Dipole Moment and Force Constants of NSCl from Microwave Spectrum

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Dipole moment of $^{15}N^{32}S^{35}Cl$ has been determined to be $\mu_a=0.564_5\pm0.0085$, $\mu_b=1.74_7\pm0.035$, $\mu_{total}=1.83_6\pm0.036$D by analyzing the Stark effect of the $1_{1,1}\leftarrow0_{0,0}$ transition.

Twenty-eight rotational transitions of $^{14}N^{32}S^{35}Cl$ in the ground state have been analyzed to determine four centrifugal distortion constants: $\tau_{aaaa}=-6.9_9\pm0.30$, $\tau_{bbbb}=-0.011_0\pm0.0013$, $\tau_{aabb}=0.17_6\pm0.014$, and $\tau_{abab}=-0.033_4\pm0.0068$ MHz. These constants are combined with the vibrational frequencies and inertia defects to recalculate force constants: $F_{11}=10.032$ md/Å, $F_{22}=1.44_4$ md/Å, $F_{33}=0.74_9$ mdÅ, and $F_{23}=-0.08_6$ md.

The microwave spectrum of NSCl has recently been reported by Beppu *et al*,[1] who determined the molecular structure and the quadrupole coupling constant of the chlorine nucleus, and also estimated force constants using the inertia defects and vibrational frequencies. However, the dipole moment has not been evaluated because the Stark effect of the rotational spectrum of NSCl is complicated by the nuclear quadrupole coupling. In the present work the Stark effect of the $1_{1,1}\leftarrow0_{0,0}$ transition of $^{15}N^{32}S^{35}Cl$ is analyzed in detail to determine the dipole moment and its components along the a- and b-axes.

The general quadratic force field may be determined combining vibrational frequencies with other physical constants such as the inertia defects.[2] The centrifugal distortion constants have also been proved useful in force field determinations.[3-11] It may be worthwhile to improve the force field estimated in Ref. 1 using the centrifugal distortion constants and to compare derived force constants with those of related molecules such as NSF.[10,11]

Experimental

The sample of NSCl was prepared by a method described in Ref. 1. The spectrometer used was of conventional Hughes-Wilson type with a 120 kHz oscillator as a Stark modulator. The spectrum was observed at room temperature.

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1) T. Beppu, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **36**, 386 (1970).
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9) A. M. Mirri and E. Mazzariol, *Spectrochim. Acta*, **22**, 785 (1965).
10) R. L. Cook and W. H. Kirchhoff, *J. Chem. Phys.*, **47**, 4521 (1967). It is to be noted that this reference uses 0.7124D of the OCS moment as a standard. Since the value given by Ref. 12 is 0.7152_1D, dipole moment of NSF (1.902D) is recalculated to be 1.910D.
11) A. M. Mirri and A. Guarnieri, *Spectrochim. Acta*, **23A**, 2159 (1967).

Dipole Moment

The Stark effect of the $1_{1,1}\leftarrow0_{0,0}$ transition of $^{15}N^{32}S^{35}Cl$ is shown in Fig. 1, where the observed frequencies of Stark components are indicated by open circles. Electric field is calibrated using the OCS molecule as

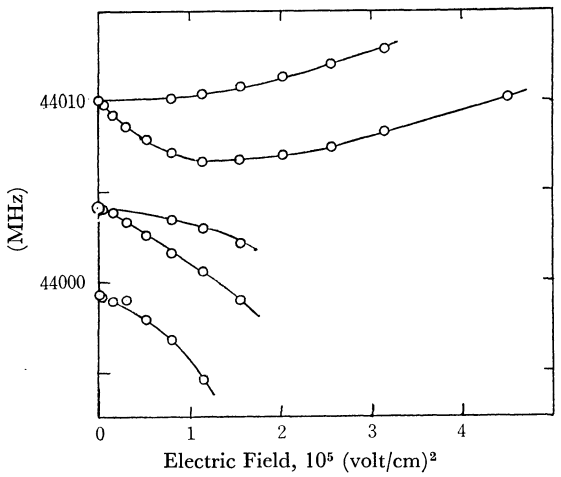

Fig. 1. Stark effect of $1_{1,1}-0_{0,0}$ of $^{15}N^{32}S^{35}Cl$.

