

interpretation of the origin of the observed transitions. We have used a carbon SCF 2p atomic wave function which avoids the parameterization introduced by using a Slater orbital with arbitrary exponent. However, in the absence of SCF functions for aromatic molecules, the use of this atomic SCF function introduces an unavoidable approximation, the quantitative effect of which we are unable to assess.

Acknowledgments. We wish to thank Dr. D. T. Longone of the University of Michigan for a gift of MLP. We are indebted to Professor Joshua Jortner for helpful discussions. This research was supported by the Directorate of Chemical Sciences AFOSR and the U. S. Public Health Service. We have also benefited from the use of facilities provided by ARPA for materials research at the University of Chicago.

Nuclear Magnetic Resonance Study of the Rotational Equilibrium in Acryloyl Fluoride

D. F. Koster

Contribution from the Mellon Institute, Pittsburgh, Pennsylvania 15213.
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Abstract: Solvent and temperature effects (+80 to -95°) on the nmr spectrum of acryloyl fluoride have been used to study the rotational equilibrium in this molecule. ΔH for an assumed *s-trans* to *s-cis* equilibrium is calculated to be 800 ± 250 cal/mole. The large uncertainty in ΔH arises mainly from the indeterminable value of ΔS . The data cannot exclude the possibility of a threefold barrier.

The rotation about the carbon-carbon single bond between sp^2 - sp^2 hybridized carbon atoms gives rise to rotational isomers of varying stability. A variety of techniques, such as infrared,¹⁻³ Raman,⁴ microwave,⁵ and ultraviolet^{6,7} spectroscopy have been used to study conformations in butadiene and substituted butadienes, while ultrasonic relaxation techniques⁸ have been applied to the study of acrolein and several substituted acroleins. Nmr techniques, however, which have been extremely valuable in elucidating conformational equilibria in cyclohexane^{9,10} and substituted ethanes,¹¹ have been only recently applied to problems of this type. Anet and Ahmad¹² have investigated benzaldehyde and several *para*-substituted benzaldehydes, and Dahlqvist and Forsén¹³ have reported results for 2-furaldehyde. We wish to report here the results for a similar study on the molecule acryloyl fluoride.

The equilibrium process in acryloyl fluoride is assumed to be between an *s-trans* and an *s-cis* form, although the data do not rule out a skew form in place of the *s-cis* one. The rotational barrier is evidently lower here than it is in the case of benzaldehyde¹² and 2-furaldehyde,¹³ and an averaged spectrum is observed over



the temperature range $+37$ to -95° . Changes in the three-bond HF coupling constant (3J_s), however, can be used to follow the equilibrium. A method similar to that used to study the internal rotation in substituted ethanes^{11,14} allows one to deduce a value for ΔH , although inclusion of a ΔS term in the analysis introduces considerable uncertainty in the calculation of ΔH by this method. The chemical shifts are quite temperature and solvent dependent, an effect which is probably due to intermolecular attraction in the liquid.

Experimental Section

Materials. The sample of acryloyl fluoride was prepared as described by Brügel.¹⁵ The absence of stray nmr peaks and agreement with its reported boiling point (34.5° at 760 mm) was taken as a criterion of its purity.

Sample Preparation. The samples were vacuum degassed and sealed in 5-mm o.d. nmr tubes. Variable temperature studies were made on a sample containing approximately 50% fluorotrichloromethane as a solvent. Room temperature spectra were also analyzed for the pure compound and 5% solutions of the compound in the respective solvents fluorotrichloromethane, carbon disulfide, and acetonitrile. A trace of TMS was added to each sample as an internal reference.

Spectra. The proton spectra taken above -60° were recorded at 60 MHz on a Varian A-60 equipped with the V-6040 variable-temperature accessory. The temperature was calibrated against the methanol peaks separation before and after recording the spectrum. The spectra were sidebanded with a General Radio 1161-A frequency synthesizer, and the average of four separate spectra at each temperature was used in the calculations. A Varian DP-60, equipped with a variable-temperature probe, was used to record the 60-MHz proton spectrum at -95° . Temperature calibration

(1) J. G. Aston, G. J. Szasz, H. W. Woolley, and F. G. Breckwedde, *J. Chem. Phys.*, **14**, 67 (1946).

