The Rotational Spectrum of Monothioformic Acid. I. *cis*- and *trans*-HC(:O)SH [1, 2]

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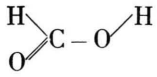
(Z. Naturforsch. **31 a**, 422–337 [1976]; received March 11, 1976)

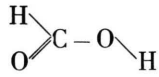
The rotational spectra of the two abundant isomers of monothioformic acid, *cis*- and *trans*-HC(:O)SH, have been assigned in the frequency region 8–250 GHz. Over 90 *a*-type transitions and over 60 *b*-type transitions have been measured for each rotamer. The *a*-type transitions belong to the ^qR_K, $^qQ_1$, $^qQ_2$, $^qQ_3$ and $^qQ_4$ branches and the *b*-type absorption lines encompass the $K_a = 1-0$, 2–1, 3–2, 4–3 and 5–4 rotational sub-bands. The rotational constants and all quartic and sextic centrifugal distortion constants have been determined for each rotamer using Watson's reduced Hamiltonian. In addition to the measured line positions the frequencies of some selected low-J transitions, not observed in this work but of potential astrophysical interest, have been listed as an aid in the interstellar search for monothioformic acid.

I. Introduction

Rotational isomerism has been the subject of numerous spectroscopic investigations in recent years [1]. Although this phenomenon is common for larger molecules it is quite rare for small molecules. The simplest molecule in which it can occur is one having four atoms arranged in a nonlinear chain. Nitrous acid, HONO, is an example of such a molecule for which the existence of two rotamers has been experimentally demonstrated in the gas phase [2]. Among the five-atomic molecules which could exhibit rotational isomerism, formic acid, HCOOH, is of particular interest. Various *ab initio* and semi-empirical calculations [3] indicate that there should be minima in the torsional potential at both the *cis* and *trans* planar configurations:



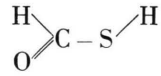
cis-HC(:O)OH



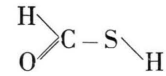
trans-HC(:O)OH

Although numerous experimental studies have been carried out, the question as to whether the *cis* rotamer exists in the gas phase in addition to the abundant *trans* rotamer has not yet been completely settled. The detection of *cis* formic acid was claimed in a recent infrared study of the reaction products from the gas phase ozonolysis of 1,2-dichloroethylene [4]. However, only *trans* formic acid has been detected by microwave spectroscopy despite the fact that Lide [5] has carefully searched for the *cis* rotamer. In the light of this controversy it seemed of interest to investigate the rotational spectrum of the closely related molecule monothioformic acid, HCOSH.

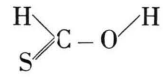
In analogy with formic acid monothioformic acid could exist in one or more of four different planar forms, namely:



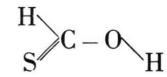
cis-HC(:O)SH



trans-HC(:O)SH



cis-HC(:S)OH



trans-HC(:S)OH

An early investigation of the infrared and proton nuclear magnetic resonance spectra of the liquid suggested that the thiol form, HC(:O)SH, was the more abundant, but gave no indication as to whether one or two rotamers were present [6]. In a preliminary communication we reported the identification of both the *cis* and *trans* rotamers of HC(:O)SH through observation of their rotational spectra [7]. The present paper is the first in a series of papers in which a complete account of our work on monothioformic acid will be given. It contains the analysis of the microwave and millimeter wave spectra of the parent isotopic species of the *cis* and *trans* thiol rotamers in their ground vibrational states.

[1] This work was supported in part by funds from the Deutsche Forschungsgemeinschaft.

[2] Presented in part at the "Fourth Colloquium on High Resolution Molecular Spectroscopy", Tours, France, September 15–19 (1975), as Paper C 6.

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In the following paper the rotational spectra of three isotopically substituted species, DC(:O)SH, HC(:O)SD, HC(:O)^{34}SH, together with the molecular structure of each rotamer are presented. Subsequent papers will deal with the measurement of molecular electric dipole moments, determination of the energy difference between the ground vibrational states of the two rotamers and the investigation of the rotational spectra of H^{13}C(:O)SH and HC(:^{18}O)SH. In addition, a detailed study of the infrared spectrum of monothioformic acid is currently in progress.

Recently formic acid has been detected in emission from the molecular cloud in the direction of the galactic center radio source Sagittarius B2 (Sgr B2) by Winnewisser and Churchwell [8] through observation of the $2_{11} - 2_{12}$ transition. This discovery, together with the previous observation of several sulfur-containing molecules, notably CS, SO, H_2S, OCS, H_2CS [9] and SO_2 [10], in the same interstellar cloud, makes a thorough search for monothioformic acid seem warranted. A search for the $2_{11} - 2_{12}$ transition of *cis*- and *trans*-HC(:O)SH in various galactic sources has been conducted. To aid in future interstellar searches, this paper contains not only a complete listing of all measured HC(:O)SH transition frequencies but also predictions of some additional low-J transitions not observed in the present work but of potential astrophysical interest.

II. Experimental Procedures

The monothioformic acid samples employed in the present investigation were prepared using a somewhat modified version of the procedure described by Engler and Gattow [6]. The preparation involves three basic steps which are summarized in the following reaction scheme:

$$\mathrm{HCOOH} + \mathrm{C_6H_5OH} + \mathrm{CH_3C(:O)OC(:O)CH_3} \xrightarrow{\mathrm{NaHCOO}} \mathrm{HC(:O)OC_6H_5} + 2\,\mathrm{CH_3COOH} \quad (1)$$

$$\mathrm{HC(:O)OC_6H_5} + \mathrm{NaSH} \longrightarrow \mathrm{NaHCOS} + \mathrm{C_6H_5OH} \quad (2)$$

$$\mathrm{NaHCOS} + \mathrm{H_3PO_4(aq)} \longrightarrow \mathrm{HCOSH}\uparrow + \mathrm{NaH_2PO_4(aq)} \quad (3)$$

In the first step, phenol was reacted with an equimolar mixture of formic acid and acetic anhydride in the presence of a small amount of sodium formate catalyst to produce phenylformate [11]. The reaction was allowed to proceed at room temperature, with stirring, for about 48 hours. The phenyl formate was then separated from the reaction mixture by fractional distillation under vacuum. In the second step, the purified phenyl formate was added dropwise, with stirring, to an equimolar amount of sodium hydrogen sulfide suspended/dissolved in ethanol. After completion of this reaction (1 – 2 hours), the ethanol and phenol were distilled off under vacuum over a period of about 12 hours. In the final step, an excess of a 50% aqueous solution of orthophosphoric acid was added dropwise to the solid sodium monothioformate to liberate the monothioformic acid. The reaction flask was cooled to – 5 °C throughout and the evolved gases were trapped at – 95 °C under vacuum. Crude product was collected for at least five hours and then purified by fractional distillation. The overall yield of purified monothioformic acid was typically about 40%. The purity of the fractionally distilled samples, as monitored on the microwave and infrared spectrometers, was estimated to be better than 95%.

Gaseous samples for the spectroscopic studies were taken from the vapor above the liquid at – 63 °C. No decomposition or polymerization of the liquid was observed even after prolonged periods at this temperature. All frequency measurements were made at room temperature with sample pressures of less than 10 millitorr. The gaseous samples were stable in the glass free space cell but decayed slowly (with a half-life of several hours) in the gold plated X-band Stark cell.

Microwave measurements were made in the frequency region 8 – 36 GHz using a Hewlett Packard model 8460 A MRR spectrometer. Three different backward wave oscillators (BWO) were used to generate microwave power in the X, P and K bands (8 – 26.5 GHz). The 26 – 36 GHz region was covered by doubling the frequency of the P-band BWO radiation. This was accomplished by applying P band power to a parametric varactor diode in a crossed wave guide mount, details of which will be discussed elsewhere [12]. Sufficient power for spectroscopic purposes was obtainable over the whole of the 26 – 36 GHz range. All measurements were carried out in a two meter X-band Stark cell employing square wave modulation of the electric field at 33.333 kHz. The absorption signals were observed after phase sensitive lock-in amplification of the detector output.

In the frequency region from 70 to 250 GHz a millimeter wave video detection spectrometer was employed. The millimeter wave radiation was gen-

erated by harmonic multiplication of the fundamental frequencies produced by different OKI microwave (28 – 42 GHz) reflex klystrons belonging to the V12 series. A dedicated PDP 8/I computer was employed for data acquisition and reduction in order to obtain high sensitivity and accurate frequency measurements. The spectrometer and its mode of operation have been described in detail previously [13, 14].

All frequency measurements, both microwave and millimeter wave, were found to be reproducible to within ± 30 kHz.

III. Rotational Spectra and Assignment

The rotational spectrum of monothioformic acid is rich over the entire microwave and millimeter wave region. This is due to the presence of two rotational isomers, both of which have fairly small rotational constants, and both of which exhibit strong *a*- and *b*-type spectra. No *c*-type transitions were observed for either rotamer. In addition to the ground state rotational spectra, transitions between rotational levels in the excited vibrational states $v_7 = 1$ and $v_9 = 1$ were also observed. Although some of these vibrational satellite lines have been measured they will not be discussed here. The microwave spectrum in the frequency region 8 – 12.4 GHz is shown in Figure 1. The most important features of this spectrum are the two $1_{01} - 0_{00}$ transitions near 11.7 GHz. All of the strong absorption lines which fall in this region have been assigned to the ground state of either the *cis* or the *trans* rotamer of HC(:O)SH. Some of these assignments are indicated in Figure 1. Despite the density of transitions, the assignment process was relatively straightforward because the important low-J transitions are all reasonably strong and hence were easily located.

1) The a-type Spectrum

The two rotational isomers of HC(:O)SH were both found to be near prolate asymmetric top molecules, with $\varkappa = -0.980834$ for the *cis* rotamer and $\varkappa = -0.980319$ for the *trans* rotamer. Their *a*-type spectra are thus typical of such slightly asymmetric rotors. An overview of the *a*-type spectrum of HC(:O)SH is given in Fig. 2 in the form of Fortrat diagrams for the two rotamers.

Strong R-branch transitions were found at intervals of roughly $(B+C)$ throughout the centimeter and millimeter wave regions. The assignment of the low-J lines of this branch was confirmed by making use of the Stark effect. A recorder trace showing the $J = 2 \leftarrow 1$ *a*-type R-branch transitions is presented in Figure 3. The $K_a = 0$ components fall near the center of this figure while the $K_a = 1$ components, split by the inertial asymmetry of the molecule, lie near both edges.