a standard.[12] In the limit of the zero field the transition consists of three lines corresponding to $F=3/2\leftarrow3/2$, $5/2\leftarrow3/2$, and $1/2\leftarrow3/2$, whereas two Stark lobes, $M_I=\pm3/2$ and $\pm1/2$, are observed at strong field. In the intermediate region there are five Stark lobes, of which three are $M_F=\pm1/2$ and two $M_F=\pm3/2$. Analysis is carried out according to a procedure described previously,[13] where the rotational constants are fixed to the values reported in Ref. 1: $A=40\ 355.96$, $B=4\ 019.65$, and $C=3\ 649.36$ MHz. A least-squares analysis gives the a and b components of dipole moment and the bb component of the quadrupole coupling constant of the chlorine nucleus as follows: $\mu_a=0.564_5\pm0.0085$D, $\mu_b=1.74_7\pm0.035$D, and $\chi_{bb}=23.8_4\pm0.50$ MHz, where errors are 2.5 times the standard deviations. The frequencies of the Stark lobes calculated using these parameters are drawn by solid lines in Fig. 1 and compared with the observed in Table 1. The χ_{bb} constant may be compared favorably with the value already reported,[1] 23.51 MHz. The total dipole moment is $\mu_{total}=1.83_6\pm0.036$D.

12) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).
13) E. Hirota and Y. Morino, This Bulletin, **34**, 341 (1961).

TABLE 1. STARK EFFECT OF THE $1_{1,1}\leftarrow 0_{0,0}$ TRANSITION OF $^{15}N^{32}S^{35}Cl$ (MHz)

square of field[a]	obsd	obsd −calcd	obsd	obsd −calcd[b]	obsd	obsd −calcd[b]
$M_F=\pm 1/2$						
0.0	44 010.10	+0.01	44 004.15	+0.02	43 999.36	+0.00
4.70	44 009.77	−0.13			43 999.17	−0.07
14.10	44 009.30	−0.22			43 998.90	−0.08
29.77	44 008.68	−0.22			43 999.00	+0.51
51.70	44 007.90	−0.20			43 997.91	+0.18
79.90	44 007.23	−0.01	44 003.46	−0.24	43 996.75	+0.08
114.37	44 006.73	+0.10	44 003.00	−0.14	43 994.60	−0.68
155.10	44 006.82	+0.28	44 002.20	+0.31		
202.10	44 007.05	+0.16				
255.37	44 007.50	+0.01				
314.90	44 008.29	+0.02				
452.77	44 010.23	+0.00				
$M_F=\pm 3/2$						
0.0	44 010.10	+0.01	44 004.15	+0.02		
4.70			44 004.05	+0.02		
14.10			44 003.83	+0.02		
29.77			44 003.28	−0.11		
51.77			44 002.63	−0.08		
79.90	44 010.19	+0.07	44 001.65	−0.08		
114.37	44 010.40	−0.01	44 000.60	+0.18		
155.10	44 010.82	−0.02	43 999.00	+0.22		
202.10	44 011.34	−0.08				
255.37	44 012.10	−0.03				
314.90	44 012.90	−0.06				

a) In 10^3 (volt/cm)^2.
b) Calculated frequencies are obtained using $\mu_a=0.564_5$D, $\mu_b=1.74_7$D, and $\chi_{bb}=23.8_4$ MHz.