(2) G. J. Szasz and N. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953).

(3) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1964).

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(5) D. Lide, Jr., *J. Chem. Phys.*, **37**, 2074 (1962).

(6) A. Roedig and R. Kloss, *Ann.*, **612**, 1 (1958).

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(9) F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 145 (1964).

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(11) H. S. Gutowsky, *Pure Appl. Chem.*, 793 (1963).

(12) F. A. L. Anet and M. U. Ahmad, *J. Am. Chem. Soc.*, **86**, 119 (1964).

(13) K. Dahlqvist and S. Forsén, *J. Phys. Chem.*, **69**, 4062 (1965).

(14) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **37**, 1466 (1962).

(15) W. Brügel, *Z. Elektrochem.*, **64**, 1149 (1960).

Table I. Nmr Parameters for $\text{H}_2\text{C}=\text{CH}-\text{CF}=\text{O}^a$
(1,2) (3) (4)

	Temperature, °C								
	+80 ^b	+37	+18	0	-17.5	-30	-45	-58	-95
$W(1)^c$	-370.29	-370.54	-374.76	-375.85	-377.16	-378.53	-379.42	-381.14	...
$W(2)$	-392.98	-393.70	-395.94	-396.68	-397.43	-398.28	-398.85	-399.96	...
$W(3)$	-365.66	-365.50	-368.37	-369.03	-369.66	-370.46	-370.95	-371.92	...
J_{12}	0.64	0.82	0.76	0.63	0.64	0.64	0.63	0.65	0.59
$J_{13}(\text{cis})$	10.61	10.56	10.66	10.68	10.60	10.63	10.54	10.50	10.51
J_{14}	3.08	2.92	2.77	2.81	2.80	2.68	2.62	2.43	2.04
J_{23}	17.37	17.34	17.28	17.32	17.29	17.26	17.20	17.20	17.06
J_{24}	-0.36	-0.37	-0.37	-0.41	-0.38	-0.40	-0.36	-0.36	-0.29
J_{34}	8.10	8.51	8.97	9.35	9.62	10.00	10.24	10.76	11.83

^a Approximately 50% in CFCl_3 . ^b Approximately 50% in hexachloroacetone. ^c Hz downfield from TMS at 60 MHz.

was checked with a copper-constantan thermocouple. The fluorine spectrum was measured only at room temperature and on the same spectrometer operating at 56.4 MHz. All spectra recorded on the DP-60 were taken in the frequency sweep mode. The field-frequency lock was accomplished with a Research Specialties Inc. spin decoupler. The frequency was swept by externally controlling the General Radio 1161-A frequency synthesizer.

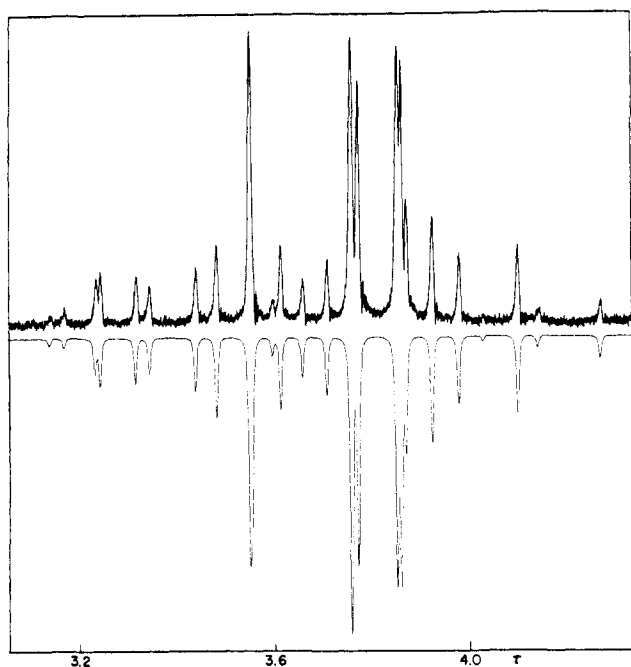


Figure 1. Observed (top) and calculated ambient temperature proton magnetic resonance spectrum of acryloyl fluoride (60 MHz).

