dimethylsulfoxide

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$^{33}$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$_{2}$O. 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$_{2}$SO). 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$_{2}$O. 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.\textsuperscript{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.\textsuperscript{2} Furthermore, accurate measurements of $^{33}$S linewidths are often aggravated by acoustic ringing of the NMR probes.\textsuperscript{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\textsuperscript{5} or methods involving NMR techniques, such as linewidth measurements\textsuperscript{6-8} or measurements on a dielectrically aligned liquid.\textsuperscript{9} \textit{Ab initio} quantum chemical calculations have been reported for some small molecules.\textsuperscript{10,11} Here, we report \textit{ab initio} calculations of the sulfur-33 quadrupole coupling parameters for a model system, dihydrogen sulfoxide (H$_{2}$SO). 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.\textsuperscript{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),\textsuperscript{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 $\eta$ the asymmetry parameter of the field gradient tensor, $(q_{zz}-q_{xy})/q_{zz}$. The maximum value $\eta$ can attain is unity, and its contribution to the relaxation rate can often be neglected.

$$T_{1}^{-1} = T_{1}^{-1} = \frac{3\pi^{2}}{10} \frac{2I+3}{F(2I-1)} \left( 1 + \frac{\eta^2}{3} \right) \left( \frac{e^{2}qQ}{h} \right)^{2} \tau_{c}$$

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\((e^2 qQ/h)\) is called the nuclear quadrupole coupling constant (NQCC). \(\tau_r\) 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

\[
\hat{q}_{ab} = (3r_a \hat{r}_b - \delta_{ab} \hat{r}^2)/r^5
\]

[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 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 \(\mu\)s) and the acquisition time was 6 ms. 90° pulses of 45 \(\mu\)s 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 \(\mu\)s delay between the end of the pulse and the beginning of the acquisition (we have tested some acoustic ringing elimination procedures\(^{3,13}\) 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:

\[
\begin{align*}
\text{f}_{\text{real}}(t) &= p_1 \cos(2\pi p_2 t + p_3) \exp \left(-\frac{t}{p_4}\right) + p_5 \\
\text{f}_{\text{imag}}(t) &= p_1 \sin(2\pi p_2 t + p_3) \exp \left(-\frac{t}{p_4}\right) + p_5
\end{align*}
\]

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; $2.2 \cdot 10^5$ 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 $^{35}$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. 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. Annuiziata and Barbarella have measured a linewidth of 5520 ± 230 Hz at 35°C, whereas Retcofsky and Friedel 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 SCF MO calculations for a model system, viz. the H$_2$SO 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. 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, and for oxygen and hydrogen from Snyder and Basch. The second basis set (DZP) also included polarization functions (exponents 0.54 for S, 1.33 for O, and 0.8 for p on H). The largest basis set (TZP) consisted of the same primitive Gaussian set of Veillard for sulfur, contracted to 6s and 5p functions, the 5s and 3p contracted set of Dunning for oxygen, and the 5s primitive set of Huzinaga for hydrogen, contracted to 3s. 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. All the calculations were performed using a VAX 11/750 computer.

The SCF calculations were performed using an S–O distance of 1.485 Å taken from a microwave study on DMSO by Tyske, 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 $^{35}$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. 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$_2$SO, 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.

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<th>Angles</th>
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<th>O (a.u.)</th>
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<td>$q_{yy}$</td>
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DZ geom.

<table>
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<td>1.301</td>
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3$^\circ$
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 TIZP basis set and a nuclear quadrupole moment of $-0.055$ barn, the $^{35}$S NQCC becomes $-31$ MHz, which is in reasonable agreement with that for other tetravalent sulfur nuclei; e.g. the $^{35}$S NQCC in sulfur dioxide is $-30$ MHz [using $Q(35S) = -0.062$ barn] according to ab initio MO-SCF calculations, and $-25.71$ MHz according to a microwave study. Similarly, applying a $^{17}$O quadrupole moment of $-0.026$ barn 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.

**Discussion**

Inserting the NQCC and $\eta$ 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 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$_2$O (Table 3b). In the case of oxygen-17, the experimental values of the quadrupolar interaction parameters (NQCC = $9.446$ MHz and $\eta = 0.232$) reported for diphenyl sulfoxide 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 $35^\circ$ 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.

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