TABLE 2. ROTATIONAL SPECTRUM OF NSCl IN THE GROUND STATE (MHz)

Transition	obsd line center	calcd	distortion correction	obsd −calcd
$1_{1,0}$ — $1_{0,1}$	37 983.1[a]	37 983.05	−1.69	0.05
$2_{1,1}$ — $2_{0,2}$	38 361.72[a]	38 361.61	−1.47	0.11
$3_{1,2}$ — $3_{0,3}$	38 934.40[a]	38 934.68	−1.17	−0.28
$4_{1,3}$ — $4_{0,4}$	39 708.73[a]	39 708.48	−0.80	0.25
$5_{1,4}$ — $5_{0,5}$	40 690.41[a]	40 691.29	−0.41	−0.88
$6_{1,5}$ — $6_{0,6}$	41 893.52[a]	41 893.33	−0.04	0.19
$7_{1,6}$ — $7_{0,7}$	43 327.0[a]	43 326.68	0.24	0.32
$8_{1,7}$ — $8_{0,8}$	45 005.0[a]	45 005.14	0.35	−0.14
$1_{1,1}$ — $0_{0,0}$	45 460.22[a]	45 460.24	−1.70	−0.02
$2_{1,2}$ — $1_{0,1}$	52 937.9[a]	52 937.61	−1.55	0.29
$3_{1,3}$ — $2_{0,2}$	60 228.4[a]	60 228.29	−1.36	0.11
$1_{1,1}$ — $2_{0,2}$	21 904.86	21 904.83	−1.63	0.03
$2_{1,2}$ — $3_{0,3}$	13 687.89	13 688.09	−1.26	−0.20
$6_{0,6}$ — $5_{1,5}$	11 958.30	11 958.17	−1.78	0.13
$7_{0,7}$ — $6_{1,6}$	20 801.36	20 801.51	−3.67	−0.15
$8_{0,8}$ — $7_{1,7}$	29 768.26	29 768.40	−6.10	−0.14
$9_{2,8}$ —$10_{1,9}$	24 744.92	24 745.48	−1.62	−0.56
$10_{2,9}$ —$11_{1,10}$	14 923.31	14 922.54	5.86	0.77
$14_{1,13}$—$13_{2,12}$	15 490.03	15 489.52	−36.69	0.51
$15_{1,14}$—$14_{2,13}$	25 920.70	25 920.94	−50.13	−0.24
$12_{2,10}$—$13_{1,13}$	30 601.97	31 601.92	0.31	0.05
$13_{2,11}$—$14_{1,14}$	27 486.13	27 486.10	3.00	0.03
$14_{2,12}$—$15_{1,15}$	23 807.70	23 807.66	4.92	0.04
$15_{2,13}$—$16_{1,16}$	20 594.13	20 594.33	5.72	−0.20
$16_{2,14}$—$17_{1,17}$	17 872.57	17 872.24	5.05	0.33
$17_{2,15}$—$18_{1,18}$	15 665.16	15 665.32	2.50	−0.16
$18_{2,16}$—$19_{1,19}$	13 994.59	13 994.64	−2.34	−0.05
$19_{2,17}$—$20_{1,20}$	12 877.96	12 877.95	−9.92	0.01

a) Ref. 1.

Centrifugal Distortion Constants and Force Constants

The line centers of all transitions assigned to the parent species, $^{14}N^{32}S^{35}Cl$, in the ground state are listed in Table 2. The hyperfine structures, where resolved, are corrected for using the quadrupole coupling constants previously reported.[1]

The first-order perturbation theory is applied to determine three rotational constants and four distortion constants. Higher-J transitions may include larger contributions of the distortion effects, but simultaneously the higher-order terms such as the P^6 terms should be taken into consideration to determine the P^4 terms precisely.[6] In the present analysis the transitions of J up to 20 are included. The values of parameters obtained by a least-squares analysis[14] are listed in Table 3, where the errors are 2.5 times the standard deviations. The line frequencies calculated using these

TABLE 3. ROTATIONAL CONSTANTS AND CENTRIFUGAL DISTORTION CONSTANTS OF $^{14}N^{32}S^{35}Cl$ IN THE GROUND STATE (MHz)[a]

A	41 723.3_4 ±0.16	τ_{aaaa}	−6.9_9 ±0.30
B	4 114.15_4±0.026	τ_{bbbb}	−0.011_0±0.0013
C	3 738.60_5±0.021	τ_{aabb}	0.17_6 ±0.014
		τ_{abab}	−0.033_4±0.0068

a) Errors are 2.5 times the standard deviations.