Spectral Analysis. The nmr spectrum of acryloyl fluoride is reported by Brügel,¹⁵ but the parameters given there are inconsistent with those reported for most vinylic couplings. A reanalysis of the ABCX spectrum was performed by treating it as a superposition of two ABC spectra. The two ABC spectra were located by the method of Castellano and Waugh¹⁶ and the lines assigned to a trial spectrum calculated by the computer program LAOCOON II.¹⁷ The program was then used to iterate to a least-squares error fit of the observed spectrum. The complete ABCX spectrum was then calculated, and the agreement with the observed spectrum, as shown in Figures 1 and 2, was very good. The appearance of the spectrum is quite sensitive to temperature and solvent changes, and for each such change a recalculation of the spectrum was necessary.

Results and Discussion

The nmr parameters found to fit the observed spectrum best, taken at eight temperatures, are given in

- (16) S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1961).
(17) S. Castellano and A. A. Bothner-By, *ibid.*, **41**, 3863 (1964).

Table I. The chemical shifts, especially $W(1)$, are quite temperature dependent. It is felt that these changes do not represent solely conformational changes but can be attributed also to increased association at lower temperatures. This point will be discussed further in the section on solvent effects.

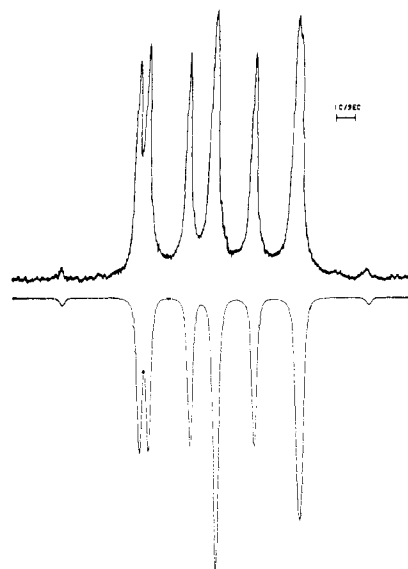


Figure 2. Observed (top) and calculated ambient temperature fluorine magnetic resonance spectrum of acryloyl fluoride (56.4 MHz).

The coupling constants, except for J_{14} and J_{34} , are essentially temperature independent. The small change in the geminal coupling is probably real and becomes more noticeable as the solvent polarity is changed. It has been suggested¹⁸ that the HCCF coupling constant follows an angular dependence similar to that of the HH coupling.¹⁹ This being the case, 3J_s in isomer I should be greater than in II. The increase in 3J_s with decreasing temperature is consistent with a more stable isomer I as expected. The long-range couplings 4J_c and 4J_t ²⁰ (the four bond couplings following *cis* and *trans* paths, respectively, through the double bond) should also be sensitive to conformational changes.^{21,22}

(18) J. C. Schug, P. E. McMahon, and H. S. Gutowsky, *ibid.*, **33**, 843 (1960).

(19) M. Karplus, *ibid.*, **30**, 11 (1959).

(20) The nomenclature is that of J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

(21) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(22) A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3451 (1965).

Although this is noted here in 4J_t , 4J_c is invariant. In a similar study of several 3-fluoro-1,3-butadienes,²³ 4J_t proved to be invariant while 4J_c changed only modestly. It is felt that changes in these long-range couplings should be used with caution in monitoring conformational equilibria.

The change in 4J_t here is in the correct direction if one assumes that this coupling is a maximum when H and F are separated by a zig-zag²⁴ arrangement of the bonds, as in II. The decrease in 4J_t at low temperatures



again argues in favor of I as the lowest energy form. It is interesting that the magnitude of 4J_t lies between that of analogous HF coupling in fluoroprene²⁵ (+1.19 Hz), which is reportedly *s-trans*,⁵ and the *meta*-HF coupling in aromatic compounds²⁶ (+6 to +7 Hz) which corresponds to a *cis* conformation of the double bonds.