The higher-J *a*-type R-branch transitions, which fall in the millimeter wave region, were also easily located and assigned. For each $J+1 \leftarrow J$ transition the K_a components form two sub-band heads. The pattern is essentially the same for each of the two rotamers. The first band head occurs at $K_a = 2$ and

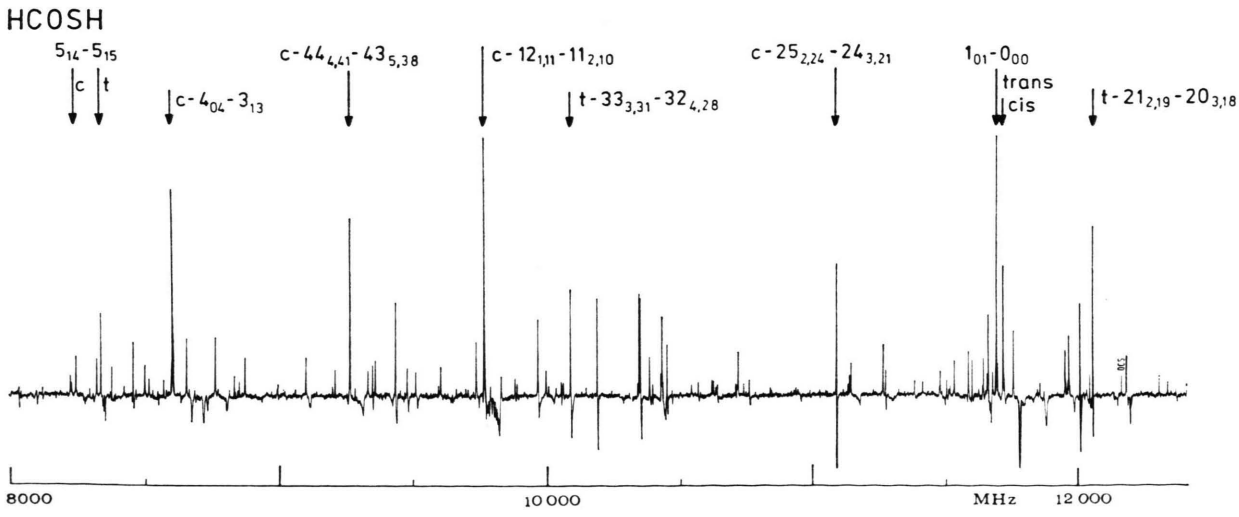

Fig. 1. Survey scan of the absorption spectrum of monothioformic acid from 8 to 12.4 GHz.

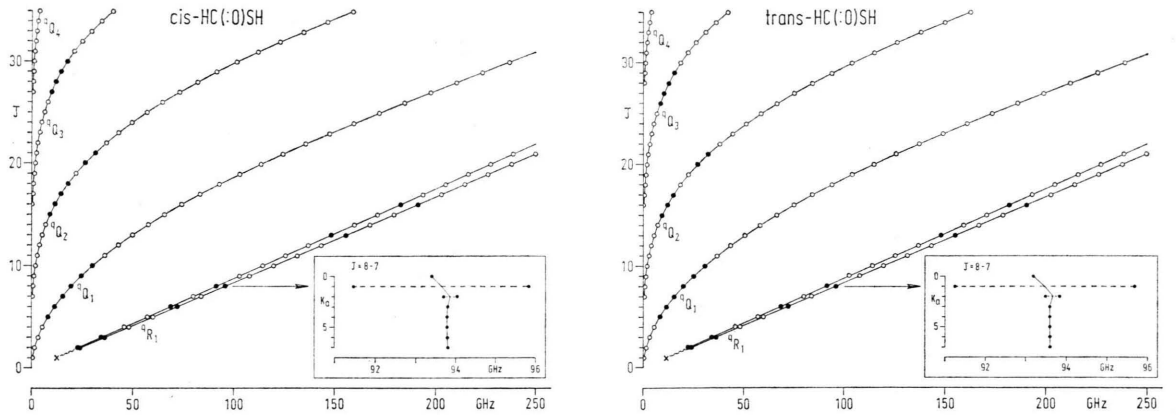

Fig. 2. Fortrat diagrams for the *a*-type transitions of the *cis* and *trans* rotamers of HC(:O)SH. The solid and open circles indicate measured and predicted line positions respectively. For the R-branch only the positions of the $K_a=1$ components are indicated. The inserts show the complete K_a pattern for the $J=8\leftarrow 7$ transitions.

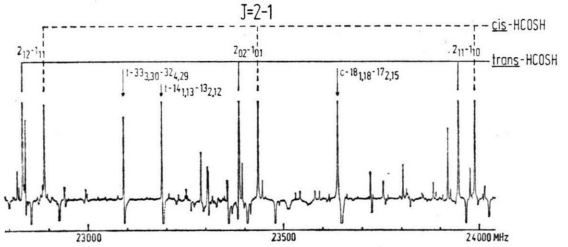

Fig. 3. Absorption spectrum of HCOSH in the region 22.8—24.0 GHz.

is due to the inertial asymmetry of the molecule. The second band head, which falls near $K_a=5$, is caused by centrifugal distortion contributions to the rotational energy; primarily from the term with the coefficient Δ_{JK}. As J increases this band head shifts gradually towards higher values of K_a. These features are summarized in Fig. 4, where the K_a patterns for several $J+1\leftarrow J$ transitions are plotted. Figure 5 illustrates in more detail the formation

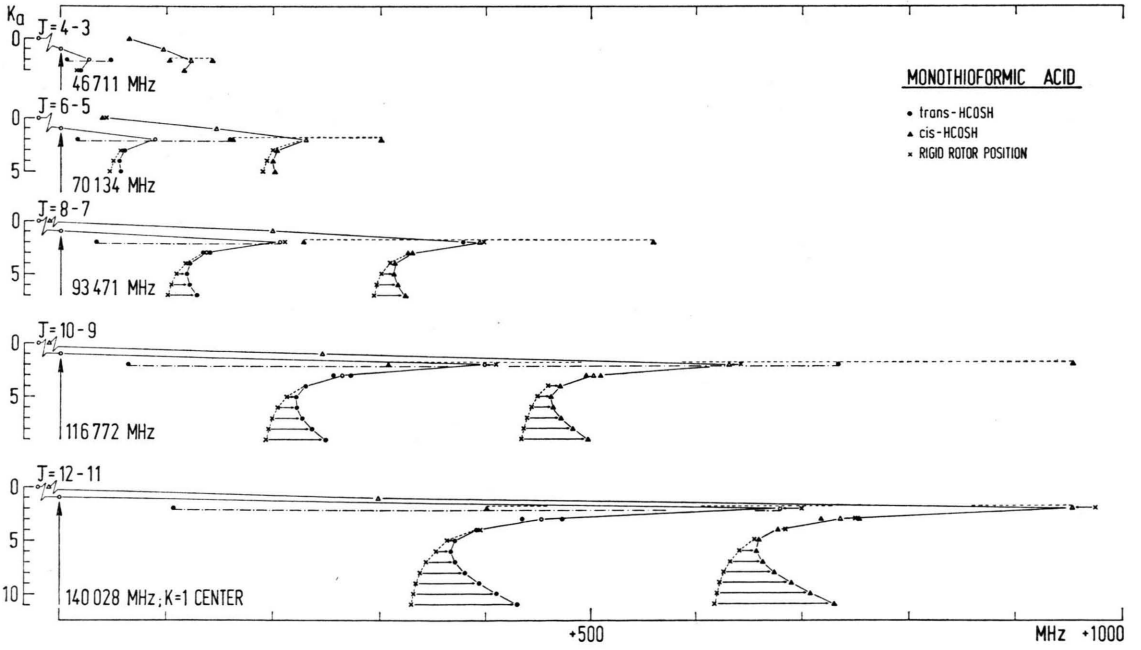

Fig. 4. Comparison of five *a*-type R-branch transitions of *trans*- and *cis*-HC(:O)SH. The center positions of the $K_a=1$ doublets of the different $J+1\leftarrow J$ transitions have been aligned (vertical arrows). For the higher-J values the $K_a=0$, 1 and 2 components of the *trans* and *cis* rotamers overlap. Deviations from the rigid rotor positions for $K_a>4$ are indicated by arrows.

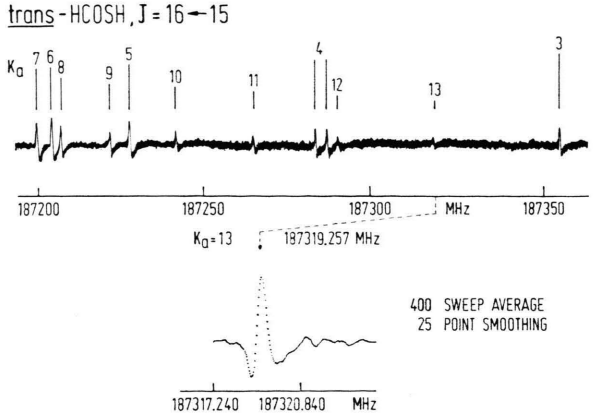

Fig. 5. Oscilloscope display of a portion of the $J=16\leftarrow15$ *a*-type R-branch transition of *trans*-HC(:O)SH. The second band head near $K_a=7$ is clearly visible. A 400 sweep compputer average of the absorption profile of the $K_a=13$ line is given.

of the second band head in the K_a pattern of the $J=16\leftarrow15$ transition of the *trans* rotamer. The upper part of this figure shows the calculated line positions, the lower part shows an oscilloscope display of the millimeter wave spectrum. The formation of such band heads has been previously observed in the spectra of other near prolate asymmetric top molecules [15, 16].

In addition to the R-branch lines numerous *a*-type Q-branch transitions belonging to the ${}^qQ_1$, ${}^qQ_2$, ${}^qQ_3$ and ${}^qQ_4$ branches were also observed for each rotamer in the microwave region.