14) E. Hirota, T. Tanaka, A. Sakakibara, Y. Ohashi, and Y. Morino, *J. Mol. Spectrosc.* **34**, 222 (1970).

parameters are compared with the observed in Table 2. The average deviation is 0.18 MHz.

In Ref. 1 the four force constants, three diagonal and one off-diagonal, are determined using two vibrational frequencies, ω_1 and ω_2, and two vibrational increments of the inertia defects, Δ_2 and Δ_3. It may thus be interesting to see whether four distortion constants obtained in the present work are useful in determining two remaining force constants, F_{12} and F_{13}. This is unfortunately not the case.

A least-squares analysis is carried out using ω_1, ω_2, Δ_2, Δ_3, τ_{aaaa}, τ_{bbbb}, τ_{aabb}, and τ_{abab} as input data with the following weights: 1.0 for ω_1, 2.0 for ω_2, 1000.0 for Δ_2 and Δ_3, 0.5 for τ_{aaaa}, 130.0 for τ_{bbbb}, 10.0 for τ_{aabb}, and 25.0 for τ_{abab}. The units used here are cm^{-1} for ω, amu Å^2 for Δ, and MHz for τ. The inertia defect should be accurate to about 0.005 amu Å^2, and the weights for the distortion constants might therefore be too small. Calculation with weights of distortion constants increased by a factor of ten gives, however, force constants which agree with the former results within 2.5 times the standard deviations. When F_{12} or F_{13} or both are included as parameters, a least-squares analysis is not convergent. However, a negative F_{12} (about -0.5 md/Å) and a positive F_{13} (about 0.3 md) give much closer fitting to the observed constants, provided that the four force constants are adjusted accordingly. The result shown in Table 4 is obtained assuming both F_{12} and F_{13} equal to zero. Agreement between the observed and the calculated constants is satisfactory except for τ_{bbbb} and τ_{abab}, for which the discrepancies exceed the error limits (see Table 4). A larger discrepancy remains for ω_3, although the "observed" value is estimated, but not measured directly.[15] It is difficult to increase the calculated ω_3 to 273 cm^{-1}, because of the conditions imposed by the inertia defect.

Table 4. Force constants of NSCl

Force constant	Present[a]	Ref. 1
F_{11}(md/Å)	10.032 ± 0.003	10.03_1
F_{22}(md/Å)	$1.44_4\pm0.013$	1.46_5
F_{33}(mdÅ)	$0.74_9\pm0.036$	0.76_7
F_{23}(md)	$-0.08_6\pm0.022$	-0.067
Constant	**obsd**	**calcd**
$\omega_1(cm^{-1})$	1325	1325
$\omega_2(cm^{-1})$	414	414
$\omega_3(cm^{-1})$	(273)[b]	253.6
Δ_1(amuÅ^2)	(-0.006_8)[c]	-0.0063
Δ_2(amuÅ^2)	0.120_4	0.1240
Δ_3(amuÅ^2)	0.359_9	0.3627
τ_{aaaa}(MHz)	-6.9_9	-6.9_1
τ_{bbbb}(MHz)	-0.011_0	-0.0154
τ_{aabb}(MHz)	0.17_6	0.179
τ_{abab}(MHz)	-0.033_4	-0.0482

a) Errors are 2.5 times the standard deviations.
b) Estimated (Ref. 15). c) Calculated, see Ref. 1.

Discussion

The total dipole moment of NSCl is $1.83_6\pm0.036$D, which is very close to that of NSF, 1.910D.[10]