Temperature Effects. Although an averaged spectrum is obtained at all temperatures, changes in 3J_s can be used to follow the rotational equilibrium. If it is assumed that only conformational changes are affecting 3J_s , the observed coupling constant, J , can be written

$$J = PJ_t + (1 - P)J_c \quad (1)$$

or on rearranging

$$J = J_c + P(J_t - J_c) \quad (2)$$

where P and $1 - P$ are the populations, and J_t and J_c are the 3J_s couplings in the *s-trans* and *s-cis* conformers, respectively. The equilibrium constant, K , is given by the expression

$$K = (1 - P)/P \quad (3)$$

or

$$P = \frac{1}{1 + K} = \frac{1}{1 + \exp[(\Delta S/R) - (\Delta H/RT)]} \quad (4)$$

At this point it is often assumed¹¹ that entropy changes are small and can be neglected. In acryloyl fluoride one is tempted to make this assumption since the rotation about the single bond corresponds to an interchange of only a fluorine and oxygen atom. Aside from the fact that the vibrational frequencies in the two forms may differ sufficiently, other factors such as differences in molecule-molecule and solvent-molecule attractions in the two forms may give rise to a ΔS term. For this reason a more general treatment in which ΔS is retained is given here.

According to eq 2 a plot of J vs. P will be linear provided the correct values for ΔS and ΔH are chosen. A program was therefore written to calculate values of P at the experimental temperatures T for a series of ΔS and ΔH values. The program entered these values

(23) A. A. Bothner-By and D. F. Koster, to be published.

(24) C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1962).

(25) A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3445 (1965).

(26) H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *ibid.*, **79**, 4596 (1957).

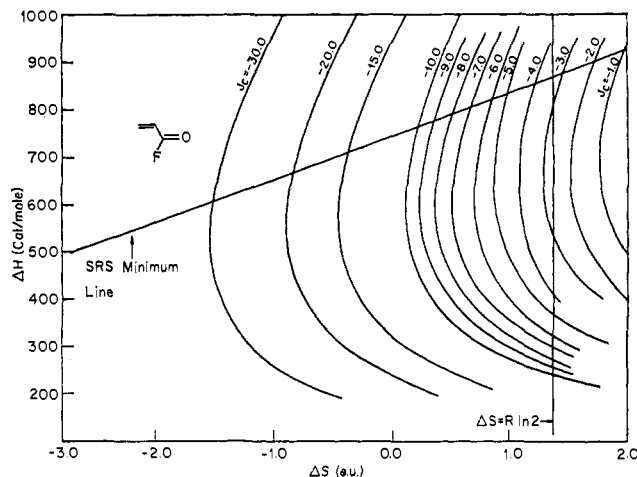
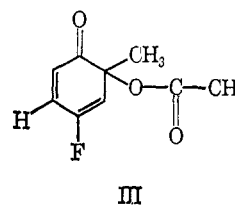


Figure 3. ΔH vs. ΔS for the minimum in the sum of the residual squared (SRS).

of P along with observed coupling constants J into eq 2 and performed the appropriate least-squares fit. The sum of the residuals squared (SRS) from the least-squares fit for each ΔS and ΔH value were arranged in a two-dimensional map so that ΔS and ΔH values lying on the same SRS contour could be linked. Unfortunately, such a treatment does not afford a unique or even narrow range of allowed ΔH and ΔS values, as is shown in Figure 3. The sloping line represents the minimum in the SRS, with each value of ΔS and ΔH along this line satisfying the data equally well. The values of J_c are seen to follow a series of curved contours. Since the large negative values are unrealistic (those less than -10 to -15 Hz) this portion of the curve can be excluded. If a suitable analogous *s-cis* compound was available, the range on J_c could be narrowed to give a more reliable ΔS and ΔH . In the absence of such a molecule a crude assumption can be made. In fluoroprene²⁵ the 3J_s HF coupling is +25.19 Hz, while in the near *s-cis* butadiene (III)²⁷ this coupling falls to +7 Hz, a reduction of 18 Hz. Along the line



representing the minimum in the SRS, J_t (3J_s in isomer I) is 14.5 ± 0.5 Hz. If, as a first approximation, it is assumed that the HF angular dependence in acryloyl fluoride follows about that in the fluorobutadienes, then J_c should be approximately -3.5 Hz. This value of J_c would put ΔH at approximately 850 cal/mole and $\Delta S = 1.3$ eu. The approximations involved here are quite severe, however, and about all that can be deduced is that $\Delta S > 0$ and $\Delta H = 800 \pm 250$ cal/mole. It also appears that J_c will be negative. The results obtained from infrared measurements²⁸ on acryloyl fluoride give a considerably lower value for ΔH (~ 300 cal/mole) and an approximate ΔS of 1.8 eu. The latter

(27) E. Moser and A. A. Bothner-By, to be published.

