I. Chabay and G. Holzwarth, *Appl. Opt.*, **14**, 454 (1975).
(22) From the ΔA and $\Delta\epsilon$ values given in ref 8 we estimate the pathlength used to be 57 μm.
(23) L. Rosenfeld, *Z. Phys.*, **52**, 161 (1928); E. U. Condon, *Rev. Mod. Phys.*, **9**, 432 (1937); W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).
(24) In this paper a $\Delta A/A$ value is taken to be the ratio of the *peak* ΔA to the *peak A*, irrespective of whether ΔA and A peak at the same frequency. $\Delta A/A$ values given are absolute values; signs can be obtained from the figures.
(25) D. S. McClure, "Electronic Spectra of Molecules and Ions in Crystals", Academic Press, New York, N.Y., 1959.
(26) P. Pino, F. Ciardelli, and M. Zandomeneghi, *Annu. Rev. Phys. Chem.*, **21**, 561 (1970).
(27) B. Bosnich, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **94**, 4750 (1972); M. Diem, J. L. Fry, and D. F. Burrow, *ibid.*, **95**, 253 (1973); L. D. Barron, M. P. Bogaard, and A. D. Buckingham, *ibid.*, **95**, 603 (1973); *Nature (London)*, **241**, 113 (1973); L. D. Barron and A. D. Buckingham, *J. Chem. Soc., Chem. Commun.*, 152 (1973); W. Hug, S. Kint, G. F. Bailey, and J. R. Scherer, *J. Am. Chem. Soc.*, **97**, 5589 (1975).

Nuclear Magnetic Resonance Spectroscopy. Spin–Lattice Relaxation of the Acetic Acid Carboxyl Carbon[1]

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Abstract: The carbon-13 spin–lattice relaxation times of the carboxyl carbons of acetic acid and its deuterated analogues (CH_3COOD, CD_3COOH, CD_3COOD) have been measured by nuclear magnetic resonance spectroscopy. These measurements reveal that the methyl protons and the hydroxyl proton contribute roughly equally to the total dipolar relaxation of neat acetic acid. Spin–rotation relaxation is also observed in these molecules. The T_1 and NOE values for the carboxyl carbon of acetic acid in aqueous solution each demonstrate a small concentration dependence in the region of high acid concentration. Although samples of 1 M acetic acid contaminated with paramagnetic metal ions show a marked pH dependence of T_1 and NOE, the T_1 and NOE values for purified samples are invariant with respect to pH. Some chemical implications of the above behavior are discussed.

Traditionally, nuclear magnetic resonance spectroscopists have usually been concerned with the measurement of chemical shifts, resonance intensities, and coupling constants. In recent years, yet another parameter, the spin–lattice relaxation time (T_1), has become of interest in carbon-13 NMR spectroscopy.[2] Although T_1 values may yield important information concerning molecular dynamics, their measurement is often fraught with difficulties. The presence of oxygen in solution, contamination by other paramagnetic impurities, vortex formation in the sample, temperature variation, and instrumental problems often lead to variable results for T_1 studies of the same molecule performed under different conditions. The value of T_1 for the carboxyl carbon of neat acetic acid, for example, has been determined by several groups[3] under various conditions, and the reported values range from 18.5 to 41.1 s.

A more detailed study of the spin–lattice relaxation behavior of acetic acid is reported here. Such a study is particularly appropriate in view of the recently discovered extreme sensitivity of carboxyl carbon T_1 values to contamination by trace paramagnetic metal ion impurities.[3e,4,5] By means of selective deuteration experiments, the relative contributions of various mechanisms to the relaxation of the acetic acid carboxyl carbon atom have been studied, and in addition the effects of dilution and pH changes upon the values of T_1 for this nucleus have been investigated.

Results and Discussion

Acetic Acid and Its Deuterated Analogues. In order to investigate the relative contributions to dipole–dipole relaxation (T_1^{DD}) from the methyl and hydroxyl protons of neat acetic acid, T_1 values (T_1^{obsd}) and nuclear Overhauser enhancements (NOE $(1 + \eta)$) for the carboxyl carbon atom of the molecules CH_3COOH, CH_3COOD, CD_3COOH, and CD_3COOD were measured. In each case, the dipole–dipole relaxation arising from the protons and the spin–lattice relaxation due to other mechanisms (T_1^{other}) were calculated by use of eq 1 and 2.

$$T_1^{DD} = T_1^{obsd}\frac{1.988}{\eta} \quad (1)$$

$$\frac{1}{T_1^{obsd}} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{other}} \quad (2)$$

The T_1 values were measured at 15.09 MHz on our "Brukarian" spectrometer by the progressive saturation technique, and are deemed accurate to ±10%[6] (see Experimental Section). The accuracy of the NOE measurements is approximately ±5%. Because carboxyl carbon T_1 values are known to be extremely sensitive to paramagnetic metal ion impurities, the samples (obtained from commercial sources) were distilled three or more times, and all glassware, vortex plugs, etc., were decontaminated as described elsewhere,[4] and in the Experimental Section. Deoxygenation was achieved by purging with nitrogen, or by the freeze–thaw technique.