2) The b-type Spectrum

Over sixty *b*-type transitions belonging to the $K_a=1-0$, $2-1$, $3-2$, $4-3$ and $5-4$ rotational sub-bands have been measured and assigned for each rotamer of HC(:O)SH. These transitions are widely scattered over the frequency region from 8 to 250 GHz, as shown by the Fortrat diagrams given in Figure 6. A few of the *b*-type branches, notably the ${}^rP_1$ and ${}^rQ_1$ branches, form band heads, but they are not as localized and hence as easily recognized as those found in the K_a pattern of the *a*-type R-branch transitions. Several low-J transitions belonging to the ${}^rP_0$ branch fall in the microwave region, and were assigned first on the basis of approximate frequency predictions. Confirmation of these assignments was obtained from observed Stark effect patterns. Additional *b*-type transitions of the remaining branches were then located using a bootstrap pro-

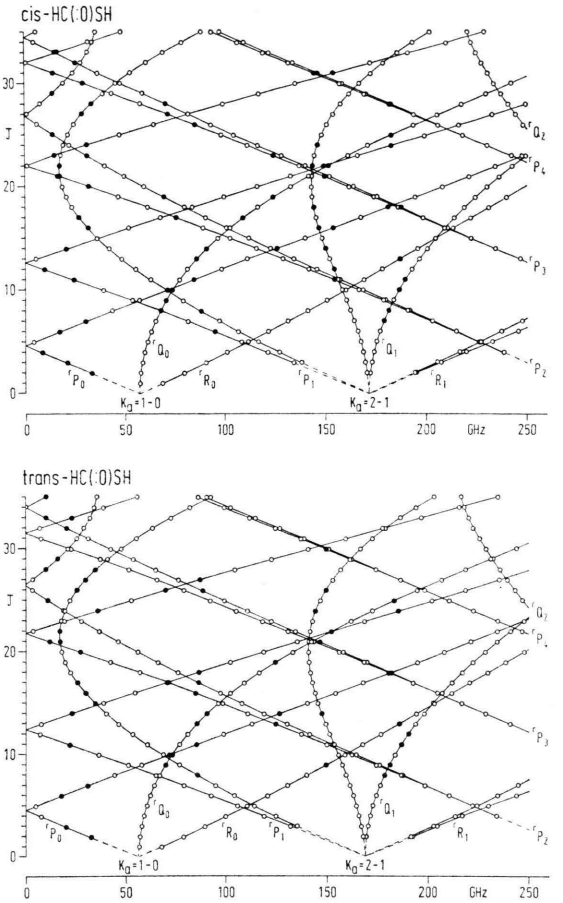

Fig. 6. Fortrat diagrams for the *b*-type transitions of *cis*- and *trans*-HC(:O)SH. Closed and open circles indicate measured and calculated line positions respectively.

cedure. This is an iterative process which starts with a least squares fit to the easily assigned low-J transitions. Rotational and centrifugal distortion constants obtained in this fit are used to predict the frequencies and standard deviations of higher-J transitions which can then be measured and included in a second least squares fit. The cycle is repeated several times with new sets of progressively higher-J lines being included in each successive fit. Simultaneously the Hamiltonian is gradually expanded by the addition of higher order terms. This procedure was used to assign the majority of the *b*-type transitions as well as the high-J *a*-type Q-branch transitions.

The rotational spectrum of monothioformic acid could thus be characterized as a confusion of strong absorption lines scattered throughout the microwave and millimeter wave regions. Only when the

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-HCOSH IN MHz

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE
** A TYPE R BRANCH **						
1(0, 1) -	0(0, 0)	11694.9370(1.0)	11694.9335(0.0003)	0.0035	0.390	0.000
2(0, 2) -	1(0, 1)	23385.8700(1.0)	23385.8653(0.0005)	0.0047	1.170	0.390
2(1, 2) -	1(1, 1)	22834.3900(1.0)	22834.3748(0.0005)	0.0152	3.017	2.255
2(1, 1) -	1(1, 0)	23945.5300(1.0)	23945.5400(0.0005)	-0.0100	3.072	2.274
3(0, 3) -	2(0, 2)	35068.8500(1.0)	35067.9959(0.0008)	0.8041	2.340	1.170
3(1, 3) -	2(1, 2)	34248.8200(1.0)	34248.8189(0.0008)	0.0011	4.159	3.017
3(1, 2) -	2(1, 1)	35915.4800(1.0)	35915.4955(0.0008)	-0.0155	4.270	3.072
3(2, 2) -	2(2, 1)	35085.5400(1.0)	35085.5069(0.0007)	0.0331	9.837	8.667
3(2, 1) -	2(2, 0)	35101.9400(1.0)	35101.9824(0.0007)	-0.0424	9.838	8.667
4(0, 4) -	3(0, 3)		46737.7354(0.0010)		3.899	2.340
4(1, 4) -	3(1, 3)		45659.9985(0.0010)		5.682	4.159
4(1, 3) -	3(1, 2)		47882.0475(0.0010)		5.868	4.270
5(0, 5) -	4(0, 4)		58390.7193(0.0012)		5.847	3.899
5(1, 5) -	4(1, 4)		57066.8704(0.0012)		7.586	5.682
5(1, 4) -	4(1, 3)		59844.0176(0.0012)		7.864	5.868
6(0, 6) -	5(0, 5)	70022.8340(1.0)	70022.8385(0.0014)	-0.0045	8.182	5.847
6(1, 6) -	5(1, 5)	68468.4250(1.0)	68468.4301(0.0014)	-0.0051	9.870	7.586
6(1, 5) -	5(1, 4)	71800.1650(1.0)	71800.1699(0.0014)	-0.0049	10.259	7.864
6(2, 5) -	5(2, 4)	70150.2740(1.0)	70150.2894(0.0013)	-0.0154	15.687	13.348
6(2, 4) -	5(2, 3)	70294.1710(1.0)	70294.1694(0.0013)	0.0016	15.697	13.352
6(3, 4) -	5(3, 3)	70193.5080(1.0)	70193.5069(0.0012)	0.0011	25.059	22.718
6(3, 3) -	5(3, 2)	70194.5750(1.0)	70194.5750(0.0012)	-0.0050	25.059	22.718
6(4, 3) -	5(4, 2)	70189.0020(1.0)	70188.9875(0.0011)	0.0145	38.171	35.830
6(4, 2) -	5(4, 1)	70189.0020(0.0)	70188.9902(0.0011)	0.0118	38.171	35.830
6(5, 2) -	5(5, 1)	70189.9120(1.0)	70189.9019(0.0012)	0.0101	55.024	52.683
6(5, 1) -	5(5, 0)	70189.9120(0.0)	70189.9019(0.0012)	0.0101	55.024	52.683
7(0, 7) -	6(0, 6)		81630.0866(0.0016)		10.905	8.182
7(1, 7) -	6(1, 6)		79863.7203(0.0016)		12.534	9.870
7(1, 6) -	6(1, 5)		83749.3010(0.0016)		13.052	10.259
8(0, 8) -	7(0, 7)	93208.6240(1.0)	93208.6279(0.0017)	-0.0039	14.014	10.905
8(1, 8) -	7(1, 7)	91251.8470(1.0)	91251.8400(0.0017)	0.0070	15.577	12.534
8(1, 7) -	7(1, 6)	95690.0320(1.0)	95690.0300(0.0017)	0.0020	16.244	13.052
8(2, 7) -	7(2, 6)	93505.0980(1.0)	93505.0854(0.0016)	0.0126	21.536	18.417
8(2, 6) -	7(2, 5)	93848.9870(1.0)	93848.9895(0.0016)	-0.0025	21.565	18.434
8(3, 6) -	7(3, 5)	93605.8430(1.0)	93605.8336(0.0014)	0.0064	30.913	27.791
8(3, 5) -	7(3, 4)	93610.6520(1.0)	93610.6355(0.0014)	0.0165	30.913	27.791
8(4, 5) -	7(4, 4)	93592.5090(0.0)	93592.5074(0.0013)	0.0016	44.025	40.903
8(4, 4) -	7(4, 3)	93592.5090(0.0)	93592.5316(0.0013)	-0.0226	44.025	40.903
8(5, 4) -	7(5, 3)	93589.8870(1.0)	93589.8936(0.0014)	-0.0066	60.877	57.756
8(5, 3) -	7(5, 2)	93589.8870(0.0)	93589.8936(0.0014)	-0.0066	60.877	57.756
8(6, 3) -	7(6, 2)	93592.8080(1.0)	93592.8048(0.0018)	0.0032	81.467	78.345
8(6, 2) -	7(6, 1)	93592.8080(0.0)	93592.8048(0.0018)	0.0032	81.467	78.345
8(7, 2) -	7(7, 1)	93598.9330(1.0)	93598.9415(0.0023)	-0.0085	105.787	102.665
8(7, 1) -	7(7, 0)	93598.9330(0.0)	93598.9415(0.0023)	-0.0085	105.787	102.665
9(0, 9) -	8(0, 8)		104754.8872(0.0019)		17.509	14.014
9(1, 9) -	8(1, 8)		102631.9522(0.0018)		19.001	15.577
9(1, 8) -	8(1, 7)		107620.9890(0.0018)		19.834	16.244
9(2, 8) -	8(2, 7)	105173.6900(1.0)	105173.6786(0.0017)	0.0114	25.044	21.536
9(2, 7) -	8(2, 6)	105663.2460(1.0)	105663.2609(0.0017)	-0.0149	25.089	21.565
9(3, 7) -	8(3, 6)	105315.9230(1.0)	105315.9230(0.0015)	-0.0140	34.426	30.913
9(3, 6) -	8(3, 5)	105324.6970(1.0)	105324.7199(0.0015)	-0.0229	34.427	30.913
9(4, 5) -	8(4, 5)	105296.5040(0.0)	105296.4719(0.0014)	0.0321	47.537	44.025
9(4, 5) -	8(4, 4)	105296.5040(0.0)	105296.5299(0.0014)	-0.0259	47.537	44.025
9(5, 5) -	8(5, 4)	105290.9230(1.0)	105290.9219(0.0015)	0.0011	64.390	60.877
9(5, 4) -	8(5, 3)	105290.9240(0.0)	105290.9220(0.0015)	0.0020	64.390	60.877
9(6, 4) -	8(6, 3)	105292.8230(1.0)	105292.8225(0.0019)	0.0005	84.979	81.467
9(6, 3) -	8(6, 2)	105292.8230(0.0)	105292.8225(0.0019)	0.0005	84.979	81.467
9(7, 3) -	8(7, 2)	105298.9170(1.0)	105298.9142(0.0024)	0.0028	109.300	105.787
9(7, 2) -	8(7, 1)	105298.9170(0.0)	105298.9142(0.0024)	0.0028	109.300	105.787
10(0,10) -	9(0, 9)		116265.6610(0.0019)		21.387	17.509
10(1,10) -	9(1, 9)		114003.2914(0.0019)		22.804	19.001
10(1, 9) -	9(1, 8)		119540.7134(0.0019)		23.821	19.834
11(0,11) -	10(0,10)	127738.2390(1.0)	127738.2452(0.0020)	-0.0062	25.648	21.387
11(1,11) -	10(1,10)	125365.1670(0.0)	125365.1705(0.0019)	-0.0035	26.985	22.804
11(1,10) -	10(1, 9)		131447.6518(0.0019)		28.206	23.821
12(0,12) -	11(0,11)		139170.5697(0.0020)		30.290	25.648
12(1,12) -	11(1,11)		136716.9861(0.0020)		31.546	26.985
12(1,11) -	11(1,10)		143340.1573(0.0020)		32.987	28.206

