Table IV. The Diagonal Elements in the Total, χ_{xx}, Paramagnetic, χ_{xx}^{p}, and Diamagnetic, χ_{xx}^{d}, Susceptibility Tensor in the Principal Inertial Axis System in Formic Acid[a]

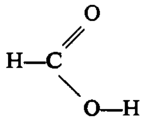
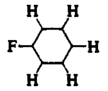
Principal inertial axis	Total	Paramagnetic	Diamagnetic
a	$-(18.8 \pm 0.8)$	28.8 ± 0.1	$-(47.6 \pm 0.8)$
b	$-(16.8 \pm 0.8)$	106.5 ± 0.1	$-(123.3 \pm 0.8)$
c	$-(24.2 \pm 0.8)$	117.2 ± 0.1	$-(141.4 \pm 0.8)$

[a] The units are 10^{-6} erg/(G^2 mole).

The in-plane molecular quadrupole moments in formic acid are the largest values known at this time. The large negative value is along a line which passes approximately through both oxygen atoms. The large positive value is along a line which passes near to both hydrogen atoms. Thus, it is evident that the negative charge builds up at the oxygen extremities, and the positive charge shows up at the hydrogen extremities. This interpretation is consistent with the results on similar molecules.

The average values of a^2, b^2, and c^2 are also interesting to compare with other molecules. As formic acid is planar, the average value of c^2 gives a direct indication of the out-of-plane electron density. The value of $\langle c^2 \rangle = (3.5 \pm 0.3) \times 10^{-16}$ cm^2 is compared in Table V to other molecules.

Table V

Ref	Molecule	Out-of-plane (off-axis) value of $\langle x^2 \rangle$, 10^{-16} cm^2
This work		3.5
a	N—N—O	3.0
a	O—C—O	3.0
5	O—C—S	4.5
b		8.4

[a] R. Shoemaker, W. Hüttner, and W. H. Flygare, *J. Chem. Phys.*, in press. [b] W. Hüttner and W. H. Flygare, *ibid.*, in press.

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The Microwave Spectrum, Structure, and Dipole Moment of *cis*-Thionylimide

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Abstract: The microwave spectrum of thionylimide, HNSO, has been observed and assigned to the planar *cis* form. The structural parameters are $d_{NH} = 1.029 \pm 0.01$ Å, $d_{NS} = 1.512 \pm 0.005$ Å, $d_{SO} = 1.451 \pm 0.005$ Å, $\angle HNS = 115.8 \pm 1°$, and $\angle NSO = 120.4 \pm 0.5°$, where the uncertainties are estimated to account for the effects of zero-point vibrations. The dipole moment and its components along the principal axes in the $HN^{15}SO$ isotopic species are $\mu_a = 0.893 \pm 0.003$ D, $\mu_b = 0.181 \pm 0.005$ D, and $\mu = 0.911 \pm 0.003$ D, where the uncertainties are the standard deviations of the reported values, from the least-squares analysis. Since no attempts were made to make a complete assignment of the impure sample, no comments can be made about the possible existence of *trans*-HNSO.

Thionylimide, HNSO, was first prepared by Schenk[1] by treating NH_3 with $SOCl_2$ and was later investigated by Becke-Goehring, Schwarz, and Spiess[2] who suggested a structure analogous to SO_2 with an NH group replacing one of the oxygen atoms. Most recently, Richert[3] has carried out a study of the infrared spectrum of HNSO, confirming the SO_2-like structure and obtaining valence force constants, bond orders, and estimates of the bond angles.

During the investigation of the microwave spectrum of NSF reported in a previous paper,[4] it was found that the appearance of certain transitions in the microwave spectrum could be correlated with certain peaks in the mass spectrum. The mass spectral cracking pattern suggested that the impurity might be HNSO. Richert and Glemser[5] have reported that HNSO is formed as an intermediate product in the hydrolysis of NSF. Hydrolysis experiments carried out in the mass spectrometer and the microwave absorption cell confirmed this.

Although a previous study of HNSO yielded a tentative structure[4] and showed that the conformation of HNSO

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(1) P. W. Schenk, *Ber.*, **65**, 94 (1942).

(2) M. Becke-Goehring, R. Schwarz, and W. Spiess, *Z. Anorg. Allg. Chem.*, **293**, 294 (1958).

(3) H. Richert, *ibid.*, **309**, 171 (1961).

(4) W. H. Kirchhoff, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1962, pp III-1, 28.

(5) O. Glemser and H. Richert, *Z. Anorg. Allg. Chem.*, **307**, 313 (1961).

was *cis* rather than *trans*, the structure rested on a rather shaky identification of certain weak transitions to the N^{15} species. Also, if the possibility of NSOH as the OH analog of NSF were to be admitted, then the microwave spectrum did not contain enough information to unambiguously choose between the two isomers. In the present study the microwave spectra of all the isotopically substituted species have been studied and a careful measurement of the dipole moment made. The HNSO form has been confirmed.

Sample Preparation

HNSO was prepared both by the gas-phase reaction of $SOCl_2$ with NH_3 and by the hydrolysis of NSF in the microwave absorption cell. The reaction of NH_3 with $SOCl_2$ used NH_3 dried over sodium. Low pressures of the reactants (12 torr of NH_3 and 4 torr of $SOCl_2$) were found to give a greater yield of HNSO and less SO_2. Since HNSO is unstable toward polymerization at temperatures above its melting point, it could not be condensed once it was prepared. It was found that in the gas phase, the sample was usable for a week. During this time the amount of HNSO slowly decreased whereas the amount of SO_2 remained relatively constant. Thus, it appears that SO_2 is formed during the initial reaction only.

DNSO was also prepared both by the reaction of ND_3 with $SOCl_2$ and by the hydrolysis of NSF with D_2O. $HN^{15}SO$ was prepared by the reaction of $N^{15}H_3$ with $SOCl_2$ and $HNSO^{18}$ by the hydrolysis of NSF with H_2O^{18}.

The Microwave Spectrum of HNSO

The microwave spectrum of HNSO was found to consist of strong *a*-type transitions and weak *b*-type transitions. The low J transitions were identified by their Stark effects and the assignments were confirmed by a fit to a rigid-rotor model. The assignments of the spectra of the isotopically substituted species DNSO, $HN^{15}SO$, and $HNSO^{18}$ were made by the Stark effect and by comparison of the spectra of isotopically enriched compounds with the spectrum of the normal isotopic species. Since S^{34} has a natural abundance of approximately 4%, the spectrum of $HNS^{34}O$ should be easily seen. Two possible candidates for the S^{34} species were observed. The ratio of the intensity of the $0_{0,0} \rightarrow 1_{0,1}$ transition for each candidate to the intensity of the $0_{0,0} \rightarrow 1_{0,1}$ transition of the normal isotopic species was measured at Dry Ice temperature and room temperature. The ratios at Dry Ice temperature were 0.051 and 0.041 and at room temperature were 0.05 and 0.17, respectively. The theoretical ratio is 0.0444 and should be the same at both temperatures. The first candidate exhibited the proper temperature dependence to be assigned as the S^{34} species. That the measured intensity ratio does not agree with the ratio obtained from isotopic abundances arises from nonlinearities in the detection system of the microwave spectrometer which make the measurement of the intensity ratio of two transitions with very different intensities somewhat uncertain. The second species exhibited behavior expected for an excited vibrational state of the normal isotopic species (which, because it has a slightly different average structure from the molecule in the ground vibrational state, will exhibit a slightly different microwave spectrum). The relative intensity of the vibrational satellite and the S^{34} species was measured carefully at Dry Ice temperature where both species have roughly the same intensity, and using the relative isotopic abundance of S^{34} of 0.0444, it was found that relative intensity of the vibrational satellite to the ground-state transition was 0.0353. Assuming a Boltzman distribution for the excited vibrational states, this relative intensity would predict the energy of the excited state to be 461 cm^{-1} above the gound state. Richert and Glemser have observed a vibrational transition, ν_5, centered at 453 cm^{-1}.[3] The vibrational satellite was thus assigned to the $v_5 = 1$ vibrational state of the normal isotopic species.

Many of the observed transitions consisted of multiplets which are caused by the coupling of the spin of the nitrogen nucleus to the over-all rotation of the molecular framework by means of the interaction of the quadrupole moment of the nitrogen nucleus with the electron cloud of the molecule. From the magnitude of the separation of the hyperfine components, the diagonal elements of the quadrupole coupling tensor (eQq_a, eQq_b, and eQq_c) were calculated.

In Table I are presented the assigned rotational transitions of all the isotopic species studied as well as those of the vibrational state $v_5 = 1$. All transition frequencies were measured by beating the klystron frequency against a multiple of a 100-kHz standard frequency at NBS which is accurate to one part in 10^8. The major error in frequency measurement arose from placing the line centers. The accuracy of the transition frequencies was estimated to be ± 0.1 MHz. The larger differences between calculated and observed frequencies arose from the effects of centrifugal distortion.

In Table II are given the rotational constants and moments of inertia for the various species. A few comments on the calculation of these parameters follow. In species where quadrupole structure was resolved, the quadrupole coupling constants were first evaluated by fitting the splittings by the method of least squares to the constants eQq_a and eQq_c. The third constant eQq_b was evaluated from the relation $eQq_a + eQq_b + eQq_c = 0$. Because isotopic substitution causes rotation only about the c principal axis, eQq_c should not change. In the case of DNSO where the quadrupole structure was poorly resolved, use was made of this by assuming the value of eQq_c obtained in the normal isotopic species. The observed transitions were then corrected for quadrupole effects. For the S^{34} species, the quadrupole coupling constants of the normal species were used, and it was assumed that the strongest components were being measured. The rotational constants B and C were calculated from the $1_{11} \rightarrow 2_{12}$ and $1_{10} \rightarrow 2_{11}$ transitions for all species except N^{15} for which, in addition, the combination $(2_{02} \rightarrow 2_{11}) - (1_{01} \rightarrow 1_{10}) = 2_{11} - 1_{10}$ was included. This gave a consistent set of B and C for all species and for which it was assumed that centrifugal distortion effects would tend to cancel. For the normal and N^{15} species, the *b*-type transitions were used to calculate the A rotational constant. For the remaining species A was calculated from the difference between the $1_{01} \rightarrow 2_{02}$ transition and the average of the $1_{11} \rightarrow 2_{12}$ and $1_{10} \rightarrow 2_{11}$ transition frequencies. Since this difference

Table I. Assigned Rotational Transitions of *cis*-HNSO

Isotope	Transition		ν, MHz	
	$J_{K_-,K_+} \rightarrow J'_{K'_-,K'_+}$	$F \rightarrow F'$[a]	Obsd[b]	Calcd
$HN^{14}S^{32}O^{16}$	$0_{0,0} \rightarrow 1_{0,1}$	$1 \rightarrow 0$	18075.50	18075.71
		$1 \rightarrow 1$	18074.42	18074.58
		$1 \rightarrow 2$	18074.82	18075.03
	$1_{1,1} \rightarrow 2_{1,2}$	$1 \rightarrow 2$ $2 \rightarrow 2$	34484.95	34484.95
		$2 \rightarrow 3$	34485.45	34485.45
		$0 \rightarrow 1$ $1 \rightarrow 1$	34485.73	34485.72
	$1_{0,1} \rightarrow 2_{0,2}$	$0 \rightarrow 1$ $2 \rightarrow 2$	36097.57	36097.93
		$2 \rightarrow 3$ $1 \rightarrow 2$	36098.03	36098.35
		$1 \rightarrow 1$	36098.77	36099.10
	$1_{1,0} \rightarrow 2_{1,1}$	$2 \rightarrow 3$ $2 \rightarrow 2$	37814.57	37814.56
		$1 \rightarrow 2$ $1 \rightarrow 1$	37814.11	37814.12
		$0 \rightarrow 1$	37815.27	37815.24
	$2_{1,2} \rightarrow 3_{0,3}$	...	16185.66	16185.66
	$3_{1,3} \rightarrow 4_{0,4}$	...	36274.93	36276.43
	$5_{1,4} \rightarrow 4_{2,3}$	...	18310.28	18311.63
	$4_{1,4} \rightarrow 4_{1,3}$	...	16637.53	16638.76
	$6_{1,6} \rightarrow 6_{1,5}$	...	34866.57	34872.43
$DN^{14}S^{32}O^{16}$	$0_{0,0} \rightarrow 1_{0,1}$	$1 \rightarrow 0$	17307.39	17307.42
		$1 \rightarrow 1$	17306.42	17306.44
		$1 \rightarrow 2$	17306.77	17306.84
	$1_{1,1} \rightarrow 2_{1,2}$	$1 \rightarrow 2$ $2 \rightarrow 2$	32838.23	32838.23
		$2 \rightarrow 3$	32838.71	32838.70
	$1_{0,1} \rightarrow 2_{0,2}$	$2 \rightarrow 3$ $1 \rightarrow 2$	34542.97	34543.36
		$1 \rightarrow 1$	34543.63	34544.01
	$1_{1,0} \rightarrow 2_{1,1}$	$2 \rightarrow 3$ $2 \rightarrow 2$	36388.55	36388.58
		$1 \rightarrow 2$ $1 \rightarrow 1$	36388.15	36388.09
		$0 \rightarrow 1$	36389.18	36389.20
$HN^{15}S^{32}O^{16}$	$0_{0,0} \rightarrow 1_{0,1}$	...	17508.98	17509.03
	$1_{1,1} \rightarrow 2_{1,2}$	...	33441.32	34441.32
	$1_{0,1} \rightarrow 2_{0,2}$	...	34971.21	34971.60
	$1_{1,0} \rightarrow 2_{1,1}$	...	36594.75	36594.82
	$1_{0,1} \rightarrow 1_{1,0}$	...	40902.05	40902.05
	$2_{0,2} \rightarrow 2_{1,1}$	...	42525.72	42525.27
	$4_{1,4} \rightarrow 4_{1,3}$	...	15760.51	15761.48
	$6_{1,6} \rightarrow 6_{1,5}$	...	33034.58	33039.98
$HN^{14}S^{34}O^{16}$	$0_{0,0} \rightarrow 1_{0,1}$	$1 \rightarrow 2$	18038.61	18038.71
	$1_{1,1} \rightarrow 2_{1,2}$	$2 \rightarrow 3$	34376.03	34376.02
	$1_{0,1} \rightarrow 2_{0,2}$	$2 \rightarrow 3$	36021.29	36021.66
	$1_{1,0} \rightarrow 2_{1,1}$	$2 \rightarrow 3$	37778.72	27778.70
$HN^{14}S^{32}O^{18}$	$1_{1,1} \rightarrow 2_{1,2}$	$1 \rightarrow 2$ $2 \rightarrow 2$	32700.38	32700.37
		$2 \rightarrow 3$	32700.87	32700.87
		$0 \rightarrow 1$ $1 \rightarrow 1$	32701.11	32701.19
	$1_{0,1} \rightarrow 2_{0,2}$	$0 \rightarrow 1$ $2 \rightarrow 2$	34189.55	34189.95
		$2 \rightarrow 3$ $1 \rightarrow 2$	34190.04	34190.42
		$1 \rightarrow 1$	34190.82	34191.23
	$1_{1,0} \rightarrow 2_{1,1}$	$2 \rightarrow 3$ $2 \rightarrow 2$	35769.61	35769.61
		$1 \rightarrow 2$ $1 \rightarrow 1$	35769.15	35769.15
		$0 \rightarrow 1$	35770.33	35770.33
$HN^{14}S^{32}O^{16}$ $\nu_5 = 1$	$0_{0,0} \rightarrow 1_{0,1}$	...	18061.83	18061.92
	$1_{1,1} \rightarrow 2_{1,2}$	...	34447.66	34447.66
	$1_{0,1} \rightarrow 2_{0,2}$	...	36071.98	36072.37
	$1_{1,0} \rightarrow 2_{1,1}$	...	37800.00	37800.00

[a] In cases where the quadrupole structure is not resolved or, as in the N^{15} species, does not exist, no F quantum numbers are reported. [b] The estimated uncertainties in the measured transitions are ±0.10 MHz.

was quite small, centrifugal distortion was expected to have a significant effect on the calculated value of A. For the normal and N^{15} species, the $1_{01} \rightarrow 2_{02}$ frequency was calculated and the deviation from the observed value was noted. This deviation, 0.39 MHz, was then added to the $1_{01} \rightarrow 2_{02}$ transition of each of the remaining species, and the A rotational constant was calculated from this corrected frequency. It was assumed that an estimated uncertainty of ± 0.2 MHz would account for the residual effects of centrifugal distortion and measurement error. The uncertainties reported for A reflect this uncertainty of ± 0.2 MHz. It should also be pointed out that the value of the inertial defect, $\Delta = I_c - I_b - I_a$, for the $\nu_5 = 1$ species in comparison to the inertial defect for the isotopic species confirms the assignment of this species to an excited vibrational state.

The Structure of HNSO

The value of the inertial defect was found to be consistent with a planar structure for HNSO.[6] Therefore the three moments of inertia were not independent, and the structural calculations could be made with any two of the three moments. Because b-type transitions were weak, they were not observed in several of the isotopic species, and as a result the A rotational constant was poorly determined for these species. Hence I_b and I_c for each of the isotopic species were used in the calculation of the structure.

Since an isotopic substitution was made at each nucleus, Kraitchman's equation[7] should yield the Cartesian coordinates in the principal axis system of the normal isotopic species for each atom and hence the structure of the molecule. However, it is known that the averaging effects of zero-point vibrations differ for two isotopic species and that the distances obtained by Kraitchman's method, the so-called substitution distances, can be seriously in error if an atom lies close to a principal axis.[8,9] Indeed, the B rotational constant for the S^{34} species was greater than that for the S^{32} species, thus indicating an imaginary coordinate for the distance of the sulfur atom from the b axis. The magnitude of this decrease, -0.0012 uÅ^2, is less than the corresponding decrease of -0.0021 uÅ^2 in SO_2[10] where the sulfur atom is directly on the b axis. Such a change in SO_2 would correspond to an apparent shrinkage of the SO bond length of 3×10^{-5} Å.

In order to obtain the structure of HNSO, use must be made of the fact that the Cartesian coordinates must satisfy the center of mass condition. From the condition $\sum_i m_i a_i = 0$, the relative signs of the a coordinates may be obtained even though this condition is not satisfied exactly because of the averaging effects of zero-point vibrations. The conditions $\sum_i m_i b_i = 0$ is imposed to obtain the b coordinate of the sulfur atom. Several values for b_S may be obtained, depending on the choice of relative signs of the remaining coordinates. Only two combinations give structures which are chemically

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(6) D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **40**, 3142 (1964).

(7) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).

(8) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

(9) D. R. Herschbach and V. W. Laurie, *ibid.*, **37**, 1668 (1962).

(10) J. Bellet, Thesis, Laboratoire de Spectroscopie Hertzienne de la Faculté des Sciences de Lille, Masson & Cie, Editeurs, Paris, 1965, p 27.

Table II. Rotational Constants and Moments of Inertia for *cis*-HNSO[a]

	$HN^{14}S^{32}O^{16}$	$DN^{14}S^{32}O^{16}$	$HN^{15}S^{32}O^{16}$	$HN^{14}S^{34}O^{16}$	$HN^{14}S^{32}O^{18}$	$HN^{14}S^{32}O^{16}$ $v_5 = 1$
A, MHz	49316.00 ± 0.1	49299 ± 96	48868.19 ± 0.1	48051 ± 140	48006 ± 176	49966 ± 159
B, MHz	9869.77 ± 0.04	9540.86 ± 0.04	9542.89 ± 0.03	9870.00 ± 0.04	9325.98 ± 0.04	9869.04 ± 0.04
C, MHz	8205.19 ± 0.04	7765.92 ± 0.04	7966.14 ± 0.04	8168.64 ± 0.04	7791.59 ± 0.04	8192.87 ± 0.04
eQq_a, MHz	−1.50 ± 0.07	−1.30 ± 0.09	...	...	−1.62 ± 0.10	...
eQq_b, MHz	−0.07 ± 0.17	−0.27[b]	...	...	+0.08 ± 0.19	...
eQq_c MHz	+1.57 ± 0.14	+1.57 (assumed)	...	...	+1.54 ± 0.16	...
I_a, uÅ^2 [c]	10.24771 ± 0.00002	11.948 ± 0.027	10.34161 ± 0.00002	10.517 ± 0.031	10.527 ± 0.039	10.114 ± 0.032
I_b, uÅ^2	51.20445 ± 0.00021	52.96967 ± 0.00022	52.95837 ± 0.00016	51.20326 ± 0.00021	54.19010 ± 0.00023	51.20821 ± 0.00021
I_c, uÅ^2	61.59222 ± 0.00030	65.07616 ± 0.00034	63.44048 ± 0.00032	61.86781 ± 0.00030	64.86170 ± 0.00033	61.68483 ± 0.00030
$\Delta = I_c - I_a - I_b$, uÅ^2	0.14006 ± 0.00046	0.158 ± 0.027	0.14050 ± 0.00044	0.148 ± 0.031	0.145 ± 0.039	0.363 ± 0.032

[a] The reported uncertainties for all the rotational constants are based on an assumed uncertainty of ±0.1 MHz for each of the measured frequencies with the exception of the A constants for $DN^{14}S^{32}O^{16}$, $HN^{14}S^{34}O^{16}$, $HN^{14}S^{32}O^{18}$, and the vibrational state $v_5 = 1$ which are based on an uncertainty of ±0.2 MHz for the $1_{01} \rightarrow 2_{02}$ transitions from which they were evaluated. The uncertainties in the moment of inertia and the inertial defects are based on the uncertainties in the corresponding rotational constants. [b] Calculated from $eQq_a + eQq_b + eQq_c = 0$. [c] All mass units are based on $m(C^{12}) = 12.00000000$. The conversion factor from MHz to uÅ^2 is 505,376.

feasible. These are the structures with the oxygen and nitrogen atoms on opposite sides of the b axis and the hydrogen atom bonded either to the oxygen atom or nitrogen atom with the sulfur atom placed on the opposite side of the b axis from the hydrogen. These two structures are presented in Table III. Both structures yield bond distances and angles which are plausible and reasonable but the two structures are chemically quite different. Becke-Goehring, Schwarz, and Spiess have claimed the existence of both NSOH and HNSO,[2] but chemical arguments as well as the mass spectral cracking pattern favor the HNSO form. However, the following arguments will show that it is possible to choose between the two forms on the basis of the microwave information alone.

Since the Kraitchman equations in the rigid-rotor approximation yield the Cartesian coordinates of the isotopically substituted atoms in the principal axis system of the normal isotopic molecule, it is thus possible to calculate the sulfur a coordinate from the value of I_b and from the condition that $I_{ab} = \sum_i m_i a_i b_i = 0$. The results of these two calculations are also included in Table III. It should be noted that for both models there is inconsistency in the sulfur coordinate depending on the method of calculation used. The effects of vibrational averaging are responsible for this, and Costain[8] has shown that for the calculation of the coordinate of an atom located near a principal axis, fitting the coordinate to the moment of inertia gives large errors. However, it should be noted that the value calculated from the condition $I_{ab} = 0$ is a totally unreasonable value for the sulfur coordinate in the HOSN model, a value well beyond the effects of vibrational averaging. This evidence is enough to exclude the HOSN model. However, one more calculation may be performed. Using the structure obtained from the center of mass condition for each model, the SO and SN bond distances were allowed to shrink uniformly for the S^{34} isotopic substitution in order to account for the decrease in I_b on substitution. For the HOSN model, a shrinkage of 0.00039 Å was required as opposed to 0.00002 Å for the HNSO model. The corresponding value in SO_2 is, as mentioned earlier in this paper, 0.00003 Å. The necessary shrinkage for the HOSN model is an order of magnitude greater, and hence the HNSO form is again favored.

Table III. Two Possible Structures of HNSO[a]

	b Coordinate, Å		
H	−1.3455 ± 0.0003	S	+0.3783 ± 0.0004
N	−0.3166 ± 0.0010	O	−0.3960 ± 0.0004
	a Coordinate, Å		
N	−1.3352 ± 0.0001	O	+1.2355 ± 0.0001
	cis-HNSO Form		*cis*-NSOH Form
H	−1.3066 ± 0.0001		+1.3066 ± 0.0001
	From center of Mass Condition $\Sigma_i m_i a_i = 0$		
S	+0.0079 ± 0.0001		−0.0745 ± 0.0001
	Calculated from I_b		
S	+0.0571 ± 0.0014		−0.0571 ± 0.0014
	Calculated from $I_{ab} = 0$		
S	−0.0110 ± 0.0017		−0.3041 ± 0.0020

[a] The uncertainties indicated are those due to uncertainties of ±0.1 MHz in the transition frequencies and do not reflect the larger uncertainties arising from centrifugal distortion and vibrational averaging effects.

In Table IV is given the structure of *cis*-HNSO along with the calculated moments of inertia. The error limits reported for the distances and angles are those that are associated with uncertainties of ±0.1 MHz in the transition frequencies and hence reflect the reproducibility of these numbers if the same measurements and calculations were repeated. The interpretation of these parameters depends on the effects of vibrational averaging and values for equilibrium or ground-state average parameters may differ from these by as much as ±0.01 Å for the NH distance, ±0.005 for the SO and SN distances, ±1° for the HNS angle, and ±0.5° for the NSO angle by comparison with more extensive studies on simpler molecules.[11,12]

The Dipole Moment of *cis*-HNSO

The Stark effect of the $M = 0$ component of the $1_{0,1} \rightarrow 2_{0,2}$ transition and the $M = 0$ component of the $1_{1,1} \rightarrow 2_{1,2}$ transition of $HN^{15}SO$ along with the $M = 0$ and 1 components of the $1_{0,1} \rightarrow 2_{0,2}$ transition of the normal isotopic species were quantitatively measured

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(11) V. W. Laurie and D. R. Herschbach, *J. Chem. Phys.*, **37**, 1687 (1962).

(12) L. Pierce, N. Di Cianni, and R. H. Jackson, *ibid.*, **38**, 730 (1963).

Table IV. The Structure of *cis*-HNSO with the Calculated First and Second Moments[a]

$d_{NH} = 1.0293 \pm 0.0009$ Å
$d_{NS} = 1.5123 \pm 0.0005$ Å
$d_{SO} = 1.4513 \pm 0.0004$ Å
$\angle HNS = 115.8 \pm 0.2°$
$\angle NSO = 120.41 \pm 0.06°$
$\Sigma_i m_i a_i = 0$ (assumed)
$\Sigma_i m_i b_i = -0.0302$
$\Sigma_i m_i a_i b_i = -0.0379$
$I_a = 10.3106$ $\quad I_a$ (calcd) $- I_a$ (obsd) $= -0.0629$
$I_b = 51.1026$ $\quad I_b$ (calcd) $- I_b$ (obsd) $= +0.1019$
$I_c = 61.5922$ $\quad I_c$ (calcd) $- I_c$ (obsd) $= +0.1790$

[a] The uncertainties in the molecular parameters are those due to uncertainties of ±0.1 MHz in the transition frequencies. The effects of centrifugal distortion and, more importantly, vibrational averaging make the interpretation of these values as average distances or equilibrium distances uncertain to ±0.01 Å for d_{NH}, ±0.005 Å for d_{SO} and d_{SN}, ±1° for $\angle$HNS, and ±0.5° for $\angle$NSO.

using a precision dc voltage supply in order to evaluate the dipole moment of *cis*-HNSO. Because the transitions of the N^{15} species are free from quadrupole splittings, the value of the dipole moment was determined for this species. Less accurate measurements were made on the transitions of the normal species. The value of dipole moment should not change for the two species, but since the principal axes are rotated slightly on isotopic substitution the values of the components of the dipole moment along the principal axes will change, and it is thus theoretically possible to calculate the relative signs of μ_a and μ_b from this change. It was found that the data did not allow the relative signs of the μ_a and μ_b to be determined beyond question.

The Stark effect in an asymmetric rotor varies as the square of the applied voltage. The next term in the perturbation expansion of the Stark effect varies as the fourth power of voltage, but this quartic term is usually ignored. However, the presence of even a small quartic term can have a striking effect on the value of the quadratic term when this quartic term is ignored in a least-squares fit. Typically, if the average contribution over the voltage range studied of the quartic term is equal to the standard deviation, then the value of the quadratic constant obtained in the least-squares fit of a quadratic function to the observed Stark effect will be in error by more than four times the standard deviation of that constant. Yet inclusion of the quartic constant in the fit will change the over-all standard deviation of the fit by only 3%. In a situation like this, a better value for the quadratic constant is obtained by subtracting the zero-field frequency from each measurement, dividing the resulting shift by the square of the applied voltage, and averaging the ratios. If enough data points are available, fitting the observed Stark effect to a quartic equation gives a still better value. The quartic term can be calculated theoretically, but its evaluation is very tedious even for low J transitions.

In Tables V–VII are given the results of several calcu-

Table V. Stark Effect Parameters in *cis*-$HN^{15}SO$[a]

Type of calculation	Transition	Zero-field intercept, MHz	Quadratic constant × 10^5 MHz/(V/cm)^2	Quartic constant × 10^{16}(MHz)^2/(V/cm)^4
Least-squares fit of $v = v_0 + aE^2$	$1_{0,1} \rightarrow 2_{0,2}$; $M = 0$	34971.15 ± 0.06	−0.1868 ± 0.0004	...
	$1_{1,1} \rightarrow 2_{1,2}$; $M = 0$	33441.37 ± 0.06	+0.1274 ± 0.0003	...
Least-squares fit of $v = v_0 + aE^2 + bE^4$	$1_{0,1} \rightarrow 2_{0,2}$; $M = 0$	34971.23 ± 0.09	−0.1887 ± 0.0016	+6.5 ± 5.2
	$1_{1,1} \rightarrow 2_{1,2}$; $M = 0$	33441.31 ± 0.08	+0.1286 ± 0.0012	−3.5 ± 3.5
Average value of $\Delta v/E^2$	$1_{0,1} \rightarrow 2_{0,2}$; $M = 0$	34971.21 (measd)	−0.1874 ± 0.0003	...
	$1_{1,1} \rightarrow 2_{1,2}$; $M = 0$	33441.32 (measd)	+0.1282 ± 0.0003	...

[a] The uncertainties presented are the standard deviations of the averages or least-squares values.

Table VI. Stark Effect Parameters in *cis*-HNSO (Normal Isotopic Species)[a]

				Quadratic constant calculated from N^{15} species	
Type of calculation	Transition	Zero-field intercept, MHz	Quadratic constant × 10^5MHz/(V/cm)^2	μ_a and μ_b have same sign × 10^5 MHz/(V/cm)^2	μ_a and μ_b have opposite sign × 10^5 MHz/(V/cm)^2
Least-squares fit of $v = v_0 + aE^2$	$1_{01} \rightarrow 2_{02}$; $M = 0$	36098.01 ± 0.14	−0.1858 ± 0.0011	−0.1864 ± 0.0005	−0.1844 ± 0.0005
	$1_{01} \rightarrow 2_{02}$; $M = 1$	36098.19 ± 0.11	+0.1257 ± 0.0006	+0.1264 ± 0.0002	+0.1293 ± 0.0002
Average value of $\Delta v/E^2$	$1_{0,1} \rightarrow 2_{0,2}$; $M = 0$	36098.00 (measd)	−0.1856 ± 0.0005	−0.1869 ± 0.0004	−0.1850 ± 0.0004
	$1_{0,1} \rightarrow 2_{0,2}$; $M = 1$		+0.1276 ± 0.0007	+0.1269 ± 0.0002	+0.1298 ± 0.0002

[a] The uncertainties presented are the standard deviations of the averages or least-squares values.

Table VII. Dipole Moment Values in *cis*-HNSO[a]

	$HN^{15}SO$			$HN^{14}SO$		
Type of calculation	μ_a, D	μ_b, D	μ, D	μ_a, D	μ_b, D	μ, D
Least-squares fit of $v = v_0 + aE^2$	0.8885 ± 0.0008	0.1798 ± 0.0013	0.9065 ± 0.0009	0.8851 ± 0.0017	0.1888 ± 0.0042	0.9050 ± 0.0020
Least-squares fit of $v = v_0 + aE^2 + bE^4$	0.8929 ± 0.0029	0.1810 ± 0.0052	0.9111 ± 0.0033	...	...	...
Average value of $\Delta v/E^2$	0.8904 ± 0.0007	0.1791 ± 0.0013	0.9082 ± 0.0008	0.8886 ± 0.0014	0.1808 ± 0.0031	0.9068 ± 0.0011

[a] The uncertainties reported are the standard deviations of the averages or least-squares values.

lations of the Stark coefficients for the measured transitions. Three calculations were performed: (1) least-squares fit of the observed frequencies to $\nu = \nu_0 + aE^2$; (2) least-squares fit of the observed frequencies to $\nu = \nu_0 + aE^2 + bE^4$; (3) averaging the values of $\Delta\nu/E^2$. In these expressions, ν_0 is the evaluated intercept, a the quadratic constant, b the quartic constant, and $\Delta\nu$ the frequency shift calculated using the measured zero-field absorption frequency. The value of the electric field, E, was calculated from the applied voltage, V, by measuring the Stark effect of OCS using the Marshall and Weber value of the dipole moment of OCS, 0.7124 D.[13,14]

Several items should be noted in studying Tables V–VII. First, the uncertainties reported are the standard deviations of the values obtained from the least-squares fits, or, for calculation 3, from the averaging procedure. The variation in standard deviation for a single parameter arises from the fact that the different calculations involve different numbers of variable parameters. Thus, the quartic fit, involving three parameters, gives the largest standard deviation in the quadratic constant and zero-field intercept. In both $HN^{15}SO$ measurements, the quartic fit gave an intercept in better agreement with the measured value. The shift in the quadratic constant from one type of calculation to another was greater than any of the standard deviations for any of the calculations, although the spreads for the values overlapped. These facts, along with the direction of the shift in the constants all are consistent with the existence of a small quartic term even though that term is poorly determined as shown in Table V. For $HN^{14}SO$ the situation is less clear. Because of quadrupole broadening, the measurements were less accurate. Also, fewer measurements were taken, making the quartic fit almost meaningless. For the $M = 1$ lobe, the value of the zero-field intercept with its associated standard deviation did not overlap the measured zero-field transition. The gap between the quadratic constant evaluated from a least-squares fit of $\nu_0 + aE^2$ and that from the average of $\Delta\nu/E^2$ is equal to three standard deviations. These facts indicate that there may be an important quartic term and that the quadratic constant could be as large as 0.129–0.130 × 10^{-5} MHz/(V/cm)^2. Also given in Table VI are the values of the quadratic constant for $HN^{14}SO$ calculated from the data for $HN^{15}SO$ assuming μ_a and μ_b having the same or opposite signs. Although the evidence favors the situation where μ_a and μ_b have the same signs, if the quadratic constant for the $M = 1$ lobe of the $1_{01} \rightarrow 2_{02}$ transition in $HN^{15}SO$ is indeed as high as 0.129 × 10^{-5} MHz/(V/cm)^2, then the opposite signs would be favored. As to which values to accept, those obtained for the quartic fit for $HN^{15}SO$, *viz.*, $\mu_a = 0.893 \pm 0.03$ D, $\mu_b = 0.181 \pm 0.005$ D, and $\mu = 0.911 \pm 0.03$ D where the uncertainties quoted are the standard deviations from the least-squares fit, should be favored. It should finally be stressed that, because of the limited number of data points, 10 for each $HN^{15}SO$ Stark lobe and 5 and 7 respectively for the $M = 1$ and $M = 0$ lobes of $HN^{14}SO$, the indication of a quartic constant may be purely a statistical fluctuation. Indeed, for a trial calculation using 100 data points with errors generated from a random number table, an appreciable quartic contribution arose from these errors. Thus, if accurate dipole moments are to be obtained, it is advisable to calculate the quartic constant and evaluate the quadratic constant by an iterative method.

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(13) S. A. Marshall and J. Weber, *Phys. Rev.*, **105**, 1502 (1957).

(14) A more recent measurement of the OCS dipole moment has been measured by Dr. John S. Muenter at Harvard University who reported in a private communication a value of 0.71521 ± 0.00020. Thus, the values reported here may have to be multiplied by a factor of 0.71521/0.7124.