The results of this study are presented in Table I. It must be emphasized at this point that in spite of the rigorous purification procedures employed, all T_1 values reported in Table I and elsewhere in this paper may be only lower limits. If residual contamination by paramagnetic metal ions or by oxygen is great enough, T_1 values in the absence of contamination may be larger than reported. However, in all cases the reported values are reproducible for multiple samples, and other evidence (see below) indicates that even if some individual T_1 or NOE values are somewhat in error, the trends observed cannot be ascribed to contamination by paramagnetic impurities.

The first line of the table reports results for CH_3COOH. These values for T_1 and NOE agree, within experimental error, with those reported by Farrar et al.[3d] Other values for T_1 and NOE reported in the literature are smaller than

Table I. T_1 and NOE Values for Neat Acetic Acids (Carboxyl Carbon)

Compd	T_1^{obsd}, s	NOE $(1+\eta)$	T_1^{DD}, s	T_1^{other}, s
CH_3COOH	40	2.43	56	142
CH_3COOD	60	1.95	126	115
CD_3COOH	61	2.16	105	146
CD_3COOD	137	1.11	>2000	145

those obtained here, although where NOE values have been measured,[3c] the dipolar relaxation times are in good agreement. These shorter values are likely the result of contamination by oxygen or other paramagnetic impurities, or by vapor formation.[3d] Thus, the dominant relaxation mechanism for the carboxyl carbon atom of CH_3COOH is dipolar.

The remaining results in Table I refer to specifically deuterated molecules. If we make the reasonable assumption that the major effect of deuteration upon the spin-lattice relaxation time of the carboxyl carbon is loss of dipolar relaxation from the replaced protons, then we may use the results of the deuteration experiments to determine the relative contributions of the various protons to T_1^{DD}. Replacement of the hydroxyl proton by deuterium results in a T_1^{DD} value of 126 s. This residual dipolar relaxation must arise from the methyl protons. Similarly, replacement of the methyl protons by deuterons yields a value for T_1^{DD} of 105 s for relaxation due to the hydroxyl proton. The total dipolar relaxation for this system is given by eq 3, where $T_1^{DD}(OH)$ and $T_1^{DD}(CH_3)$ are the contributions to

$$\frac{1}{T_1^{DD}(\text{total})} = \frac{1}{T_1^{DD}(OH)} + \frac{1}{T_1^{DD}(CH_3)} \qquad (3)$$

T_1^{DD}(total) of the hydroxyl and methyl protons, respectively. Substituting from Table I, a value for T_1^{DD}(total) of 57 s is obtained. This value is in good agreement with the value of 56 s found for acetic acid.

Table I shows that the methyl protons and the hydroxyl protons contribute roughly equally to the relaxation of the carboxyl carbon atom. This is true even though there are three methyl protons and only one hydroxyl proton. Several factors make the hydroxyl proton more efficient than a single methyl proton. The hydroxyl proton is closer to the carboxyl carbon than is the methyl proton, and T_1^{DD} is dependent upon the sixth power of the carbon-hydrogen internuclear distance.[2] In addition, rapid internal rotation of the methyl group may lead to a reduction in $T_1^{DD}(CH_3)$.[7] Finally, in dimeric acetic acid, hydrogen-bonded protons may help to relax the carboxyl carbon.

In CH_3COOD and CD_3COOH, T_1^{DD} and T_1^{other} are of roughly equal importance, whereas in CD_3COOD, where dipolar relaxation is essentially eliminated, T_1^{other} accounts for all the relaxation. Chemical-shift anisotropy relaxation has been found to be unimportant for acetic acid.[3c,d] Scalar coupling relaxation has been suggested as a possible contributing mechanism for neat acetic acid.[3d] However, Table I reveals that within experimental error, replacement of the hydroxyl proton by a deuteron has no effect on T_1^{other}. Thus, scalar coupling may be ruled out as a significant relaxation mechanism for neat acetic acid, and T_1^{other} may be ascribed to spin-rotation relaxation plus any contribution from residual paramagnetic impurities.