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-HCOSH

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE
13(0,13) -	12(0,12)	150561.3170(1.0)	150561.3293(0.0020)	-0.0123	39.312	30.290
13(1,13) -	12(1,12)	148058.2230(1.0)	148058.2232(0.0020)	-0.0032	36.484	31.546
13(1,12) -	12(1,11)	155216.4780(1.0)	155216.4797(0.0020)	-0.0017	38.165	32.987
13(2,12) -	12(2,11)	151771.8850(1.0)	151771.7778(0.0018)	0.0272	42.964	37.902
13(2,11) -	12(2,10)	153213.8670(1.0)	153213.7990(0.0018)	0.0080	43.148	38.037
13(3,11) -	12(3,10)	152183.8620(1.0)	152183.8649(0.0017)	-0.0029	52.386	47.319
13(3,10) -	12(3, 9)	152240.7120(1.0)	152240.7198(0.0017)	-0.0078	52.391	47.313
13(4,10) -	12(4, 9)	152131.2750(1.0)	152131.2719(0.0017)	0.0031	65.491	60.417
13(4, 9) -	12(4, 8)	152132.1210(1.0)	152132.1070(0.0017)	0.0140	65.491	60.417
13(5, 9) -	12(5, 8)	152104.0070(1.0)	152103.9916(0.0018)	0.0154	82.342	77.268
13(5, 8) -	12(5, 7)	152104.0070(0.0)	152103.9977(0.0018)	0.0093	82.342	77.268
13(6, 8) -	12(6, 7)	152096.4760(1.0)	152096.4686(0.0021)	0.0074	102.931	97.857
13(6, 7) -	12(6, 6)	152096.4760(0.0)	152096.4687(0.0021)	0.0073	102.931	97.857
13(7, 7) -	12(7, 6)	152099.2100(1.0)	152099.1996(0.0026)	0.0104	127.252	122.178
13(7, 6) -	12(7, 5)	152099.2100(0.0)	152099.1996(0.0026)	0.0104	127.252	122.178
13(8, 6) -	12(8, 5)	152108.2870(1.0)	152108.2791(0.0031)	0.0079	155.298	150.224
13(8, 5) -	12(8, 4)	152108.2870(0.0)	152108.2791(0.0031)	0.0079	155.298	150.224
13(9, 5) -	12(9, 4)	152121.8940(1.0)	152121.8915(0.0036)	0.0025	187.062	181.987
13(9, 4) -	12(9, 3)	152121.8940(0.0)	152121.8915(0.0036)	0.0025	187.062	181.987
13(10, 4) -	12(10, 3)	152139.0890(1.0)	152139.0884(0.0041)	0.0006	222.534	217.460
13(10, 3) -	12(10, 2)	152139.0890(0.0)	152139.0884(0.0041)	0.0006	222.534	217.460
13(11, 3) -	12(11, 2)	152159.3280(1.0)	152159.3265(0.0047)	0.0015	261.707	256.631
13(11, 2) -	12(11, 1)	152159.3280(0.0)	152159.3265(0.0047)	0.0015	261.707	256.631
13(12, 2) -	12(12, 1)	152182.2620(1.0)	152182.2684(0.0056)	-0.0064	304.569	299.493
13(12, 1) -	12(12, 0)	152182.2620(0.0)	152182.2684(0.0056)	-0.0064	304.569	299.493
15(1,14) -	14(1,13)	178913.0220(1.0)	178913.0169(0.0020)	0.0051	49.706	43.738
16(0,16) -	15(0,15)	184484.5930(1.0)	184484.6221(0.0020)	-0.0321	52.644	46.491
16(1,16) -	15(1,15)	182014.6940(1.0)	182014.6940(0.0020)	0.0000	53.567	47.495
16(1,15) -	15(1,14)	190729.1590(1.0)	190729.1642(0.0020)	-0.0052	56.068	49.706
16(2,15) -	15(2,14)	186619.7040(1.0)	186619.6921(0.0019)	0.0119	60.478	54.253
16(2,14) -	15(2,13)	189194.4000(1.0)	189194.3940(0.0019)	0.0060	60.878	54.567
16(3,14) -	15(3,13)	187359.6150(1.0)	187359.6251(0.0019)	-0.0101	69.961	63.712
16(3,13) -	15(3,12)	187520.4340(1.0)	187520.4214(0.0019)	0.0126	69.978	63.723
16(4,13) -	15(4,12)	187281.8990(1.0)	187281.8972(0.0020)	0.0018	83.060	76.813
16(4,12) -	15(4,11)	187285.5520(1.0)	187285.5613(0.0020)	-0.0093	83.060	76.813
16(5,12) -	15(5,11)	187225.6990(0.0)	187225.6667(0.0023)	0.0323	99.906	93.660
16(5,11) -	15(5,10)	187225.6990(0.0)	187225.7092(0.0023)	-0.0102	99.906	93.660
16(6,11) -	15(6,10)	187203.9400(1.0)	187203.9309(0.0027)	0.0091	120.493	114.249
16(6,10) -	15(6, 9)	187203.9400(0.0)	187203.9312(0.0027)	0.0088	120.493	114.249
16(7,10) -	15(7, 9)	187199.9060(1.0)	187199.9174(0.0032)	-0.0114	144.814	138.570
16(7, 9) -	15(7, 8)	187199.9060(0.0)	187199.9174(0.0032)	-0.0114	144.814	138.570
16(8, 9) -	15(8, 8)	187206.3750(1.0)	187206.3654(0.0036)	0.0096	172.861	166.616
16(8, 8) -	15(8, 7)	187206.3750(0.0)	187206.3654(0.0036)	0.0096	172.861	166.616
16(9, 8) -	15(9, 7)	187219.9170(1.0)	187219.9040(0.0039)	0.0130	204.626	198.381
16(9, 7) -	15(9, 6)	187219.9170(0.0)	187219.9040(0.0039)	0.0130	204.626	198.381
16(10, 7) -	15(10, 6)	187238.7530(1.0)	187238.7814(0.0040)	-0.0284	240.100	233.855
16(10, 6) -	15(10, 5)	187238.7530(0.0)	187238.7814(0.0040)	-0.0284	240.100	233.855
16(11, 6) -	15(11, 5)	187262.0070(1.0)	187262.0023(0.0041)	0.0047	279.275	273.029
16(11, 5) -	15(11, 4)	187262.0070(0.0)	187262.0023(0.0041)	0.0047	279.275	273.029
16(12, 5) -	15(12, 4)	187288.9240(1.0)	187288.9572(0.0046)	-0.0332	322.140	315.893
16(12, 4) -	15(12, 3)	187288.9240(0.0)	187288.9572(0.0046)	-0.0332	322.140	315.893
16(13, 4) -	15(13, 3)	187319.2570(1.0)	187319.2474(0.0062)	0.0096	368.684	362.436
16(13, 3) -	15(13, 2)	187319.2570(0.0)	187319.2474(0.0062)	0.0096	368.684	362.436
16(14, 3) -	15(14, 2)	187352.6090(1.0)	187352.5951(0.0093)	0.0139	418.895	412.645
16(14, 2) -	15(14, 1)	187352.6090(0.0)	187352.5951(0.0093)	0.0139	418.895	412.645
18(1,17) -	17(1,16)	214286.1830(1.0)	214286.1956(0.0022)	-0.0126	69.971	62.823
19(0,19) -	18(0,18)	218073.7250(1.0)	218073.7387(0.0023)	-0.0137	73.349	66.075
19(1,19) -	18(1,18)	215866.2820(1.0)	215866.2812(0.0023)	0.0008	74.040	66.839
** A TYPE Q BRANCH **						
1(1, 0) -	1(1, 1)		555.5930(0.0001)		2.274	2.255
2(1, 1) -	2(1, 2)		1666.7582(0.0002)		3.072	3.017
3(1, 2) -	3(1, 3)		3333.4348(0.0003)		4.270	4.159
4(1, 3) -	4(1, 4)		5555.4838(0.0006)		5.868	5.682
5(1, 4) -	5(1, 5)	8332.6200(1.0)	8332.6311(0.0008)	-0.0111	7.864	7.586
6(1, 5) -	6(1, 6)	11664.3920(1.0)	11664.3909(0.0011)	0.0011	10.259	9.870
7(1, 6) -	7(1, 7)	15549.9750(1.0)	15549.9715(0.0014)	0.0035	13.052	12.534
8(1, 7) -	8(1, 8)	19988.1600(1.0)	19988.1615(0.0018)	-0.0015	16.244	15.577
9(1, 8) -	9(1, 9)	24977.2000(1.0)	24977.1983(0.0021)	0.0017	19.834	19.001
10(1, 9) -	10(1,10)	30514.6200(1.0)	30514.6203(0.0025)	-0.0003	23.821	22.804
15(2,13) -	15(2,14)	9433.9300(1.0)	9433.9274(0.0016)	0.0026	54.567	54.253
16(2,14) -	16(2,15)	12008.6250(1.0)	12008.6292(0.0018)	-0.0042	60.878	60.478
17(2,15) -	17(2,16)	15035.5100(1.0)	15035.5066(0.0021)	0.0034	67.591	67.089
20(2,18) -	20(2,19)	27130.6800(1.0)	27130.6920(0.0027)	-0.0120	90.145	89.240
21(2,19) -	21(2,20)	32245.5300(1.0)	32245.5317(0.0029)	-0.0017	98.470	97.394

