

Figure 1. Two-dimensional Fourier transform spectrum of 10 mol % DCCCN in Merck Phase V at 30.5 °C. The F_2 domain shows a section (540 Hz) of the regular NMR spectrum folded about the transmitter frequency positioned at $\Delta\omega = 155$ Hz off resonance. The F_1 domain presents the double quantum signal at F_1 of $2\Delta\omega$. The experiment was performed at 9.21 MHz in ~ 2 h, using 8k data points to cover a spectral width of 20 KHz in the F_2 domain. The evolution period t_1 was incremented in 200 steps of 1 ms. For the first pulse, $\omega_1 = 4.6$ kHz ($\sim\omega_Q/4$) and $t_{p1} = 200$ μ s, while for the monitoring pulse, $\omega_1 = 17$ kHz and $t_{p2} = 15$ μ s.

spectrum appears along the F_2 axis. The F_2 widths of the two lines are influenced¹¹ not only by the transverse decay rates $R_2(1,0) = R_2(0,-1)$ and static field inhomogeneity, but also by thermal gradients which cause a spread in ω_Q . The line separation in the folded spectrum equals twice the resonance offset, $\Delta\omega = 155$ Hz. Along the F_1 axis the double quantum phase coherence is observed as predicted,^{1,2,4} at $2\Delta\omega$ and the line is broadened by twice the static field inhomogeneity. Since the double quantum precession frequency does not depend on ω_Q , the inhomogeneous broadening from thermal gradients is absent. This property has been exploited in several elegant deuterium studies of solid^{2,4,12} and liquid crystals.¹³

By measurement of the line width in the F_1 domain in Figure 1 and correcting for the static inhomogeneity ($2\delta\omega_0 = 3.6$ Hz) we obtained $R_2(1,-1) = 20 \pm 2$ s⁻¹ for a 10 mol % solution of DCCCN in Merck Phase V at 30.5 °C. A similar experiment yielded $R_2(1,-1) = 13.4 \pm 1.4$ s⁻¹ for 10 mol % CDCl₃ in the same solvent at 32.3 °C.

Relations between Redfield relaxation elements¹⁴ for a single ordered deuteron and the three spectral densities of motion, $J_0(0)$, $J_1(\omega_0)$, and $J_2(2\omega_0)$, have recently been published.^{11,15,16} It may be shown that the 2Q coherence decay rate $R_2(1,-1)$ is given by a single Redfield relaxation element:

$$R_2(1,-1) = (3\pi^2/20)(e^2qQ/h)^2\{J_1(\omega_0) + 2J_2(2\omega_0)\} \quad (1)$$

A nonselective inversion recovery experiment yields the quantity $J_1(\omega_0) + 4J_2(2\omega_0)$ while $J_1(\omega_0)$ can be obtained separately using selective pulses to monitor the difference magnetization created by selective inversion of either doublet component.^{11,17} From such spin lattice relaxation experiments we have obtained¹⁸ $J_1(\omega_0) = 170 \pm 10$ ps, $J_2(2\omega_0) = 83 \pm 5$ ps for DCCCN and $J_1(\omega_0) = 161 \pm 11$ ps, $J_2(2\omega_0) = 85 \pm 7$ ps for CDCl₃. Using these values, eq 1, and published values^{19,20} for (e^2qQ/h) we calculate $R_2(1,-1) = 20.1 \pm 0.8$ s⁻¹ for DCCCN and $R_2(1,-1) = 13.3 \pm 0.7$ s⁻¹ for CDCl₃, in excellent agreement with the values observed in the double quantum experiment.

It appears, then, that accurate double quantum decay rates may be obtained, provided that the static field inhomogeneity is known and not too large. Otherwise, echo techniques^{21,22} must be used. In the present case no new information was obtained, but the 2Q experiment may be viewed as a valuable check on the interesting observation that $J_1(\omega_0) > J_2(2\omega_0)$ even though the motion appears to be well within the extreme narrowing limit ($\tau_c = 1/2J_0(0)$ with present definitions). In ordered systems with two deuterons, the complete characterization of the molecular dynamics requires knowledge of MQ

relaxation rates.²³ A general discussion of complex spin systems with an elegant application to paramagnetic relaxation will soon be published by Wokaun and Ernst.²²

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G. Bodenhausen, N. M. Szeverenyi
R. L. Vold, R. R. Vold*

Department of Chemistry
University of California, San Diego
La Jolla, California 92093

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A MINDO/3 Study of Some Hydrogen-Bonded Systems

Sir:

A study of some sample hydrogen-bonded systems was made using the MINDO/3 geometry optimizing method of Bingham, Dewar, and Lo.¹ The systems chosen for study are tabulated in Table I along with the heats of formation of the monomer and dimer.

The calculations for the hydrogen-bonded dimers were performed using the optimized geometries of the monomers as found by the MINDO/3 method.¹ The monomers were then set at orientations predicted to be the most stable according to ab initio studies. The intermolecular distance between the monomers was optimized by initiating the distance $R_{x-x'}$ at 1.00 Å less than the ab initio best $R_{x-x'}$ listed in Table I. The distance $R_{x-x'}$ is the distance between the second row atoms involved in the hydrogen bond which can be represented as $x \cdots H-x$. It can be seen from the tabulated results that the optimization procedure of MINDO/3 using standard options as given in the program separates the monomers to a distance beyond that considered normal for hydrogen bonding. At these intermolecular distances which are predicted to be the most stable, it can be seen that the dimer system has either the same stability as two independent monomers or is less stable than two isolated monomers.

Table I. Systems Studied and Heats of Formation of Monomer and Dimer

dimer system	MINDO/3	MINDO/3	ΔE , kcal/mol (ab initio)	R_{x-x} , Å	
	ΔH_f for dimer	ΔH_f for monomers		ab	MIN- DO/3
(H ₂ O) ₂ , linear	-107.3	-107.2	-6.09 ^a	2.73 ^a	5.43
(H ₂ O) ₂ , bifurcated	-107.2	-107.2	-4.45 ^b	3.00 ^b	5.31
(H ₂ O) ₂ , cyclic	-107.2	-107.2	-4.0 ^b	2.90 ^b	5.62
NH ₃ →OH ₂	-62.9	-63.0	-5.89 ^c	2.91 ^c	6.68
			-5.8 ^d	3.12 ^d	
CH ₃ OH→OH ₂	-45.9	-103.7	-5.26 ^e	2.71 ^e	5.18
CH ₃ OH→NH ₃	-49.0	-59.5	-6.48 ^c	2.87 ^c	6.98

^a J. E. Del Bene and J. A. Pople, *J. Chem. Phys.*, **52**, 4858 (1970).

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^c J. E. Del Bene, *ibid.*, **95**, 5460 (1973). ^d P. A. Kollman and L. C. Allen, *ibid.*, **93**, 4991 (1971). ^e J. E. Del Bene, *J. Chem. Phys.*, **55**, 4633, (1971).

The conclusion is that MINDO/3 geometry optimization program² in its present form does not predict correct interatomic distances for heavy atoms connected by hydrogen bonds.

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Theresa Julia Zielinski*

Department of Chemistry, College of Mount Saint Vincent
Riverdale, New York 10471

Donna L. Breen

Department of Chemistry, Auburn University

Robert Rein

Department of Experimental Pathology
Roswell Park Memorial Institute, Buffalo, New York 14263

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Hydrogen Bonding in the MINDO/3 Approximation

Sir:

The MINDO/3 program has been heralded as being very reliable,¹ and, indeed, as we in our laboratories and others have found, it is a very good method for the calculation of the ground-state properties of large molecules. However, we recently uncovered a major shortcoming in the method, and we wish to warn the scientific community at large of this fact.

One of our recent studies involving the MINDO/3 method concerned the intermolecular interaction between carbonyl derivatives and water. We were surprised to find very little, if any, intermolecular interactions and as a check we decided to investigate the water dimer also to see whether MINDO/3 provides realistic results for such hydrogen-bonding problems.

We obtained the same results as those published by Dewar² for the minimization of both an isolated acetaldehyde and water units. For the water dimer, we chose the geometry given by Popkie et al.³ where the intermolecular angles α and β equal 0 and the oxygen-oxygen distance is fixed at 2.9475 Å (Figure 1). We obtained a heat of formation of -53.6 kcal/mol for the monomer and -99.7 kcal/mol for the dimer. This leads to a

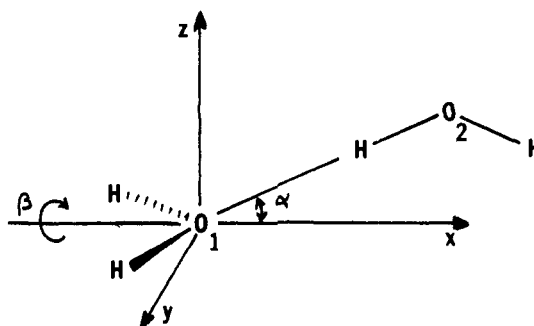


Figure 1. The geometry of a water dimer.

Table I. Dimer Orientations and Heats of Formation^a of Water Dimers^{b,c}

R_{OO} , Å	α	β	ΔH_F°
2.95	0	0	-99.7
2.85	0	0	-98.0
2.75	0	0	-96.0
2.6	0	0	-92.2
2.5	0	0	-88.9
2.95	30	0	-97.2
2.95	45	0	-98.3
2.95	52	0	-98.5
2.95	89	0	-98.2
2.95	0	90	-99.7

^a Kilocalories/mole. ^b Monomer heat of formation is -53.6 kcal/mol. ^c Molecule 1 is in the x - y plane. Molecule 2 is in the x - z plane. R_{OO} is the internuclear distance between the two oxygen atoms. α is the angle between the O₂-H₂ bond of molecule 2 and the x axis. β measures the rotation of molecule 1 around its principal axis (see Figure 1).

repulsion of 7.5 kcal/mol and contrasts with the value of -3.67-kcal/mol stabilization energy for the dimer calculated by these authors,³ -6.41 kcal/mol⁴ for STO/3G, -5.94 kcal/mol⁵ for CNDO/2, and -14.1 kcal/mol⁶ for the INDO method.

We then proceeded to minimize the distance between the two oxygen atoms in the hope that somewhere along this path we would find a minimum. We found the dimer to be unstable at all distances (Table I). Spot calculations at various intermolecular angles also failed to reveal any stable dimer structure. Although we have not made a thorough investigation of all the angular dependencies of the dimer to find a minimum, our preliminary findings show that MINDO/3 predicts a linear orientation of two water molecules to be repulsive, in contrast to the other semiempirical and ab initio techniques.

For the acetaldehyde-water pair we chose the geometry obtained by Del Bene⁷ from an STO/3G calculation (Figure 2). In contrast to a stabilization of 3.82 kcal/mol found by the

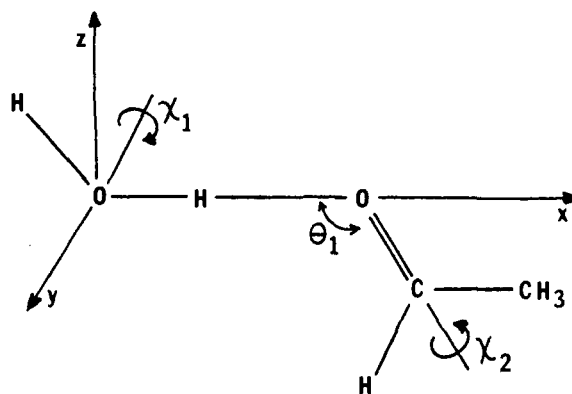


Figure 2. Geometry of the acetaldehyde-water pair.