The relatively large amount of relaxation in acetic acid arising from the hydroxyl proton means that T_1 values for carboxyl carbon nuclei obtained in aqueous solution cannot be directly compared with values obtained from solutions containing D_2O. This fact is of special significance for studies of compounds of biological interest, because such molecules are often studied in water or D_2O.

Table II. Concentration Dependence of T_1 and NOE

Mole fraction acid	−Log (mole fraction acid)	T_1, s	NOE $(1+\eta)$
	CH_3COOH in H_2O		
1.00	0.00	40	2.43
0.80	0.0969	34	2.70
0.561	0.251	30	2.63
0.245	0.611	32	2.46
0.129	0.889	30	2.36
0.054 1	1.267	33	2.39
0.037 4	1.427	45	2.25
0.018 7	1.728	47	2.21
0.009 37	2.028	45	2.11
0.004 68	2.330	47	2.08
	CH_3COOD in D_2O		
1.00	0.00	60	1.95
0.556	0.255	60	2.11

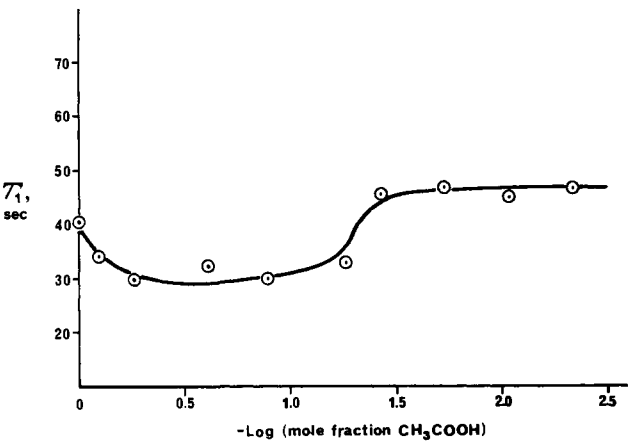

Figure 1. Concentration dependence of T_1 of the carboxyl carbon of CH_3COOH in H_2O.

Concentration Dependence of Acetic Acid T_1 Values. The results of a study of the concentration dependence of T_1 and NOE for aqueous acetic acid appear in Table II. The usual precautions to avoid contamination by paramagnetic metal ions were observed. In addition, the water used to dilute the samples was doubly distilled, and then extracted with dithizone in carbon tetrachloride to remove metal ions (see Experimental Section).

The changes in T_1 and NOE observed upon dilution of acetic acid with H_2O are small but outside experimental error. Although the individual T_1 values may be in error by as much as ±10%, the results reveal a definite trend (Table II and Figure 1). Addition of small amounts of H_2O (less than about 1 equiv) to neat acetic acid results in a decrease in T_1 accompanied by a small increase in NOE. Subsequent dilution with H_2O causes an increase in T_1 and decrease in NOE. At concentrations of 0.037 mol fraction of acid or less, dilution has no measurable effect on either T_1 or NOE. Similar nonlinear behavior is manifest in other physical methods for studying acetic acid-water mixtures. For example, dilution curves for acetic acid which have maxima or minima in the region of 0.5 mol fraction acid have been observed in low-frequency Raman spectra,[8] carbon-13 chemical shift measurements,[9] proton chemical shift measurements,[10] hydrogen relaxation time measurements,[11] and viscosity measurements.[12]

The cause is in all probability changes in aggregation of

the molecules in solution as has been postulated by several workers.[13] Thus, the cyclic dimers present in neat acetic acid may, on initial dilution with water, form new species which could be linear dimers, hydrated dimers, acid water polymers, and so on, or mixtures of these. Formation of such aggregates can explain the initial changes on dilution and subsequent further breaking up of aggregates on continued dilution could well account for the maxima or minima in the curves.

There are several ways in which water-acetic acid aggregates could affect T_1 and NOE values. One way is through slower tumbling rates which in turn would result in more efficient dipolar relaxation. This would cause an increase in NOE values and a decrease in T_1, as is observed. Subsequent dilution could result in changes in these aggregates and a reversal of T_1 and NOE behavior. Nonlinear changes in macroscopic viscosity as a function of acetic acid concentration would have similar effects of T_1 and NOE. Intimate association of water molecules with the aggregates could also result in an increase in intermolecular dipolar relaxation upon initial dilution. This possibility is supported by observations of intermolecular relaxation by water of the carboxyl carbon of glycine[4] and the carbonyl carbon of perdeuterioacetone.[14] That dilution of CH_3COOD with D_2O produces no change in T_1 or NOE within experimental error (Table II) would appear to support this consideration. However, one must remember that the mechanisms of relaxation are not identical for the deuterated and undeuterated species.