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-HCOSH

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE
26(3,23) -	26(3,24)	8453.3650(1.0)	8453.3582(0.0027)	0.0068	154.250	153.968
27(3,24) -	27(3,25)	10450.3500(1.0)	10450.3460(0.0029)	0.0040	164.866	164.518
28(3,25) -	28(3,26)	12798.6950(1.0)	12798.6996(0.0032)	-0.0046	175.884	175.457
29(3,26) -	29(3,27)	15535.8800(1.0)	15535.8701(0.0034)	-0.0101	187.304	186.785
39(4,35) -	39(4,36)	9347.8650(1.0)	9347.8651(0.0038)	-0.0001	335.136	334.825
40(4,36) -	40(4,37)	11274.5800(1.0)	11274.5797(0.0038)	0.0003	350.848	350.472
41(4,37) -	41(4,38)	13516.1150(1.0)	13516.1004(0.0038)	0.0146	366.961	366.510
42(4,38) -	42(4,39)	16107.7050(1.0)	16107.6985(0.0039)	0.0065	383.477	382.939
43(4,39) -	43(4,40)	19085.6400(1.0)	19085.6373(0.0045)	0.0027	400.395	399.759
44(4,40) -	44(4,41)	22486.6300(1.0)	22486.6309(0.0059)	-0.0009	417.718	416.968
45(4,41) -	45(4,42)	26347.2100(1.0)	26347.2221(0.0080)	-0.0121	435.445	434.566
** B TYPE R BRANCH **						
1(1, 1) -	0(0, 0)		67604.5902(0.0017)		2.255	0.000
2(1, 2) -	1(0, 1)		78744.0315(0.0019)		3.017	0.390
3(1, 3) -	2(0, 2)		89607.1851(0.0021)		4.159	1.170
4(1, 4) -	3(0, 3)		100199.1877(0.0022)		5.682	2.340
5(1, 5) -	4(0, 4)		110528.3227(0.0024)		7.586	3.899
6(1, 6) -	5(0, 5)		120606.0335(0.0026)		9.870	5.847
7(1, 7) -	6(0, 6)		130446.9153(0.0027)		12.534	8.182
8(1, 8) -	7(0, 7)		140068.6688(0.0028)		15.577	10.905
9(1, 9) -	8(0, 8)	149492.0050(1.0)	149491.9931(0.0029)	0.0119	19.001	14.014
13(1,13) -	12(0,12)	185706.2820(1.0)	185706.3013(0.0031)	-0.0193	30.484	30.290
** B TYPE Q BRANCH **						
1(1, 1) -	1(0, 1)		56465.2497(0.0016)		2.274	0.390
2(1, 1) -	2(0, 2)		57825.1244(0.0016)		3.072	1.170
3(1, 2) -	3(0, 3)		57872.6240(0.0015)		4.270	2.340
4(1, 3) -	4(0, 4)		59016.9361(0.0015)		5.868	3.899
5(1, 4) -	5(0, 5)		60470.2345(0.0015)		7.864	5.847
6(1, 5) -	6(0, 6)		62247.5859(0.0016)		10.259	8.182
7(1, 6) -	7(0, 7)		64366.8002(0.0016)		13.052	10.905
8(1, 7) -	8(0, 8)		66848.2023(0.0017)		16.244	14.014
9(1, 8) -	9(0, 9)	69714.3090(1.0)	69714.3042(0.0018)	0.0048	19.834	17.509
10(1, 9) -	10(0,10)	72989.3590(1.0)	72989.3566(0.0019)	0.0024	23.821	21.387
11(1,10) -	11(0,11)		76698.7632(0.0021)		28.206	25.648
12(1,11) -	12(0,12)		80868.3508(0.0022)		32.987	30.290
13(1,12) -	13(0,13)	85523.5190(1.0)	85523.5012(0.0024)	0.0178	38.165	35.312
14(1,13) -	14(0,14)	90688.1570(1.0)	90688.1676(0.0026)	-0.0106	43.738	40.713
15(1,14) -	15(0,15)		96383.8173(0.0028)		49.706	46.491
19(1,18) -	19(0,19)	124760.6080(1.0)	124760.6045(0.0034)	0.0035	77.510	73.349
22(1,21) -	22(0,22)	151953.6940(1.0)	151953.6533(0.0040)	0.0407	102.466	97.397
25(1,24) -	25(0,25)	183715.6510(1.0)	183715.6584(0.0058)	-0.0074	130.902	124.774
14(2,12) -	14(1,13)	147486.3530(1.0)	147486.3430(0.0032)	0.0100	48.657	43.738
24(2,22) -	24(1,23)	144615.9840(1.0)	144615.9668(0.0047)	0.0172	125.863	121.039
26(2,24) -	26(1,25)	149570.1200(1.0)	149570.1168(0.0064)	0.0032	146.137	141.148
8(2, 7) -	8(1, 8)	178635.5330(1.0)	178635.5276(0.0034)	0.0054	21.536	15.577
9(2, 8) -	9(1, 9)	181177.2510(1.0)	181177.2540(0.0034)	-0.0030	25.044	19.001
11(2,10) -	11(1,11)	187133.6670(1.0)	187133.6595(0.0033)	0.0075	33.227	26.985
12(2,11) -	12(1,12)	190551.8280(1.0)	190551.8560(0.0033)	-0.0280	37.902	31.546
** B TYPE P BRANCH **						
1(1, 1) -	2(0, 2)	32523.9800(1.0)	32523.9914(0.0014)	-0.0114	2.255	1.170
2(1, 2) -	3(0, 3)	20290.3650(1.0)	20290.3703(0.0014)	-0.0053	3.017	2.340
3(1, 3) -	4(0, 4)		7801.4538(0.0014)		4.159	3.899
5(0, 5) -	4(1, 4)		4929.2670(0.0015)		5.847	5.682
6(0, 6) -	5(1, 5)	17885.2300(1.0)	17885.2351(0.0016)	-0.0051	8.182	7.586
7(0, 7) -	6(1, 6)	31046.8900(1.0)	31046.8916(0.0017)	-0.0016	10.905	9.870
8(0, 8) -	7(1, 7)		44391.7992(0.0019)		14.014	12.534
9(0, 9) -	8(1, 8)		57894.8463(0.0020)		17.509	15.577
10(0,10) -	9(1, 9)	71528.5700(1.0)	71528.5551(0.0021)	0.0149	21.387	19.001
11(0,11) -	10(1,10)	85263.5450(1.0)	85263.5089(0.0022)	0.0361	25.648	22.804
12(0,12) -	11(1,11)		99068.9080(0.0023)		30.290	26.985
13(0,13) -	12(1,12)		112913.2512(0.0023)		35.312	31.546
14(0,14) -	13(1,13)	126765.1130(1.0)	126765.1197(0.0023)	-0.0067	40.713	36.484
15(0,15) -	14(1,14)		140594.0287(0.0023)		46.491	41.801
18(0,18) -	17(1,17)	181669.8340(1.0)	181669.8545(0.0024)	-0.0205	66.075	60.015
10(2, 9) -	11(1,10)	22047.0800(1.0)	22047.0828(0.0033)	-0.0028	28.941	28.206
14(1,13) -	13(2,12)	23187.8800(1.0)	23187.8766(0.0035)	0.0034	43.738	42.964
17(1,16) -	16(2,15)	70318.0870(1.0)	70318.0867(0.0035)	0.0003	62.823	60.478
18(1,17) -	17(2,16)	86391.5010(1.0)	86391.5675(0.0036)	-0.0665	69.971	67.089
24(1,23) -	23(2,22)	185396.8500(1.0)	185396.8498(0.0048)	0.0002	121.039	114.855

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-HCOSH

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE
7(2, 5) -	8(1, 8)	85648.2400(1.0)	85648.2259(0.0030)	0.0141	18.434	15.577
14(2,12) -	15(1,15)	34843.8200(1.0)	34843.8116(0.0037)	0.0084	48.657	47.495
15(2,13) -	16(1,16)	30002.0800(1.0)	30002.0985(0.0038)	-0.0185	54.567	53.567
16(2,14) -	17(1,17)	25886.1800(1.0)	25886.1784(0.0040)	0.0016	60.878	60.015
20(2,18) -	21(1,21)	17325.1600(1.0)	17325.1724(0.0043)	-0.0124	90.145	89.567
21(2,19) -	22(1,22)	17279.0600(1.0)	17279.0734(0.0043)	-0.0134	98.470	97.893
25(2,23) -	26(1,26)	25769.7500(1.0)	25769.7431(0.0053)	0.0069	135.799	134.940
26(2,24) -	27(1,27)	30044.9800(1.0)	30044.9619(0.0063)	0.0181	146.137	145.135
27(2,25) -	28(1,28)	35158.8600(1.0)	35158.8833(0.0079)	-0.0233	156.876	155.713
12(3,10) -	13(2,11)	124768.3280(1.0)	124768.3238(0.0039)	0.0042	47.310	43.148
15(3,13) -	16(2,14)	84946.0200(1.0)	84946.0054(0.0036)	0.0146	63.712	60.878
19(3,17) -	20(2,18)	27352.4200(1.0)	27352.4233(0.0033)	-0.0033	91.058	90.145
20(3,18) -	21(2,19)	12857.0900(1.0)	12857.0942(0.0034)	-0.0042	98.872	98.470
24(2,22) -	23(3,21)	36012.9800(1.0)	36012.9879(0.0039)	-0.0079	125.863	124.662
26(2,24) -	25(3,23)	69797.6710(1.0)	69797.6533(0.0047)	0.0177	146.137	143.809
27(2,25) -	26(3,24)	87170.0400(1.0)	87170.0498(0.0052)	-0.0098	156.876	153.968
16(3,13) -	17(2,16)	86613.3360(1.0)	86613.3325(0.0032)	0.0035	69.978	67.089
24(3,21) -	25(2,24)	11088.6550(1.0)	11088.6575(0.0034)	-0.0025	134.219	133.849
28(2,27) -	27(3,24)	10189.1650(1.0)	10189.1600(0.0047)	0.0050	169.206	164.866
29(2,28) -	28(3,25)	16084.6500(1.0)	16084.6509(0.0054)	-0.0009	176.420	175.884
41(2,40) -	40(3,37)	24263.8000(1.0)	24263.8033(0.0068)	-0.0033	340.466	339.656
42(2,41) -	41(3,38)	19097.3800(1.0)	19097.3764(0.0072)	0.0036	356.576	355.939
43(2,42) -	42(3,39)	13527.5300(1.0)	13527.5324(0.0104)	-0.0024	373.059	372.625
17(4,14) -	18(3,15)	180768.4200(1.0)	180768.4354(0.0061)	-0.0154	89.698	83.668
33(3,30) -	32(4,29)	23090.4500(1.0)	23090.4526(0.0066)	-0.0026	237.024	236.254
17(4,13) -	18(3,16)	181600.6740(1.0)	181600.6564(0.0060)	0.0176	89.698	83.634
20(4,16) -	21(3,19)	146399.6760(1.0)	146399.6941(0.0052)	-0.0181	111.961	107.078
25(4,21) -	26(3,24)	87918.4290(1.0)	87918.4198(0.0044)	0.0092	156.961	153.968
31(4,27) -	32(3,30)	20691.9200(1.0)	20691.9191(0.0046)	0.0009	223.795	223.195
32(4,28) -	33(3,31)	10088.8300(1.0)	10088.7971(0.0047)	0.0029	236.324	235.987
35(3,33) -	34(4,30)	10350.0800(1.0)	10350.0792(0.0049)	0.0008	262.914	262.569
36(3,34) -	35(4,31)	20118.6250(1.0)	20118.6008(0.0054)	0.0242	276.957	276.286
29(5,25) -	30(4,26)	149832.0360(1.0)	149832.0327(0.0108)	0.0033	216.659	211.661
39(5,35) -	40(4,36)	18856.3150(1.0)	18856.3185(0.0067)	-0.0035	351.477	350.848
42(4,38) -	41(5,37)	9966.9300(1.0)	9966.9270(0.0059)	0.0030	383.477	383.144
43(4,39) -	42(5,38)	24859.0350(1.0)	24859.0382(0.0070)	-0.0032	400.395	399.566
40(5,35) -	41(4,38)	18861.7200(1.0)	18861.7190(0.0066)	0.0010	367.140	366.510
44(4,41) -	43(5,38)	16115.9300(1.0)	16115.9300(0.0092)	0.0000	416.968	416.430