After the completion of the present work Guarnieri sent us his results on dipole-moment determination.[16] He analyzed the Stark effect of three transitions, $2_{1,1}\leftarrow 2_{0,2}$ ($F=7/2\leftarrow7/2$), $3_{1,2}\leftarrow3_{0,3}$ ($F=9/2\leftarrow9/2$), and $1_{1,1}\leftarrow 0_{0,0}$, of the parent species. For the former two transitions he measures the Stark effect of the component of the largest F value (7/2 and 9/2, respectively) which is independent of the quadrupole effect, and for the last transition only the Stark effect in the strong field is used in the analysis. Dipole moment he obtains is $\mu_a=0.57\pm0.03$D, $\mu_b=1.77\pm0.02$D, and $\mu_{total}=1.87\pm0.02$D. To compare the present results with these values it is necessary to transform the principal axes of the ^{15}N species to those of the parent species, and the angle of transformation is calculated to be $31.4_4'$ using the structural parameters of Ref. 1. When μ_a and μ_b are of the same sign, the a- and b-components of the parent species are calculated to be $\mu_a=0.580_5\pm0.01$ and $\mu_b=1.74_2\pm0.04$D, whereas they are $\mu_a=0.548_5\pm0.01$ and $\mu_b=1.75_2\pm0.04$D in the case of opposite sign (see Ref. 1 for the signs of the coordinate axes). It is seen that both cases are in agreement with Guarnieri's results within experimental errors. On the other hand, the latter case ($\mu_a\mu_b<0$) is shown to be more realistic from consideration of bond moment. As shown in Table 5, the total moment of the ^{15}N species makes an angle of 57°2′ with S–Cl and 60°40′ with S–N, when μ_a and μ_b are of the same sign, whereas the two angles are 92°50′ and 24°52′ for the case of opposite sign. The total moment of 1.83_6D is then accounted for by μ(S–Cl) of 1.80_8D and μ(S–N) of 1.74_0D for the former case and μ(S–Cl) of 0.87_2D and μ(S–N) of 2.07_1D for the latter. A similar analysis is carried out for NSF, and the result is also given in Table 5. Because the

Table 5. Bond moments of NSCl and NSF

	NSCl	NSF
I. $\mu_a\mu_b>0$		
θ_1	57°2′	58°18′
θ_2	60°40′	58°37′
μ(S–X)	1.80_8D	1.82_8D
μ(S–N)	1.74_0D	1.82_2D
II. $\mu_a\mu_b<0$		
θ_1	92°50′	72°56′
θ_2	24°52′	43°59′
μ(S–X)	0.87_2D	1.48_7D
μ(S–N)	2.07_1D	2.04_7D

θ_1: angle between μ and S–X.
θ_2: angle between μ and S–X.

bond moment of S–Cl is normally of the order of 0.7D,[17] the second case is more reasonable for NSCl, although a larger moment is expected for S–Cl because of larger fraction (57%) of a resonance form $N{=}S^+Cl^-$, as discussed in Ref. 1. As for NSF, the difference between the bond moments for the two cases is smaller, because the total moment is nearly parallel to the b-axis. Yet the second case is a bit more reasonable: although the bond moment of S–F is not known, the

15) A. Müller, G. Nagarajan, O. Glemser, S. F. Cyvin, and J. Wegener, *Spectrochim. Acta*, **23A**, 2683 (1967).
16) A. Guarnieri, personal communication; to be published.
17) C. P. Smyth, "Dielectic Behavior and Structure," McGraw-Hill, New York, N. Y. (1955).

electronegativity difference for F and S is 1.5, whereas it is 0.5 for Cl and S. Therefore, the S–F moment of 1.48_7D of NSF in the second case seems to be more reasonable. It may be interesting to note that the value of S–N, 2.04_7D for NSF and 2.07_1D for NSCl, is very close to dipole moment of the NS radical, 1.81D.[18]

It is rather disappointing that it has not been possible to determine all three off-diagonal force constants, even if the inertia defects and centrifugal distortion constants are used in addition to vibrational frequencies. The situation is similar to the case of NSF investigated by Cook and Kirchhoff,[10] although they did not take into account the inertia defects in the excited vibrational states. The F_{11} constant of NSF (10.703 md/Å) is nearly the same as that of NSCl (10.032 md/Å), just as the bond length N–S, 1.448 Å for NSF and 1.450 Å for NSCl. The force constants associated with the halogen atom decrease their values from the case of fluoride to the chloride. It may be interesting to note that F_{23} becomes negative for the chloride. In order to improve the force constants of NSCl it is indispensable to observe the ν_3 band in the infrared spectrum.

The calculation in the present work was carried out at the Computation Center at Kyushu University.

18) T. Amano, S. Saito, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **32**, 97 (1969).