The chemical shift, dipolar, and quadrupolar tensors of deuterium in potassium bicarbonate

Abraham M. Achlama

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this with the relative independence of k_{333}/ω_3 (from Ref. 4) and $\partial\alpha/\partial Q$ (from Ref. 8), we conclude that it is the components of $\partial^2\alpha/\partial Q^2$ which are dependent on the hydrogen bond strength. Strictly, our results apply to the anisotropic components of α, but we note that the overtone $I_\parallel$ and $I_\perp$ Raman spectra of pure H_2O are also skewed to high frequencies,[1] indicating that the isotropic components may be similarly affected. Assuming, reasonably, that this is not simply the result of the normal mode character of the OH motion in HDO changing with hydrogen bonding, then we infer that $\partial^2\alpha/\partial r_{OH}^2$ changes significantly with hydrogen bonding, where r_{OH} is the OH bond length. Accurate measurements would be required to determine the magnitude of the change because the possibility exists that the low overtone Raman intensity observed for strong hydrogen bonds may result from a compensation of the two contributions to $B_{xy}^{(2)}$. A similar mechanism has been suggested as the explanation of the IR overtone line shape of HDO[10] and other hydrogen bonding systems.[12] In that case it is the components of the dipole moment derivatives which compensate. The results of this work indicate that electronic rearrangements induced by hydrogen bonding have a profound effect on the second order polarizability derivatives.

[a] Alfred P. Sloan Foundation Fellow.

[b] Address, as of January 1981, Dept. of Physical Chemistry, University of Sydney, N. S. W. Australia 2006.

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The chemical shift, dipolar, and quadrupolar tensors of deuterium in potassium bicarbonate

Abraham M. Achlama

Isotope Department, The Weizmann Institute of Science, Rehovot, Israel
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The availability of very high fields and high sampling rates in today's spectrometers has enabled the application of high resolution FTNMR techniques for the study of deuterium in the solid state. The sensitivity that may be obtained allows the determination of previously unattainable parameters, e.g., the chemical shift tensor to an accuracy comparable to that of multipulse or multiquantum methods.[1]

The state of the hydrogen in potassium bicarbonate has been the subject of several studies during recent years. Poplett and Smith[2] have extensively studied this material in the polycrystalline phase using the zero field double resonance technique. However, the directional parameters are lost by this method. Feucht et al.[3] applied the multipulse line narrowing method for the study of the proton chemical shift tensor. In their study only an average tensor could be determined because not all magnetically distinguishable lines were resolved. This problem was not encountered in the present study because the quadrupolar interaction disentangles the deuterium spectrum so that unresolved

proton lines can here be measured independently. Thomas et al. have studied the crystal structure of this material by x-ray[4] and neutron diffraction[5] techniques. In the latter they have suggested the presence of two different hydrogen bonds with deuterium occupation numbers of 0.877 and 0.123. Previously, Chiba has measured the deuterium quadrupole tensor by the cw method.[6]

Reported in this study is the observation of the full chemical shift, quadrupolar, and dipolar tensors of deuterium in potassium bicarbonate. Deuterium A_2 spectrum in the solid has first been reported in barium chlorate monohydrate,[7(a)] and it is only in crystalline water molecules that full dipolar tensors have since been determined.[7(b)]

A single crystal of $KDCO_3$ ($6 \times 3 \times 3$ mm) was obtained as described by Thomas et al.[4] The space group is $P2_1/a$ with four molecules to the unit cell, forming two dimers. Each dimer contains a center of symmetry relating the two molecules between themselves. Con-
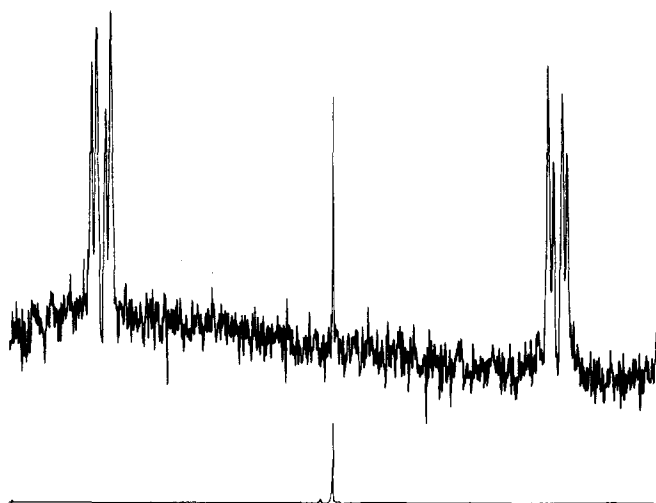
FIG. 1. FTNMR spectrum of a single crystal of KDCO₃. The narrow line at the center is due to free water trapped in the crystal. Sweep width is 125 kHz, pulse width 10 μ sec, quadrature detection mode 3 sec between pulses, and overnight accumulation. The bottom trace is of external D_2O which for this crystal orientation coincides with the internal water.