TABLE II. OBSERVED AND CALCULATED FREQUENCIES OF CIS-HCOSH IN MHz

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (HEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE
** A TYPE R BRANCH **						
1(0, 1)	- 0(0, 0)	11719.0050(1.0)	11719.0000(0.0004)	0.0050	0.391	0.000
2(0, 2)	- 1(0, 1)	23433.9450(1.0)	23433.9452(0.0007)	-0.0002	1.173	0.391
2(1, 2)	- 1(1, 1)	22888.6900(1.0)	22888.6815(0.0007)	0.0085	3.049	2.285
2(1, 1)	- 1(1, 0)	23987.5150(1.0)	23987.5256(0.0007)	-0.0106	3.104	2.304
3(0, 3)	- 2(0, 2)	35140.7600(1.0)	35140.7833(0.0011)	-0.0233	2.345	1.173
3(1, 3)	- 2(1, 2)	34330.3700(1.0)	34330.3608(0.0011)	0.0092	4.194	3.049
3(1, 2)	- 2(1, 1)	35978.5200(1.0)	35978.5535(0.0011)	-0.0335	4.304	3.104
3(2, 2)	- 2(2, 1)	35157.8000(1.0)	35157.7975(0.0010)	0.0025	9.959	8.786
3(2, 1)	- 2(2, 0)	35173.6200(1.0)	35173.6611(0.0010)	-0.0411	9.960	8.787
4(0, 4)	- 3(0, 3)		46835.4704(0.0014)		3.907	2.345
4(1, 4)	- 3(1, 3)		45768.8721(0.0014)		5.721	4.194
4(1, 3)	- 3(1, 2)		47966.2751(0.0014)		5.904	4.304
5(0, 5)	- 4(0, 4)		58513.9866(0.0017)		5.859	3.907
5(1, 5)	- 4(1, 4)		57203.2017(0.0017)		7.629	5.721
5(1, 4)	- 4(1, 3)		59949.5474(0.0017)		7.904	5.904
6(0, 6)	- 5(0, 5)	70172.3670(1.0)	70172.3628(0.0020)	0.0042	8.200	5.859
6(1, 6)	- 5(1, 5)	68632.3610(1.0)	68632.3724(0.0020)	-0.0114	9.918	7.629
6(1, 5)	- 5(1, 4)	71927.1980(1.0)	71927.1921(0.0020)	0.0059	10.303	7.904
6(2, 5)	- 5(2, 4)	70295.3990(1.0)	70295.3987(0.0018)	0.0003	15.822	13.477
6(2, 4)	- 5(2, 3)	70433.9350(1.0)	70433.9437(0.0018)	-0.0087	15.831	13.482
6(3, 4)	- 5(3, 3)	70337.4030(1.0)	70337.4059(0.0016)	-0.0029	25.340	22.993
6(3, 3)	- 5(3, 2)	70338.4010(1.0)	70338.4072(0.0016)	-0.0062	25.340	22.993
6(4, 3)	- 5(4, 2)	70333.5780(1.0)	70333.5776(0.0015)	0.0004	38.657	36.311
6(4, 2)	- 5(4, 1)	70333.5780(1.0)	70333.5800(0.0015)	-0.0020	38.657	36.311
6(5, 2)	- 5(5, 1)	70335.1440(1.0)	70335.1487(0.0015)	-0.0047	55.773	53.427
6(5, 1)	- 5(5, 0)	70335.1440(1.0)	70335.1487(0.0015)	-0.0047	55.773	53.427
7(0, 7)	- 6(0, 6)		81806.7243(0.0022)		10.928	8.200
7(1, 7)	- 6(1, 6)		80055.4511(0.0022)		12.588	9.918
7(1, 6)	- 6(1, 5)		83897.9866(0.0022)		13.101	10.303
8(0, 8)	- 7(0, 7)	93413.3420(1.0)	93413.3531(0.0024)	-0.0111	14.044	10.928
8(1, 8)	- 7(1, 7)	91471.5750(1.0)	91471.5579(0.0024)	0.0171	15.640	12.588
8(1, 7)	- 7(1, 6)	95860.6700(1.0)	95860.6548(0.0024)	0.0152	16.299	13.101
8(2, 7)	- 7(2, 6)	93699.2850(1.0)	93699.2948(0.0022)	-0.0098	21.682	18.557
8(2, 6)	- 7(2, 5)	94030.4800(1.0)	94030.5042(0.0022)	-0.0242	21.710	18.574
8(3, 6)	- 7(3, 5)	93796.8570(1.0)	93796.8659(0.0020)	-0.0089	31.206	28.077
8(3, 5)	- 7(3, 4)	93801.3410(1.0)	93801.3673(0.0020)	-0.0263	31.206	28.077
8(4, 5)	- 7(4, 4)	93784.7060(1.0)	93784.6908(0.0018)	0.0152	44.522	41.394
8(4, 4)	- 7(4, 3)	93784.7060(1.0)	93784.7128(0.0018)	-0.0068	44.522	41.394
8(5, 4)	- 7(5, 3)	93783.1020(1.0)	93783.0942(0.0019)	0.0078	61.639	58.511
8(5, 3)	- 7(5, 2)	93783.1020(1.0)	93783.0943(0.0019)	0.0077	61.639	58.511
8(6, 3)	- 7(6, 2)	93787.0280(1.0)	93787.0240(0.0022)	0.0040	82.550	79.422
8(6, 2)	- 7(6, 1)	93787.0280(1.0)	93787.0240(0.0022)	0.0040	82.550	79.422
8(7, 2)	- 7(7, 1)	93794.2620(1.0)	93794.2664(0.0029)	-0.0044	107.250	104.121
8(7, 1)	- 7(7, 0)	93794.2620(1.0)	93794.2664(0.0029)	-0.0044	107.250	104.121
9(0, 9)	- 8(0, 8)		104988.7703(0.0026)		17.546	14.044
9(1, 9)	- 8(1, 8)		102879.8729(0.0025)		19.071	15.640
9(1, 8)	- 8(1, 7)		107813.8579(0.0025)		19.895	16.299
9(4, 6)	- 8(4, 5)	105512.3010(1.0)	105512.2666(0.0020)	0.0344	48.042	44.522
9(4, 5)	- 8(4, 4)	105512.3010(1.0)	105512.3195(0.0020)	-0.0185	48.042	44.522
9(5, 5)	- 8(5, 4)	105507.9500(1.0)	105507.9571(0.0020)	-0.0071	65.158	61.639
9(5, 4)	- 8(5, 3)	105507.9500(1.0)	105507.9573(0.0020)	-0.0073	65.158	61.639
9(6, 4)	- 8(6, 3)	105511.0480(1.0)	105511.0545(0.0024)	-0.0065	86.069	82.550
9(6, 3)	- 8(6, 2)	105511.0480(1.0)	105511.0545(0.0024)	-0.0065	86.069	82.550
10(0,10)	- 9(0, 9)		116529.8389(0.0027)		21.433	17.546
10(1,10)	- 9(1, 9)		114279.6439(0.0027)		22.883	19.071
10(1, 9)	- 9(1, 8)		119756.1850(0.0027)		23.890	19.895
11(0,11)	- 10(0,10)		128033.8813(0.0028)		25.704	21.433
11(1,11)	- 10(1,10)	125670.1780(1.0)	125670.1923(0.0027)	-0.0143	27.075	22.883
11(1,10)	- 10(1, 9)		131686.1447(0.0027)		28.282	23.890
12(0,12)	- 11(0,11)		139498.8062(0.0028)		30.357	25.704
12(1,12)	- 11(1,11)		137050.9188(0.0028)		31.647	27.075
12(1,11)	- 11(1,10)		143602.1562(0.0028)		33.072	28.282
13(0,13)	- 12(0,12)	150923.2560(1.0)	150923.2321(0.0029)	0.0239	35.391	30.357
13(1,13)	- 12(1,12)	148421.3050(1.0)	148421.3073(0.0028)	-0.0023	36.597	31.647
13(1,12)	- 12(1,11)	155502.5340(1.0)	155502.5414(0.0028)	-0.0074	38.259	33.072