(28) W. G. Fateley, G. L. Carlson, and R. E. Witkowski, to be published.

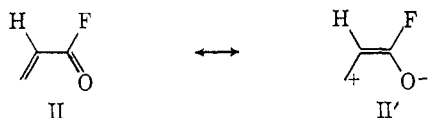
Table II. Solvent Effects on the Nmr Parameters for Acryloyl Fluoride^a

Parameter	Neat	50% in CFCl ₃	5% in CFCl ₃	5% in CS ₂	5% in CH ₃ CN
<i>W</i> (1) ^b	-373.30	-370.58	-365.85	-367.92	-377.11
<i>W</i> (2)	-395.08	-393.72	-392.39	-391.86	-396.84
<i>W</i> (3)	-367.73	-365.46	-363.78	-363.59	-370.78
<i>J</i> ₁₂	0.64	0.89	0.93	0.93	0.63
<i>J</i> ₁₃	10.63	10.55	10.57	10.60	10.60
<i>J</i> ₁₄	3.01	2.96	2.92	2.79	2.95
<i>J</i> ₂₃	17.31	17.29	17.36	17.23	17.24
<i>J</i> ₂₄	-0.35	-0.32	-0.31	-0.33	-0.28
<i>J</i> ₃₄	8.67	8.46	7.95	8.22	9.02

^a The numbering system is identical with that of Table I. ^b Hz from TMS at 60 MHz.

measurements were made in *ca.* 2% CS₂ solution which may account in part for the discrepancy.

The negative value for *J_c* may cause concern since only positive values for vicinal HF couplings are known.²⁹ The carbonyl group has, however, reduced *J_t* with respect to the analogous coupling in fluoroprene.²⁵ A similar reduction is noted in the ³*J_s* coupling in going from butadiene³⁰ to acrolein³¹ (10.41 to 7.40 Hz), and it is therefore reasonable to expect *J_c* to be less than it is in restrained *cis* systems ($\sim +7$ Hz). It is also known that the *cis* HF coupling changes sign (+ \rightarrow -) in going from fluoroethylene to trifluoroethylene.³² If acryloyl fluoride is written in the resonance form II', the negatively charged carbonyl group may be



sufficient to make *J_c* negative.

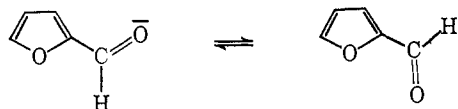
The value of ΔH obtained either by nmr or infrared is lower than those reported for acrolein and substituted acroleins⁸ (1.1-3.0 kcal/mole). A similar low ΔH value is found for several 3-fluoro-1,3-butadienes^{23,28} and in some way must be attributed to the introduction of the fluorine nucleus. One possible explanation may lie in the known resonance ability of fluorine which would tend to stabilize the *s-cis* form.



Up to this point we have assumed that the rotational barrier is a twofold one. If, however, we now assume it is threefold, that is, the less stable form is *skew* rather than *s-cis*, eq 4 becomes

$$P = \frac{1}{1 + 2K} = \frac{1}{1 + 2[\exp(\Delta S/R) - (\Delta H/RT)]} \quad (5)$$

If in (5) $\Delta S = 0$, the expression for *P* will be identical with that in (4) with $\Delta S = R \ln 2$ ($= 1.38$). It is interesting that Dahlqvist and Forsén¹³ report ΔS for the



(29) D. F. Evans, S. L. Manatt, and D. D. Elleman, *J. Am. Chem. Soc.* **85**, 238 (1963).

(30) R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectry.*, **12**, 76 (1964).

(31) A. W. Douglas and J. H. Goldstein, *ibid.*, **16**, 1 (1965).