sequently, the unit cell contains two magnetically distinguishable deuterons giving rise to two signals as observed in Fig. 1. The signals are split by the quadrupolar interaction, asymmetrically about the center. The shift of the center stems from the second order quadrupolar contribution (which is corrected for[8]) and the chemical shift. The accurate position of the center is determined by the free water trapped in the crystal while growing and serves as an internal reference for the chemical shift measurements. Each signal is further split by the deuterium–deuterium dipolar interactions within the dimer. The multiplet is not symmetric, the intensity of the smaller line being ~2/3 of the larger.[9] The lines are 2D apart with $D = -\gamma^2/4\pi^2 \langle (3\cos^2\theta -1)/r^3 \rangle$. Here r is the length of the vector joining

the two deuteriums in the dimer and θ is the angle that this vector forms with the external magnetic field H_0. For the particular orientation of H_0 in Fig. 1 the quadrupolar and dipolar interactions have the same signs. If they had opposite signs, the smaller lines would interchange with the larger ones. Since the sign of the dipolar interaction is known, it provides a means for determining the sign of the quadrupolar constant. This is found to be positive in the present case.

Thirty five different orientations were measured using a specially designed goniometer for the superconducting magnet configuration (cf. Ref. 10 for the experimental procedure). The two sets of lines were converted to a common one by taking account of the symmetry elements of the unit cell. The 70 data points were together subjected to a best-fit procedure, resulting in the tensors given in Table I. It is reassuring to note the coincidence between the principal directions of the EFG tensors measured here and by Chiba.[6] However, his quadrupolar constant is somewhat smaller. Poplett and Smith[2] measured the deuterium quadrupole constants for different deuterium ratios. Extrapolating their results to fully deuterated samples, the agreement becomes even better than in Table I. The largest component of the EFG makes an angle of 1° with the O–D bond direction (3° with O–H ··· 0). The intermediate component is at 0.5° to the normal to the plane formed by the two hydrogen bonds. Note that the dimer is not perfectly planar; the carbonate ions planes make an angle of 5° with that of the hydrogen bonds.

The anisotropies of the proton and deuterium chemical shifts are the same. Because of the lower resolution in the proton measurements, only one of the Eulerian angles could be accurately determined and it agrees with the present value within the experimental error. There is, however, a discrepancy in the isotropic parts of the chemical shift tensor, which is not understood. The difference of 8.3 ppm is larger than that between water and TMS.[12] In any case, in Fig. 1 is reproduced the trace

TABLE I. Deuterium quadrupolar, chemical shift (σ), and dipolar tensors in potassium bicarbonate.

e^2qQ/h (kHz)	σ_i (ppm)	$\Delta\sigma$ (ppm)	η	r (Å)	Principal directions[a] (deg)			Reference
					Φ	Θ	Ψ	
156.7 ± 0.2			0.18 ± 0.02		99.3	65.4	−2.6	This work
154.4 ± 0.6			0.194 ± 0.018		99.1[b]	65.2[b]	−2.5[b]	6
155.49 ± 0.18	(87.5% deuteration)		0.1856 ± 0.002					2
(²D, from D_2O)	−7.8 ± 0.2	26.4 ± 0.5	0.09 ± 0.02		94.6	66.6	−4.7	This work
(¹H, from TMS)	−16.1 ± 1	26.7	0.2 ± 0.1		90[c]	68 ± 2	0[c]	3
				2.223 ± 0.015	171.0	83.3	···	This work
				2.222	167.4	84.9	···	5

[a]Φ, Θ, and Ψ are the Eulerian angles (Goldstein's convention[11]) in an $\{x, y, z\}$ system whose axes coincide with the crystallographic $[\hat{b} \times \hat{c}]$, $\hat{b}$, $\hat{c}$ axes, respectively. The principal components are defined such that $|Z| > |Y| > |X|$.
[b]Converted from the direction cosines of Ref. 6.
[c]Average of the two unresolved magnetically distinguishable tensors.

of an external D_2O sample which coincides with our internal reference. The maximum observed difference between the external and internal references was 0.7 ppm. σ_{zz} makes an angle of 6° with the O–D bond direction, a deviation which is frequently encountered and should be taken into account when trying to identify the bond direction.