Other changes which would occur as a result of changes in the aggregates with water concentration would be in the exchange rate of the acid hydroxyl protons and the spin-rotation relaxation time. These factors could also affect the measured T_1 values, if they were of the correct magnitude. While residual paramagnetic impurities may contribute to the absolute values of the measured T_1 and NOE values, they cannot explain the observed trends because the initial decrease in T_1 is accompanied by an increase in NOE.

In summary, dilution of acetic acid with H_2O results in an initial small decrease in T_1 values and an increase in NOE for the carboxyl carbon. These changes are presumably due to solvent-solute interactions of some type. Further dilution results in an increase in T_1 until water is present in large excess at which point the T_1 becomes constant. Clearly, if further changes in monomer-dimer-aggregate equilibria occur in the high-water region, the T_1 and NOE values are not sensitive to them, at least to the accuracy of our measurements.

pH Dependence of T_1 and NOE. In our initial studies with unpurified solutions of acetic acid-sodium acetate, a strong pH dependence was found for T_1 and NOE of the carboxyl carbon (Table III). Whereas the T_1 values in strongly acid and strongly basic solution were reasonably close to those of 1 M acetic acid (0.0187 mol fraction above), there was a pronounced minimum in T_1 and NOE near pH 4.6, which is approximately the pK value of acetic acid. An interesting facet of these data is the observation that the dipolar relaxation time remains constant across the whole range of pH and is about 75 s. The same type of behavior occurs for a 1.0 M solution of acetic acid-sodium acetate in D_2O although the observed T_1 values are consistently longer than in H_2O and the NOE values are consistently smaller (Table IV). The dipolar relaxation time is again invariant across the whole pH range, although at 247 s it is significantly longer than in the H_2O solution.

We have observed a similar pH dependence of carboxyl carbon T_1 values in glycine[15] and we have attributed this to contamination by paramagnetic metal ions.[4] Indeed, addition of about 10^{-4} M $CuCl_2$ to 1 M acetic acid resulted in a greatly accentuated pH dependence with T_1 values on the order of 1 s at pH 4.5 and negligible NOE. A similar study was recently reported by Cohen and co-workers[3e] who also found a large pH dependence of T_1 for acetic acid solutions doped with Cu(II). For nondoped solutions these authors obtained much larger T_1 values, although from pH 4 to 7.6 their data varied somewhat randomly from 33.1 to 60.3 s with an average relaxation time of 44 s. Unfortunately these authors did not measure nuclear Overhauser enhancements and so were unable to make estimates of the true dipolar relaxation times.

Even in such heavily doped samples as those just described it is still possible to obtain meaningful dipolar relaxation times if one has reliable NOE data. For example, in our purposely doped sample of acetic acid-sodium acetate at pH 1.7 we find T_1 to be 12.4 s and the NOE to be 1.4. These data yield a dipolar relaxation time of 62 s, which is in good agreement with that of our "nondoped" sample.

We finally examined the pH dependence of T_1 and NOE in acetic acid solutions which had been purified as discussed above and in the Experimental Section. The results appear in Table V. Within experimental error, there is no pH dependence of either T_1 or NOE. Considering the relatively large error in T_1^{DD} the agreement over the whole pH range is quite striking. The average T_1^{DD} of 70 s is in excellent agreement with the average T_1^{DD} of 75 s from the unpurified sample.

Since it was found that in neat acetic acid replacement of the hydroxyl proton by a deuteron resulted in an increase in T_1, it might be expected that removal of the hydroxyl pro-

Table III. pH Dependence of T_1 and NOE for Unpurified 1.0 M Acetic Acid-Sodium Acetate in H_2O

pH	T_1, s	NOE $(1 + \eta)$	T_1^{DD}, s	T_1^{other}, s
0.2	38	2.10	69	84
1.4	40	2.03	80	80
4.6	22	1.59	72	31
5.6	31	1.76	74	50
6.2	36	1.86	81	66
6.6	39	2.00	77	77
9.5	47	2.25	72	151

Table IV. pH Dependence of T_1 and NOE for Unpurified 1.0 M Acetic Acid-Sodium Acetate in D_2O

pH	T_1, s	NOE $(1 + \eta)$	T_1^{DD}, s	T_1^{other}, s
1.1	64	1.69	186	98
5.62	27	1.23	237	31
5.88	33	1.26	255	38
6.09	47	1.41	231	60
6.19	51	1.42	242	64
9.83	91	1.68	269	147

Table V. pH Dependence of T_1 and NOE for Purified 1.0 M Acetic Acid-Sodium Acetate in H_2O

pH	T_1, s	NOE $(1 + \eta)$	T_1^{DD}, s	T_1^{other}, s
2.1	43	2.29	67	121
2.4	45	2.25	72	120
3.7	42	2.24	68	110
4.3	45	2.20	75	113
5.4	40	2.23	65	104
5.6	45	2.16	78	107
13.1	46	2.27	72	126
13.1	44	2.35	65	135

ton by the formation of the acetate ion would have a similar effect, and that T_1 values should increase with increasing pH. Since this is not observed, there may be some compensatory effect. This could be an increase in viscosity and such increases have been observed for acetic acid–sodium acetate solutions.[16] However, it must be remembered that whereas neat acetic acid is mostly dimeric, 1 M acetic acid may well be mostly monomeric, and the relative importance of the various relaxation mechanisms need not be the same for the two situations.

For the unpurified sample in D_2O (Table IV) the constancy of T_1^{DD} over the whole pH range is again apparent; the average value of 247 s, however, is considerably greater than in the H_2O case. The shorter T_1 values for H_2O solutions at low pH are due, at least in part, to the presence of a proton rather than a deuteron on the hydroxyl oxygen. Because acetic acid is present mainly as an anion at pH 9 and above, the shorter T_1^{DD} for the H_2O solutions in this region must be due to intermolecular relaxation from the protons of water (assuming that the correlation times of CH_3COO^- in water and D_2O are approximately equal). The magnitude of this intermolecular effect may be calculated from

$$1/T_1^{DD(inter)} = 1/T_1^{DD(H_2O)} - 1/T_1^{DD(D_2O)}$$

and comes out to be about 100 s. We have recently observed intermolecular effects of similar magnitude in aqueous solutions of glycine.[4] If one assumes that at pH 9 and above all paramagnetic metal ions are present as hydroxides[17] and do not affect T_1 and NOE values, then the larger Overhauser enhancement observed for the acetic acid carboxyl carbon in H_2O as opposed to D_2O constitutes a direct observation of an intermolecular Overhauser enhancement. This intermolecular carbon-13 NOE finds its analogy in proton NMR in the classic double resonance experiment of Kaiser[18] on a chloroform–cyclohexane solution. Germane to the intermolecular relaxation noted in the acetic acid–sodium acetate system is the conclusion of von Goldammer and co-workers[14] that intermolecular relaxation from water is important for the carbonyl carbon of perdeuterioacetone. von Goldammer's results indicated that the magnitude of the intermolecular relaxation was about 100 s.

It remains to make some comments about the effect of the paramagnetic metal impurities on the carboxyl carbon T_1 values in the unpurified samples. Since the T_1 and NOE values for the purified and unpurified samples at pH 9 and above are in close agreement, the assumption that paramagnetic metal impurities are present as hydroxides in this pH region and hence do not affect relaxation appears to be a good one. It is evident from the tables that paramagnetic metal ions have a maximal effect near pH 4.5, and that some residual contribution to relaxation may still be present at low pH.

The results reported above for acetic acid serve to emphasize the extreme precautions which must be observed if meaningful T_1 values for carboxyl nuclei are desired. However, although absolute values for T_1 may sometimes be suspect, meaningful trends can often still be observed if nuclear Overhauser enhancements are measured.

Experimental Section

NMR Measurements. All carbon-13 spin–lattice relaxation times were measured using the progressive saturation method,[19] with our pulse Fourier transform modified "Brukarian" spectrometer operating at 15.09 MHz. The 90° pulse was 12 μs. The lock signal was obtained from external D_2O in a capillary except when a deuterium-containing solution was being studied. Teflon vortex plugs were used to ensure that the samples were confined within the transmitter coils. The temperature was 30 ± 1°.

Studies of Neat Acids. Acetic acid and its deuterated analogues were all obtained from commercial sources, and were distilled three or more times before use. All tubes, glassware, vortex plugs, etc., were soaked for at least 24 h in alkaline EDTA solution to remove metal ions, and were rinsed thoroughly with doubly distilled water which was stored in a polyethylene bottle. Samples were run either in 10-mm tubes, with deoxygenation using a nitrogen purge, or in sealed bulbs, with degassing using four freeze–thaw cycles. Identical results were obtained from the two methods.