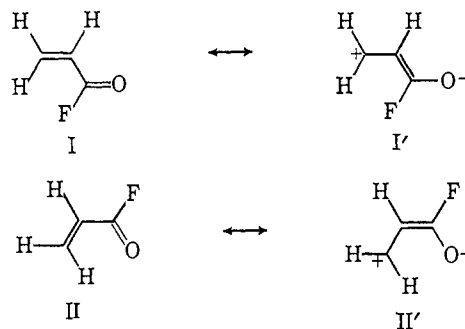
(32) D. F. Evans, *Mol. Phys.*, **5**, 183 (1962).

equilibrium in 2-furaldehyde to be 2 eu, although they do not cite the cause for such a large entropy change. The data could be fitted equally well to a threefold barrier with a smaller ΔS term. This is not to suggest that the barrier is actually a threefold one, but rather that it cannot be definitely excluded. Recently Mönning³³ has reported a microwave and far-infrared study of 2-furaldehyde and at least in the gas phase the molecule exists in two planar forms. The one in which the oxygen atoms are *trans* is the more stable.

A few comments should be made regarding the assumption that only conformational changes are affecting ³*J_s*. Two other factors which might affect ³*J_s* are (1) changes in the population of the torsional levels for torsional vibration about the carbon-carbon single bond and (2) an inherent temperature sensitivity of *J_{HF}*. The first point can be neglected since such an effect was not observed on the analogous HH coupling constant in the *cis,cis*- and *cis,trans*-1,4-dichloro-1,3-butadienes²⁵ when these compounds were reanalyzed³⁴ at -55° . However, an increase of about 0.3 Hz in ³*J_s* in acrolein itself is noted over the temperature range $+37$ to -55° ,³⁴ but again this is probably due to an increase in the *s-trans* population. An inherent temperature dependence of HF couplings has not been previously reported and was not found in the ³*J_c* and ³*J_t* HF couplings in the 3-fluoro-1,3-butadienes.²³

Solvent Effects. The spectrum was reexamined in solvents of varying polarity and concentration to see if the large temperature effects on the chemical shifts could be attributed to molecular association. The results are summarized in Table II.

The solvent effects can be more easily discussed if we consider the resonance forms I' and II' of the two rotational isomers. I', with a larger charge separation,



(33) F. Mönning, Physikalische Institut der Universität Freiburg i, Br., 8th European Congress on Molecular Spectroscopy, Copenhagen, August 1965, Abstract 410.

(34) D. F. Koster, unpublished work.

tion, would have a larger dipole moment than II'. It, therefore, should be associated to a greater extent and be favored in more polar solvents. Except for the anomaly in the 5% CS₂ solution, the chemical shifts tend to lower field as the solvent polarity increases. The greater change in $W(1)$ can be attributed to either a predominance of intermolecular hydrogen bonding to this proton or greater electron withdrawal from this bond by the carbonyl group in I'.

The solvent effects on the coupling constants also follow in that 3J_s should increase with an increase in I'. The decrease in the geminal HH coupling in highly polar solvents can be attributed to the increased electron-withdrawing ability of the carbonyl group in I', which should tend to make J_{gem} more negative.³⁵ Similar solvent effects on geminal coupling constants have been reported by Shapiro, *et al.*,³⁶ in formaldoximes.

(35) A. A. Bothner-By and J. A. Pople, *J. Chem. Phys.*, **42**, 1339 (1965).

It is difficult to evaluate to what extent association plays an important part in the chemical shift variations since they and 3J_s are both solvent and temperature dependent. A plot of any chemical shift *vs.* 3J_s as a function of solvent or temperature is essentially linear although the slope of the plots differ considerably. It is found that solvent changes have greater effect on the chemical shifts (relative to 3J_s) than do temperature changes.

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(36) B. L. Shapiro, S. J. Ebersole, and R. M. Kopehik, *J. Mol. Spectry.*, **11**, 326 (1963).

The Microwave Spectrum, Structure, Dipole Moment, and Quadrupole Coupling Constants of *trans*-Nitrous Acid^{1a}

A. Peter Cox^{1b} and Robert L. Kuczkowski^{1c}

Contribution from the Department of Physical Chemistry, The University, Bristol 8, England, and the National Bureau of Standards, Washington, D. C. Received July 18, 1966

Abstract: Mixtures of NO, NO₂, and H₂O in a wave guide cell have produced pressures of nitrous acid sufficient for the assignment of the *trans* isomer by microwave spectroscopy. Accurate values of the *B* and *C* ground-state rotational constants have been determined for the normal, deuterated, and nitrogen-15 species of *trans*-nitrous acid. The data are consistent with the expected planar configuration and on this basis the following structure has been calculated for *trans*-nitrous acid: N—O(H) = 1.433, N=O = 1.177, and O—H = 0.954 Å; ∠ONO = 110° 39' and ∠NOH = 102° 3'. Quadrupole coupling constants for the nitrogen-14 nucleus in the normal and deuterated species have been determined; the values for *trans* HNO₂ are: $\chi_{aa} = 1.91$, $\chi_{bb} = -5.39$, and $\chi_{cc} = 3.48$ Mc/sec. The components of the dipole moment in the nitrogen-15 molecule have been determined to be $\mu_a = 1.387 \pm 0.01$ and $\mu_b = 1.223 \pm 0.06$ D., and yield a value for the total dipole moment of 1.85 ± 0.06 D., inclined at an angle of $41^\circ 24' \pm 24'$ to the *a* principal axis. The structure of *trans*-nitrous acid is discussed on the basis of these data.

Nitrous acid cannot be obtained in the pure state and as a result rather little has been determined about its accurate molecular structure. Its chemical reactions in aqueous solution are very well known,^{2a} but it is only comparatively recently that the existence of nitrous acid as a gaseous species has been firmly established, mainly on the basis of the infrared^{2b,3a} and ultraviolet⁴ spectra. Detailed vibrational analyses

of the infrared spectrum³ have shown the molecule to occur in comparable amounts of *cis* and *trans* tautomeric forms, with the *trans* form being lower in energy by about 530 cal/mole. The potential barrier restricting internal rotation of the OH group for the *cis* form was found to be about 10.8 kcal/mole.^{3b} In the matrix at 20°K this barrier has been estimated as 9.7 ± 0.7 kcal/mole.⁵

In the gas phase nitrous acid can be studied only in the presence of its dissociation products NO, NO₂, and water vapor, together with N₂O₄, N₂O₃, and nitric acid. The various equilibria concerned have been studied by a number of authors.⁶ The available data indicate that at room temperature and at a pressure of

(1) (a) The results of this research were presented in part at the Ohio State Symposium on Molecular Structure and Spectroscopy, June 1965; (b) The University, Bristol; (c) National Bureau of Standards; NRC-NBS Postdoctoral Research Associate 1964-1966. Present address: Department of Chemistry, University of Michigan, Ann Arbor, Mich.

(2) (a) See, for example, T. A. Turney and G. A. Wright, *Chem. Rev.*, **59**, 497 (1959); (b) E. J. Jones, *J. Am. Chem. Soc.*, **65**, 2274 (1943); L. D'Or and P. Tarte, *J. Chem. Phys.*, **19**, 1064 (1951).

(3) (a) L. H. Jones, R. M. Badger, and G. E. Moore, *ibid.*, **19**, 1599 (1951); (b) G. E. McGraw, D. L. Bernitt, and I. C. Hisatsune, Ohio State Symposium on Molecular Structure and Spectroscopy, June 1965.

(4) P. Tarte, *Bull. Soc. Chim. Belges*, **59**, 365 (1950); L. D'Or and P. Tarte, *Bull. Soc. Roy. Sci. Liege*, **20**, 685 (1951); G. Porter, *J. Chem. Phys.*, **19**, 1278 (1951).

(5) R. T. Hall and G. C. Pimentel, *ibid.*, **38**, 1889 (1963).

(6) L. G. Wayne and D. M. Yost, *ibid.*, **19**, 41 (1951); A. P. Altshuler, *J. Phys. Chem.*, **61**, 251 (1957); P. G. Ashmore and B. J. Tyler, *J. Chem. Soc.*, 1017 (1961); D. M. Waldorf and A. L. Babb, *J. Chem. Phys.*, **39**, 432 (1963); and *Errata, ibid.*, **40**, 1165 (1964).