It was also possible to determine the deuterium–deuterium vector. Its length is the same as obtained in the neutron diffraction study; however, its direction deviates by 4° in the hydrogen bonds plane. No corrections for thermal vibrations have been attempted, which could be the source for this discrepancy. Finally, we note that no trace has been detected for the presence of two different types of hydrogen bonds.

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On the evaluation of higher-order JWKB integrals

C. K. Chan and P. Lu

Department of Physics, Arizona State University, Tempe, Arizona 85281

Recently, Barwell et al.[1] developed two simple quadrature procedures for evaluating higher-order JWKB phase integrals of the following form:

$$I_k(E) = \oint_\Gamma dr f(r)/[E - U(r)]^{k+(1/2)} , \qquad (1)$$

where k is a positive integer. $f(r)$ is a function of r, $U(r)$, and its derivatives. The contour Γ encloses the branch cut connecting the turning points r_1 and r_2. In the second approach of Barwell et al., the transformation $r = \frac{1}{2}(r_2 + r_1) + \frac{1}{2}(r_2 - r_1)z$ maps $[r_1, r_2]$ onto $[-1, 1]$ so that $I_k(E)$ can be evaluated by the following Gaussian-like integration formula:

$$I_k(E) = \frac{1}{2}(r_2 - r_1)\sum_{m=1}^{N} W_m^k F(z_m) , \qquad (2)$$

where

$$F(z) = f(r)\{(1 - z^2)/[E - U(r)]\}^{k+(1/2)} . \qquad (3)$$

$F(z)$ is approximated by a $(N-1)$th degree polynomial using N points $\{z_m\}$ on the interval $[-1, 1]$. The weights $\{W_m^k\}$ are given by

$$W_m^k = \sum_{n=0}^{N-1} (Z^{-1})_{n+1,m}[1 + (-1)^n]$$
$$\times \Gamma(n/2 + \tfrac{1}{2})\Gamma(-k + \tfrac{1}{2})/\Gamma(n/2 - k + 1) , \qquad (4)$$

where Z^{-1} is the inverse of the Vandermonde matrix Z. The coefficients of Z are $(Z)_{mn} = (z_m)^{n-1}$.

This procedure is extremely efficient because $I_k(E)$ can

be determined by N function evaluations for $F(z_m)$ if the weights $\{W_m^k\}$ are known. However, the evaluation of these weights can be very time consuming if one inverts the matrix Z numerically using popular algorithms such as the Gauss–Jordan method. The objective of this note is to develop a more efficient algorithm which is based on the explicit representation of the inverse Vandermonde matrix. As a result, the computing time used in generating the weights $\{W_m^k\}$ can be reduced.

An explicit representation for the inverse of the Vandermonde matrix[2] is given by

$$P_N(z)/[(z - z_m)P_N'(z_m)] = \sum_{m=0}^{N-1} (Z^{-1})_{n+1,m}z^n , \qquad (5)$$

where $P_N(z)$ is any polynomial which has N zeros $\{z_m\}$ on the interval $[-1, 1]$. The obvious candidate for $P_N(z)$ is the Chebyshev polynomial

$$T_N(z) = \sum_{n=0}^{N} C_n z^n , \qquad (6)$$

which has zeros given by

$$z_m = \cos[(2m - 1)\pi/2N] . \qquad (7)$$

Hence, Eq. (5) can be rewritten as

$$T_N(z)/T_N'(z_m) = \sum_{n=0}^{N} [(Z^{-1})_{n,m} - z_m(Z^{-1})_{n+1,m}]z^n . \qquad (8)$$

Comparing coefficients in Eq. (8), we obtain the following recurrence relation: