

Table II. Viscosity Dependences in Aqueous Solutions^a

Molecule	Volume, Å ³	ρ	C_{stick} , psec/cP	C_{slip} , psec/cP	C_{exptl} , psec/cP
1. HCOOH	38.5	0.6 ± 0.05	10.1	1.6 ± 0.3	6.4 ± 0.5
2. HCOO ⁻	35.2	0.6 ± 0.05	9.5	1.5 ± 0.2	3.7 ± 0.5
	76.7 ^b	0.55 ± 0.05	21	4.2 ± 0.5	
3. CH ₃ COOH	55.5	0.6 ± 0.05	14.7	2.4 ± 0.3	9.9 ± 0.6
4. CH ₃ COO ⁻	52.2	0.6 ± 0.05	14	2.2 ± 0.3	5.0 ± 0.5
	93.7 ^b	0.55 ± 0.05	25.6	5.1 ± 0.5	
5. CH ₃ COOCH ₃	71	0.58 ± 0.03	22	3.9 ± 0.6	4.5 ± 1
6. CH ₃ CH ₂ COOH	72.5	0.55 ± 0.05	23	4.5 ± 0.5	12.9 ± 2

^a All data are from ref 4. ^b Hydrated volume.

coiled or more likely that the flexibility allows for more rapid reorientation than an equivalent rigid structure.

The experimental viscosity dependences in aqueous solutions fall in between the predictions of the slip and stick models as shown in Table II. It is known that all of these molecules can form hydrogen bonds to the solvent, H₂O. Edward has estimated the hydrated volume of the CO₂⁻ group to be 41 Å³ greater than the unhydrated volume.¹³ Using these volumes, the predicted slip viscosity dependences agree very well with those measured for the two anions studied. Methyl acetate is the most weakly H bonded and has a viscosity dependence that is very nearly like that predicted by the slip model. Reorientation for the neutral acids has a considerably greater viscosity dependence than that of the corresponding anion. It is clear that it is more difficult to predict reorientation times in aqueous solutions because of the effects of H bonding on

reorientation. Reorientation in aqueous solutions may be described by hydrodynamics involving either some combination of stick and slip boundary conditions or by slip boundary conditions with an additional "hydration" volume.

In conclusion, hydrodynamics with slip boundary conditions can successfully predict the reorientation times of most small molecules in the absence of strong solute-solvent interactions. When these interactions are present, the reorientation time falls between the predictions of the slip and stick models.

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Carbon-13 Chemical Shielding Tensors in Calcium Formate

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Abstract: The ¹³C chemical shift tensors for the two crystallographically nonequivalent ions in calcium formate have been determined by high resolution solid state nmr in a single crystal, using a sensitivity enhancement technique. The eigenvectors of the tensors are found to be only approximately aligned with a coordinate system oriented along the symmetry directions of the OCO groups, indicating a strong perturbation of the ions by the crystal field and suggesting that the ions may not be planar. The principal values of the shift tensors in ppm with respect to liquid benzene (increasing toward high field), along with their approximate directions, are: -106 and -111 (along C-H), -61 and -57 (in OCO plane perpendicular to C-H), 24 and 24 (perpendicular to the OCO plane), for the first and second tensors, respectively. The equality of the isotropic shifts, -48 ppm for both, gives no hint of the observed differences between the ions.

Just as high resolution nmr in liquids has been enormously important to chemists in the study of molecular structure and dynamics in the liquid state, high resolution nmr in the solid state now promises to be an even richer source of information about molecules and their interactions with their environments. For instance, the chemical shift tensor of a nucleus in a molecule in the solid state may yield information about the local electronic environment of the nucleus and its local site symmetry. In the liquid state the directional character of these properties is lost through rapid mo-

lecular tumbling. Recent advances in experimental techniques have enabled high resolution nmr studies of dilute spins such as ¹³C in solids, with great increases in signal sensitivity.¹

Experimental Section

With this in mind, we have undertaken the determination of the ¹³C chemical shielding tensors in crystalline calcium formate. The pulse sequence used in this experiment is shown in Figure 1. It is

(1) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).

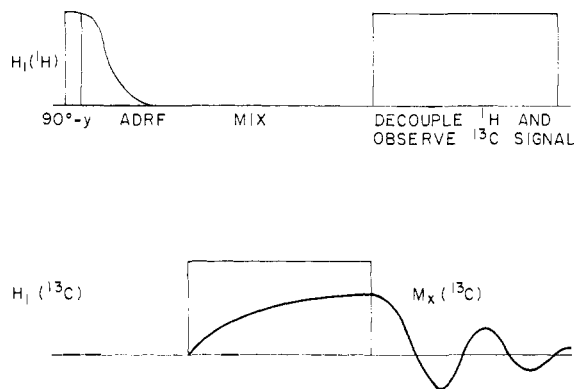


Figure 1. The pulse sequence used in the experiment

a modification of the original Hartmann-Hahn double resonance technique.² High resolution is obtained by observing the rare S spin (¹³C) decay while the abundant I spins (¹H) are decoupled by strong radiofrequency irradiation at their resonant frequency. The technique differs from the initial high resolution version of Pines, Gibby, and Waugh¹ in that thermal mixing of the S spins and the I spins is accomplished with the I spin reservoir in the dipolar state while an "off-resonance" (*i.e.*, $\gamma_I H_{II} \neq \gamma_S H_{IS}$) radiofrequency field is applied to the S spins. This method gives a substantial improvement in signal to noise compared to the usual spin-lock method. The magnitude of H_{IS} is a compromise among three factors: (1) the rate of mixing is a maximum for $H_{IS} = 0$ and decreases as H_{IS} increases;³ (2) the final equilibrium value of M_S is proportional to H_{IS} according to Curie's law; (3) the time of mixing is limited because of the finite value of T_{1D} (¹H). The amplitude of H_{IS} is adjusted to optimize the visually observed decay signal; its adjustment is relatively critical compared to the broad resonance of Hartmann-Hahn matching. The length of the mixing pulse is also varied together with H_{IS} to optimize the signal. The best H_{IS} and mixing time for calcium formate were respectively 15 G and 30 msec. Although these quantities were not optimized for each crystal orientation, it was apparent that they were not strongly dependent upon orientation. Linewidths were about 3–4 ppm.

The spectrometer is a superheterodyne apparatus with the proton and carbon lines operating at 97 and 24 MHz, respectively, corresponding to a Zeeman field of 2.37. Two orthogonal signals are obtained from the phase detector, sampled, digitized, and stored in an on-line PDP-12 minicomputer for signal accumulation and Fourier transformation. The probe contains two orthogonal coils for the generation of the H_1 fields and a goniometer which rotates the crystal about an axis perpendicular to H_0 by a worm and gear arrangement. Both the spectrometer⁴ and the probe⁵ have been described elsewhere.

The crystal is mounted in a carefully machined cube of boron nitride which in turn is seated in a matching boron nitride button that supports the crystal in the radiofrequency coils. The cube with its crystal may be removed from the button and replaced in a different orientation, making it simple to rotate the same crystal about three orthogonal axes.

Single crystals of calcium formate were grown from aqueous solutions by allowing the partially covered solutions to evaporate over about a 3-week period. The crystal actually used in the experiment was grown from a solution containing 0.1 atom % Mn²⁺ ion to shorten the proton T_1 to about 0.40 ± 0.05 sec (measured at 54 MHz) so that data could be collected more rapidly. The proton T_1 of the pure compound is 26 ± 3 sec (at 54 MHz).

Calcium formate crystallizes in the orthorhombic space group $Pcab$ ⁶ and has eight formulas per unit cell or 16 formate ions. Two formate ions are contained in the asymmetric unit, allowing the possibility of two noncongruent (*i.e.*, not symmetrically related)

(2) S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, **128**, 2042 (1962).

(3) D. A. MacArthur, E. L. Hahn, and R. Walstedt, *Phys. Rev.*, **188**, 609 (1969).

(4) J. D. Ellett, Jr., M. G. Gibby, U. Haeberlen, L. M. Huber, M. Mehring, A. Pines, and J. S. Waugh, *Advan. Magn. Resonance*, **5**, 117 (1971).

(5) S. Pausak, J. Tegenfeldt, and J. S. Waugh, *J. Chem. Phys.*, submitted for publication.

(6) I. Nitta and K. Osaki, *X-Rays (Osaka Univ.)*, **5**, 27 (1948); cited in *Struct. Rep.*, **11**, 556 (1948).

tensors. The inversion operation in $Pcab$ reduces the maximum number of observable lines to eight. All eight lines were observed in certain orientations.

The crystallographic orientation of the crystal was first determined by X-ray diffraction in order to enable the tensors obtained in the nmr experiment to be related directly to the geometry of the formate ion. The crystal in its boron nitride button was mounted in a G.E. four-circle X-ray diffractometer, and angular data were taken for 28 reflections. The orientation of the crystallographic axes with respect to the button was determined by a least-squares fit of the reflection data.

Nmr spectra were taken every five degrees for rotations of the crystal about three mutually orthogonal axes. Approximately 300 to 500 decays were coadded for each spectrum. The familiar sinusoidal rotation patterns were obtained by plotting the chemical shifts of the spectral lines *vs.* the angle of rotation of the crystal. By noting the crossings of curves in the rotation plots at angles for which the Zeeman field passes through a symmetry plane of the crystal, it was possible to assign each curve to a particular pair of inversion-related formate ions in the unit cell. The direct least-squares fitting of the tensor elements and diagonalization of the tensors was carried out by QSPL4,⁷ a program originally written for quadrupole coupling tensors and modified to accept chemical shift data. This program also varied the rotation axes to correct for possible errors arising from the cube not having right angles or the field not being perpendicular to the rotation axis, but these corrections were found to be small.

Results

The final results are indicated in Table I. The limits of error are about ± 1 ppm for the eigenvalues and

Table I. Calcium Formate ¹³C Chemical Shielding Tensors

Carbon	Eigenvalue, ^a		Eigenvector ^b			Angle, ^c deg
	ppm					
I	σ_{11}	-106	0.119	-0.743	0.659	3
	σ_{22}	-61	-0.777	0.344	0.527	5
	σ_{33}	24	0.618	0.575	0.537	6
	$\bar{\sigma}$	-48				
II	σ_{11}	-111	0.107	0.480	-0.871	14
	σ_{22}	-57	0.857	-0.489	-0.164	12
	σ_{33}	24	0.505	0.728	0.464	9
	$\bar{\sigma}$	-48				

^a Shielding in ppm with respect to liquid ¹³C₆H₆; $\bar{\sigma} = 1/3 \text{Tr}\sigma$.

^b Expressed as direction cosines with respect to the crystallographic axes. ^c Angle between eigenvector and nearest axis of molecular coordinate system defined in the text.

about $\pm 1^\circ$ for the eigenvectors (where the eigenvector components are taken as direction cosines and the error limits on these quantities are expressed in degrees). The chemical shift tensors are seen to be highly anisotropic. The eigenvalues of the two tensors are very close; however, the nonequivalence of the two formate ions is clearly shown. For both molecules, the most shielded component lies in the direction approximately perpendicular to the molecular plane.

The experiment illustrates two important points. The first point is that the formate ion is highly perturbed by the crystal field and that, at least with respect to the electronic effects which give rise to the chemical shift, the ion cannot be treated as isolated. The shift tensor is skewed with respect to the orientation it would be expected to have if it were situated at a site of C_{2v} symmetry. We define in Figure 2 a coordinate system, with basis vectors *i* bisecting the OCO angle, *k* per-

(7) J. Tegenfeldt, UUIC-B13-6, Institute of Chemistry, University of Uppsala, Uppsala, Sweden, 1973.

pendicular to the OCO plane, and $\mathbf{j} = \mathbf{k} \times \mathbf{i}$. The eigenvectors for both tensors do not coincide with these molecular axes; the most extreme case is that of σ_{11} in ion II, where the eigenvector lies 14° away from \mathbf{i} . It is not known whether or not the proton in either formate ion lies in the OCO plane.⁸ The distorted orientation of the eigenvectors of the tensor for either ion with respect to this "symmetrically" oriented axis system may possibly be an indication that the ion is in fact not planar.

The second point is that although there are clear differences between the formate ions, the isotropic shifts, $\frac{1}{3}\text{Tr}\sigma$, are essentially identical. The detailed type of information which this experiment yields (*i.e.*, the directions of the principal axes and the individual components of the chemical shift tensor) is lost in a liquid study where the anisotropic properties are obscured and only the trace of the shift tensor is observed.

The isotropic part or the ^{13}C shift in $\text{Ca}(\text{HCO}_2)_2$ changes from -48 to -44 ppm on dissolving the sample in H_2O ($1 M$), suggesting that the shieldings observed are largely properties of the electronic nature of the free formate ion. However, note that the eigenvectors of the shielding tensor are somewhat twisted away from the directions that would be imposed by the symmetry of such a free ion.

A similar change in isotropic shielding occurs when solid methyl formate ($\bar{\sigma} = -36$ ppm) is melted ($\bar{\sigma} = -32$ ppm).⁹

Notice that the anisotropic part of the shielding tensor may be far more sensitive to changes in electronic structure than the isotropic shift; the difference $\Delta\bar{\sigma}$ between $\text{Ca}^{2+}(\text{HCO}_2^-)_2$ and HCOOCH_3 ($+12$ ppm) is a result of differences between corresponding principal components $\Delta\sigma_{11} = -15$ ppm, $\Delta\sigma_{22} = +52$ ppm, and $\Delta\sigma_{33} = -2$ ppm.

(8) The proton positions were not determined in the original crystal structure analysis. In a later paper proton positions were estimated using the assumption that the proton lies in the OCO plane and that the ion is undistorted in the crystal with respect to its free state configuration. See J. Itoh, R. Kusaka, R. Kiriya, and Y. Saito, *Mem. Inst. Sci. Res., Osaka Univ.*, **14**, 1 (1957); cited in *Struct. Rep.*, **21**, 502 (1957).

(9) A. Pines, M. G. Gibby, and J. S. Waugh, *Chem. Phys. Lett.*, **15**, 373 (1972).

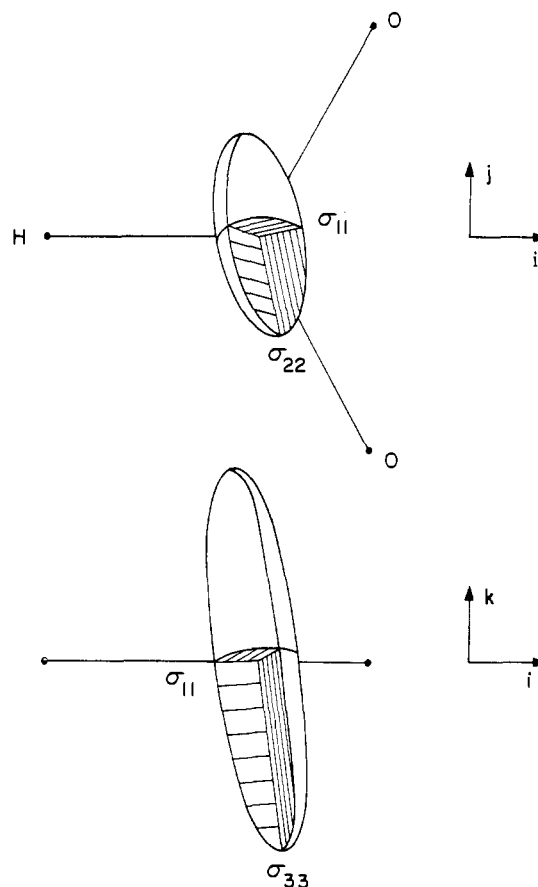


Figure 2. Schematic representation of the shielding tensor of formate ion II. The principal axes of the ellipsoids indicate the eigenvector directions. The lengths of the axes are proportional to the corresponding eigenvalues shifted to make all three eigenvalues positive. The directions \mathbf{i} , \mathbf{j} , and \mathbf{k} are defined in the text.

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