Dilution Studies. The same precautions were taken as are described above for neat acids. In addition, the water and D_2O used for dilution were doubly distilled and then extracted five times with a 0.05% solution of dithizone in carbon tetrachloride. The acetic acid used was either the triply distilled acid mentioned above, or a triply distilled sample about 90% carbon-13 enriched at the carboxyl carbon.

pH Studies. The acetic acid used in these studies was about 90% carbon-13 enriched at the carboxyl carbon, and was triply distilled before use. In addition to the precautions described above, the sodium hydroxide solution used to adjust pH was the "ultrapure" grade supplied by Alfa Inorganics. The pH data for unpurified samples were obtained with 90% carbon-13 enriched sodium acetate. The pH values were measured on a Radiometer pH meter 26 using a glass electrode.

References and Notes

(1) Supported by the National Science Foundation, and by the Public Health Service, Research Grant No. GM-11072, from the Division of General Medical Sciences.
(2) For reviews, see, G. C. Levy, *Acc. Chem. Res.*, **6**, 161–169 (1973); J. R. Lyerla, Jr., and D. M. Grant, *Int. Rev. Sci., Phys. Chem., Ser. 1*, **4**, 155–200 (1972).
(3) (a) A. Ollvson, E. Lippmaa, and J. Past, *Eestl NSV Tead. Akad. Toim. Fuus. Mat.*, **16**, 390–392 (1967); (b) T. Maruyama, M. Imanart, S. Shimizu, and K. Ishibitsu, *Magn. Reson. Relat. Phenom., Proc. Congr. AMPERE, 16th*, 299–302 (1970); (c) T. D. Alger, D. M. Grant, and J. R. Lyerla, Jr., *J. Phys. Chem.*, **75**, 2539–2540 (1971); (d) T. C. Farrar, S. J. Druck, R. R. Shoup, and E. D. Becker, *J. Am. Chem. Soc.*, **94**, 699–703 (1972); (e) J. S. Cohen, R. B. Bradley, and T. R. Clem, *ibid.*, **97**, 908–909 (1975).
(4) H. Pearson, D. Gust, I. M. Armitage, H. Huber, J. D. Roberts, R. E. Stark, R. R. Vold, and R. L. Vold, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 1599–1601 (1975).
(5) C. H. Fung, A. S. Mildvan, A. Allerhand, R. Komoroski; and M. C. Scrutton, *Biochemistry*, **12**, 620–629 (1973).
(6) I. M. Armitage, H. Huber, D. H. Live, H. Pearson, and J. D. Roberts, *J. Magn. Reson.*, **15**, 142–149 (1974).
(7) K. F. Kuhlman, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439–3448 (1970); J. R. Lyerla, Jr., D. M. Grant, and R. K. Harris, *J. Phys. Chem.*, **75**, 585–588 (1971).
(8) P. Waldstein and L. A. Blatz, *J. Phys. Chem.*, **71**, 2271–2276 (1967).
(9) G. E. Maciel and D. D. Traficante, *J. Am. Chem. Soc.*, **88**, 220–223 (1966).
(10) B. N. Bhar and G. Lindström, *J. Chem. Phys.*, **23**, 1958–1959 (1955).
(11) E. von Goldammer and M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **73**, 4–15 (1969).
(12) P. B. Davis and H. C. Jones, *J. Am. Chem. Soc.*, **37**, 1194–1198 (1915); A. E. Dunstan, *J. Chem. Soc.*, **85**, 817–827 (1904), and references cited therein.
(13) See, for example, ref 8; R. Vilcu and E. Lucinescu, *Rev. Roum. Chim.*, **14**, 283–290 (1969), and references cited therein.
(14) E. von Goldammer, H.-O. Lüdemann, and A. Müller, *J. Chem. Phys.*, **60**, 4590–4594 (1974).
(15) I. M. Armitage, H. Huber, H. Pearson, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 2096–2097 (1974).
(16) G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **59**, 5321–5328 (1973).
(17) R. E. Wasylishen and J. S. Cohen, *Nature (London)*, **249**, 847–850 (1974).
(18) R. Kaiser, *J. Chem. Phys.*, **42**, 1838–1839 (1965).
(19) R. Freeman, H. D. W. Hill, and R. Kaptein, *J. Magn. Reson.*, **7**, 82–98 (1972).