TABLE II. OBSERVED AND CALCULATED FREQUENCIES OF CIS-HCOSH

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE
13(2,12) -	12(2,11)	152091.8060(1.0)	152091.8040(0.0026)	0.0020	43.156	38.082
13(2,11) -	12(2,10)	153482.6610(1.0)	153482.6799(0.0026)	-0.0189	43.332	38.213
13(3,11) -	12(3,10)	152490.0070(1.0)	152490.0573(0.0024)	-0.0503	52.722	47.635
13(3,10) -	12(3, 9)	152543.3510(1.0)	152543.3623(0.0024)	-0.0113	52.727	47.638
13(4,10) -	12(4, 9)	152439.9620(1.0)	152439.9159(0.0023)	0.0461	66.033	60.948
13(4, 9) -	12(4, 8)	152440.7310(1.0)	152440.6780(0.0023)	0.0530	66.033	60.948
13(5, 9) -	12(5, 8)	152415.1100(1.0)	152415.1276(0.0025)	-0.0176	83.147	78.063
13(5, 8) -	12(5, 9)	152415.1100(0.0)	152415.1375(0.0025)	-0.0275	83.147	78.063
13(6, 8) -	12(6, 7)	152409.6950(1.0)	152409.7136(0.0029)	-0.0186	104.058	98.974
13(6, 7) -	12(6, 6)	152409.6950(0.0)	152409.7137(0.0029)	-0.0187	104.058	98.974
13(7, 7) -	12(7, 6)	152414.4590(1.0)	152414.5075(0.0035)	-0.0485	128.759	123.675
13(7, 6) -	12(7, 5)	152414.4590(0.0)	152414.5075(0.0035)	-0.0485	128.759	123.675
13(8, 6) -	12(8, 5)	152425.7110(1.0)	152425.7510(0.0041)	-0.0400	157.243	152.158
13(8, 5) -	12(8, 4)	152425.7110(0.0)	152425.7510(0.0041)	-0.0400	157.243	152.158
13(9, 5) -	12(9, 4)	152441.7420(1.0)	152441.6984(0.0047)	0.0436	189.501	184.416
13(9, 4) -	12(9, 3)	152441.7420(0.0)	152441.6984(0.0047)	0.0436	189.501	184.416
13(10, 4) -	12(10, 3)	152461.4160(1.0)	152461.4391(0.0053)	-0.0231	225.525	220.440
13(10, 3) -	12(10, 2)	152461.4160(0.0)	152461.4391(0.0053)	-0.0231	225.525	220.440
13(11, 3) -	12(11, 2)	152484.4760(1.0)	152484.4525(0.0060)	0.0235	265.306	260.220
13(11, 2) -	12(11, 1)	152484.4760(0.0)	152484.4525(0.0060)	0.0235	265.306	260.220
13(12, 2) -	12(12, 1)	152510.4170(1.0)	152510.4168(0.0072)	0.0002	308.832	303.745
13(12, 1) -	12(12, 0)	152510.4170(0.0)	152510.4168(0.0072)	0.0002	308.832	303.745
15(1,14) -	14(1,13)	179249.2040(1.0)	179249.2000(0.0028)	0.0040	49.822	43.843
16(0,16) -	15(0,15)	184952.3140(1.0)	184952.3160(0.0028)	-0.0020	52.767	46.598
16(1,16) -	15(1,15)	182466.5730(1.0)	182466.5953(0.0028)	-0.0223	53.722	47.635
16(1,15) -	15(1,14)	191091.6010(1.0)	191091.5845(0.0028)	0.0165	56.196	49.822
16(2,15) -	15(2,14)	187318.0510(1.0)	187318.0423(0.0027)	0.0087	60.706	54.468
16(2,14) -	15(2,13)	189506.3690(1.0)	189506.3654(0.0026)	0.0036	61.093	54.771
16(3,14) -	15(3,13)	187733.3170(1.0)	187733.3064(0.0026)	0.0106	70.333	64.070
16(3,13) -	15(3,12)	187884.0990(1.0)	187884.1083(0.0026)	-0.0093	70.349	64.081
16(4,13) -	15(4,12)	187658.1060(1.0)	187658.1050(0.0027)	0.0010	83.637	77.377
16(4,12) -	15(4,11)	187661.4580(1.0)	187661.4487(0.0027)	0.0093	83.637	77.378
16(5,12) -	15(5,11)	187605.7590(1.0)	187605.7310(0.0031)	0.0280	100.747	94.489
16(5,11) -	15(5,10)	187605.7590(0.0)	187605.7687(0.0031)	-0.0097	100.747	94.489
16(6,11) -	15(6,10)	187587.0800(1.0)	187587.0548(0.0037)	0.0252	121.656	115.399
16(6,10) -	15(6, 9)	187587.0800(0.0)	187587.0550(0.0037)	0.0250	121.656	115.399
16(7,10) -	15(7, 9)	187585.8640(1.0)	187585.8525(0.0044)	0.0115	146.357	140.100
16(7, 9) -	15(7, 8)	187585.8640(0.0)	187585.8525(0.0044)	0.0115	146.357	140.100
16(8, 9) -	15(8, 8)	187595.1490(1.0)	187595.1362(0.0049)	0.0128	174.842	168.585
16(8, 8) -	15(8, 7)	187595.1490(0.0)	187595.1362(0.0049)	0.0128	174.842	168.585
16(9, 8) -	15(9, 7)	187611.6590(1.0)	187611.6635(0.0053)	-0.0045	207.102	200.844
16(9, 7) -	15(9, 6)	187611.6590(0.0)	187611.6635(0.0053)	-0.0045	207.102	200.844
16(10, 7) -	15(10, 6)	187633.7460(1.0)	187633.7512(0.0054)	-0.0052	243.129	236.870
16(10, 6) -	15(10, 5)	187633.7460(0.0)	187633.7512(0.0054)	-0.0052	243.129	236.870
16(11, 6) -	15(11, 5)	187660.4270(1.0)	187660.4441(0.0055)	-0.0171	282.912	276.652
16(11, 5) -	15(11, 4)	187660.4270(0.0)	187660.4441(0.0055)	-0.0171	282.912	276.652
16(12, 5) -	15(12, 4)	187691.1570(1.0)	187691.1593(0.0062)	-0.0023	326.441	320.180
16(12, 4) -	15(12, 3)	187691.1570(0.0)	187691.1593(0.0062)	-0.0023	326.441	320.180
16(13, 4) -	15(13, 3)	187725.5270(1.0)	187725.5167(0.0085)	0.0103	373.705	367.443
16(13, 3) -	15(13, 2)	187725.5270(0.0)	187725.5167(0.0085)	0.0103	373.705	367.443
16(14, 3) -	15(14, 2)	187763.2500(1.0)	187763.2532(0.0128)	-0.0032	424.690	418.427
16(14, 2) -	15(14, 1)	187763.2500(0.0)	187763.2532(0.0128)	-0.0032	424.690	418.427
18(1,17) -	17(1,16)	214703.9250(1.0)	214703.9318(0.0029)	-0.0068	70.126	62.964
19(0,19) -	18(0,18)	218649.3780(1.0)	218649.3616(0.0031)	0.0164	73.525	66.232
19(1,19) -	18(1,18)	216408.6690(1.0)	216408.6897(0.0031)	-0.0207	74.246	67.028
** A TYPE Q BRANCH **						
1(1, 0) -	1(1, 1)		549.4332(0.0001)		2.304	2.285
2(1, 1) -	2(1, 2)		1648.2772(0.0002)		3.104	3.049
3(1, 2) -	3(1, 3)		3296.4699(0.0004)		4.304	4.194
4(1, 3) -	4(1, 4)		5493.8729(0.0006)		5.904	5.721
5(1, 4) -	5(1, 5)	8240.2200(1.0)	8240.2186(0.0010)	0.0014	7.904	7.629
6(1, 5) -	6(1, 6)	11535.0400(1.0)	11535.0384(0.0013)	0.0016	10.303	9.918
7(1, 6) -	7(1, 7)	15377.5700(1.0)	15377.5739(0.0017)	-0.0039	13.101	12.588
8(1, 7) -	8(1, 8)	19766.6900(1.0)	19766.6708(0.0021)	0.0192	16.299	15.640
9(1, 8) -	9(1, 9)	24700.0600(1.0)	24700.0558(0.0026)	0.0042	19.895	19.071
10(1, 9) -	10(1,10)	30177.2000(1.0)	30177.1969(0.0031)	0.0031	23.890	22.883
15(2,13) -	15(2,14)	9098.9300(1.0)	9098.9300(0.0017)	0.0000	54.771	54.468
16(2,14) -	16(2,15)	11587.2550(1.0)	11587.2532(0.0021)	0.0018	61.093	60.706
17(2,15) -	17(2,16)	14515.0500(1.0)	14515.0822(0.0024)	-0.0322	67.816	67.332
18(2,16) -	18(2,17)	17914.6700(1.0)	17914.6778(0.0028)	-0.0078	74.943	74.345
20(2,18) -	20(2,19)	26238.5400(1.0)	26238.5183(0.0035)	0.0217	90.406	89.531
21(2,19) -	21(2,20)	31206.3400(1.0)	31206.3411(0.0039)	-0.0011	98.744	97.703

TABLE II. OBSERVED AND CALCULATED FREQUENCIES OF CIS-HCOSH

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE
27(3,24) -	27(3,25)	9629.7650(1.0)	9629.7650(0.0036)	0.0000	165.404	165.076
28(3,25) -	28(3,26)	12046.0000(1.0)	12046.0088(0.0040)	-0.0088	176.438	176.036
29(3,26) -	29(3,27)	14632.1700(1.0)	14632.1974(0.0044)	-0.0274	187.876	187.388
30(3,27) -	30(3,28)	17624.6650(1.0)	17624.6777(0.0048)	-0.0127	199.717	199.129
44(4,40) -	44(4,41)	20692.7150(1.0)	20692.7185(0.0092)	-0.0035	418.862	418.172
45(4,41) -	45(4,42)	24270.7200(1.0)	24270.7120(0.0119)	0.0080	436.613	435.803
** B TYPE R BRANCH **						
1(1, 1) -	0(0, 0)		68511.2796(0.0022)		2.285	0.000
2(1, 2) -	1(0, 1)		79680.9611(0.0024)		3.049	0.391
3(1, 3) -	2(0, 2)		90577.3767(0.0027)		4.194	1.173
4(1, 4) -	3(0, 3)		101205.4655(0.0029)		5.721	2.345
5(1, 5) -	4(0, 4)		111573.1969(0.0032)		7.629	3.907
6(1, 6) -	5(0, 5)		121691.5827(0.0034)		9.918	5.859
7(1, 7) -	6(0, 6)		131574.6710(0.0036)		12.588	8.200
8(1, 8) -	7(0, 7)		141239.5046(0.0037)		15.640	10.928
13(1,13) -	12(0,12)	187076.7910(1.0)	187076.7900(0.0041)	0.0010	36.597	30.357
** B TYPE Q BRANCH **						
1(1, 0) -	1(0, 1)		57341.7128(0.0019)		2.304	0.391
2(1, 1) -	2(0, 2)		57895.2931(0.0019)		3.104	1.173
3(1, 2) -	3(0, 3)		58733.1633(0.0019)		4.304	2.345
4(1, 3) -	4(0, 4)		59863.8681(0.0019)		5.904	3.907
5(1, 4) -	5(0, 5)		61299.4289(0.0019)		7.904	5.859
6(1, 5) -	6(0, 6)		63054.2583(0.0019)		10.303	8.200
7(1, 6) -	7(0, 7)		65145.5206(0.0020)		13.101	10.928
8(1, 7) -	8(0, 8)	67592.8310(1.0)	67592.8224(0.0021)	0.0086	16.299	14.044
9(1, 8) -	9(0, 9)	70417.9300(1.0)	70417.9099(0.0022)	0.0201	19.895	17.546
10(1, 9) -	10(0,10)	73644.2530(1.0)	73644.2560(0.0024)	-0.0030	23.890	21.433
11(1,10) -	11(0,11)		77296.5194(0.0026)		28.282	25.704
12(1,11) -	12(0,12)		81399.8694(0.0028)		33.072	30.357
13(1,12) -	13(0,13)	85979.2090(1.0)	85979.1787(0.0031)	0.0303	38.259	35.391
14(1,13) -	14(0,14)	91058.1080(1.0)	91058.1050(0.0034)	0.0030	43.843	40.805
15(1,14) -	15(0,15)		96658.0950(0.0037)		49.822	46.598
17(1,16) -	17(0,17)	109489.9030(1.0)	109489.9109(0.0043)	-0.0079	62.964	59.312
19(1,18) -	19(0,19)	124564.6800(1.0)	124564.6692(0.0048)	0.0108	77.680	73.525
22(1,21) -	22(0,22)	151351.7780(1.0)	151351.8201(0.0055)	-0.0421	102.687	97.639
25(1,24) -	25(0,25)	182725.4340(1.0)	182725.4553(0.0079)	-0.0213	131.185	125.090
12(2,11) -	12(1,11)	154101.6090(1.0)	154101.6042(0.0040)	0.0048	38.213	33.072
14(2,12) -	14(1,13)	150158.5840(1.0)	150158.5734(0.0039)	0.0106	48.852	43.843
16(2,14) -	16(1,15)	146795.1210(1.0)	146795.1070(0.0038)	0.0140	61.093	56.196
18(2,15) -	18(1,17)	144390.9430(1.0)	144390.9406(0.0039)	0.0024	74.943	70.126
22(2,20) -	22(1,21)	143841.5790(1.0)	143841.5700(0.0049)	0.0090	107.485	102.687
24(2,22) -	24(1,23)	146283.8360(1.0)	146283.8104(0.0064)	0.0256	126.180	121.300
7(2, 5) -	7(1, 7)	178932.8610(1.0)	178932.8631(0.0044)	-0.0021	18.557	12.588
8(2, 7) -	8(1, 8)	181160.6020(1.0)	181160.6001(0.0043)	0.0019	21.682	15.640
10(2, 9) -	10(1,10)	186473.0740(1.0)	186473.0728(0.0042)	0.0012	29.103	22.883
11(2,10) -	11(1,11)	189561.4270(1.0)	189561.4350(0.0042)	-0.0080	33.398	27.075
** B TYPE P BRANCH **						
1(1, 1) -	2(0, 2)	33358.3800(1.0)	33358.3344(0.0016)	0.0456	2.285	1.173
2(1, 2) -	3(0, 3)	21106.2300(1.0)	21106.2326(0.0016)	-0.0026	3.049	2.345
3(1, 3) -	4(0, 4)	8601.1200(1.0)	8601.1230(0.0017)	-0.0030	4.194	3.907
5(0, 5) -	4(1, 4)		4143.9914(0.0018)		5.859	5.721
6(0, 6) -	5(1, 5)	17113.1600(1.0)	17113.1525(0.0020)	0.0075	8.200	7.629
7(0, 7) -	6(1, 6)	30287.5000(1.0)	30287.5044(0.0022)	-0.0044	10.928	9.918
8(0, 8) -	7(1, 7)		43645.4063(0.0024)		14.044	12.588
9(0, 9) -	8(1, 8)		57162.6188(0.0026)		17.546	15.640
10(0,10) -	9(1, 9)	70812.5900(1.0)	70812.5848(0.0028)	0.0052	21.433	19.071
11(0,11) -	10(1,10)	84566.8110(1.0)	84566.8222(0.0029)	-0.0112	25.704	22.883
12(0,12) -	11(1,11)		98395.4361(0.0030)		30.357	27.075
13(0,13) -	12(1,12)		112267.7495(0.0031)		35.391	31.647
14(0,14) -	13(1,13)	126153.0630(1.0)	126153.0350(0.0031)	0.0280	40.805	36.597
15(0,15) -	14(1,14)		140021.3166(0.0032)		46.598	41.927
16(0,16) -	15(1,15)	153844.2100(1.0)	153844.1908(0.0032)	0.0192	52.767	47.635
18(0,18) -	17(1,17)	181252.5960(1.0)	181252.5852(0.0032)	0.0108	66.232	60.186
5(2, 4) -	6(1, 5)	95157.9110(1.0)	95157.9172(0.0039)	-0.0062	13.477	10.303
10(2, 9) -	11(1,10)	24609.7250(1.0)	24609.7311(0.0040)	-0.0061	29.103	28.282
11(2,10) -	12(1,11)	9766.1200(1.0)	9766.1295(0.0041)	-0.0095	33.398	33.072
14(1,13) -	13(2,12)	20600.5100(1.0)	20600.5074(0.0043)	0.0026	43.843	43.156
22(1,21) -	21(2,20)	149431.1670(1.0)	149431.1599(0.0052)	0.0071	102.687	97.703
24(1,23) -	23(2,22)	182812.9430(1.0)	182812.9407(0.0061)	0.0023	121.300	115.292

TABLE II. OBSERVED AND CALCULATED FREQUENCIES OF CIS-HCOSH

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE
7(2, 5) -	8(1, 8)	87959.912 (1.0)	87959.8981 (0.0037)	0.0139	18.574	15.640
9(2, 7) -	10(1,10)	70695.1100 (1.0)	70695.1316 (0.0038)	-0.0216	25.241	22.883
15(2,13) -	16(1,16)	31463.6900 (1.0)	31463.7006 (0.0051)	-0.0106	54.771	53.722
16(2,14) -	17(1,17)	27177.8400 (1.0)	27177.8402 (0.0053)	-0.0002	61.093	60.186
20(2,18) -	21(1,21)	17778.6550 (1.0)	17778.6572 (0.0060)	-0.0022	90.406	89.813
21(2,19) -	22(1,22)	17486.5450 (1.0)	17486.5393 (0.0063)	0.0057	98.744	98.160
26(2,24) -	27(1,27)	28865.1300 (1.0)	28865.1192 (0.0096)	-0.0192	146.486	145.523
27(2,25) -	28(1,28)	33680.9500 (1.0)	33680.9073 (0.0120)	0.0427	157.242	156.118
10(3, 8) -	11(2, 9)	154268.3990 (1.0)	154268.4056 (0.0055)	-0.0066	38.638	33.492
16(3,14) -	17(2,15)	75441.9950 (1.0)	75441.9980 (0.0043)	-0.0030	73.333	67.816
19(3,17) -	20(2,18)	31916.8500 (1.0)	31916.8579 (0.0041)	-0.0079	91.471	90.406
20(3,18) -	21(2,19)	16696.6500 (1.0)	16696.6460 (0.0042)	0.0040	99.301	98.744
23(2,21) -	22(3,20)	14829.7450 (1.0)	14829.7461 (0.0045)	-0.0011	116.631	116.136
24(2,22) -	23(3,21)	31127.3900 (1.0)	31127.3799 (0.0047)	0.0101	126.180	125.141
31(2,29) -	30(3,28)	153987.0410 (1.0)	153987.0537 (0.0112)	-0.0127	204.265	199.129
18(3,15) -	19(2,18)	69544.8810 (1.0)	69544.8877 (0.0039)	-0.0067	84.065	81.745
22(3,19) -	23(2,22)	31055.6000 (1.0)	31055.5934 (0.0042)	0.0066	116.238	115.282
24(3,21) -	25(2,24)	14015.4700 (1.0)	14015.4683 (0.0047)	0.0017	134.706	134.239
29(2,28) -	28(3,25)	14035.1500 (1.0)	14035.1409 (0.0064)	0.0091	176.906	176.438
42(2,41) -	41(3,38)	22429.5300 (1.0)	22429.5305 (0.0102)	-0.0005	357.491	356.743
43(2,42) -	42(3,39)	16872.4650 (1.0)	16872.4695 (0.0099)	-0.0045	374.014	373.452
44(2,43) -	43(3,40)	10431.4750 (1.0)	10431.4719 (0.0095)	0.0031	390.912	390.564
47(3,44) -	48(2,47)	23719.8250 (1.0)	23719.8262 (0.0169)	-0.0012	463.021	462.230
20(4,17) -	21(3,18)	149698.4300 (1.0)	149698.4072 (0.0068)	0.0228	112.594	107.600
22(4,19) -	23(3,20)	124457.2960 (1.0)	124457.2784 (0.0059)	0.0176	129.424	125.273
25(4,22) -	26(3,23)	85209.3310 (1.0)	85209.3249 (0.0052)	0.0061	157.613	154.771
26(4,23) -	27(3,24)	71662.3160 (1.0)	71662.3105 (0.0052)	0.0055	167.794	165.484
29(4,26) -	30(3,27)	29276.3700 (1.0)	29276.3768 (0.0059)	-0.0068	200.693	199.717
30(4,27) -	31(3,28)	14484.6600 (1.0)	14484.6981 (0.0062)	-0.0381	212.445	211.962
33(3,30) -	32(4,29)	16222.8200 (1.0)	16222.8285 (0.0071)	-0.0085	237.668	237.127
17(4,13) -	18(3,16)	187552.4900 (1.0)	187552.5010 (0.0081)	-0.0110	90.289	84.033
27(4,23) -	26(3,26)	70397.5660 (1.0)	70397.5613 (0.0051)	0.0047	178.385	176.036
31(4,27) -	32(3,30)	25785.6750 (1.0)	25785.6798 (0.0059)	-0.0048	224.639	223.779
32(4,28) -	33(3,31)	15070.3300 (1.0)	15070.3158 (0.0061)	0.0142	237.190	236.687
36(3,34) -	35(4,31)	15578.6400 (1.0)	15578.6351 (0.0066)	0.0049	277.740	277.221
37(3,35) -	36(4,32)	25186.6200 (1.0)	25186.6175 (0.0068)	0.0025	292.199	291.359
27(5,23) -	28(4,24)	181878.0970 (1.0)	181878.1216 (0.0088)	-0.0246	195.423	189.357
30(5,25) -	31(4,27)	144884.6700 (1.0)	144884.6532 (0.0081)	0.0168	229.472	224.639
40(5,35) -	41(4,37)	12866.0950 (1.0)	12866.0908 (0.0093)	0.0042	368.466	368.036
43(4,39) -	42(5,38)	16247.4000 (1.0)	16247.3982 (0.0099)	0.0018	401.517	400.975
27(5,22) -	28(4,25)	182569.8000 (1.0)	182569.8106 (0.0089)	-0.0106	195.424	189.334
30(5,25) -	31(4,28)	146416.1820 (1.0)	146416.1643 (0.0080)	0.0177	229.473	224.589
40(5,35) -	41(4,38)	25937.2800 (1.0)	25937.2848 (0.0074)	-0.0048	368.488	367.623
41(5,36) -	42(4,39)	14104.8700 (1.0)	14104.8679 (0.0072)	0.0021	384.552	384.082
44(4,41) -	43(5,38)	9263.6100 (1.0)	9263.6081 (0.0090)	0.0019	418.172	417.863
45(4,42) -	44(5,39)	20760.5750 (1.0)	20760.5770 (0.0118)	-0.0020	435.803	435.111

transitions have been assigned and plotted in Fortrat diagrams, as shown in Figs. 2 and 6, does the inherent simplicity of the spectrum become apparent. The Fortrat diagrams also reveal the striking similarity between the spectra of the two rotamers.

IV. Centrifugal Distortion Analysis

The observed rotational transitions of monothioformic acid were analysed using the reduced Hamiltonian reported by Watson [17] in which $R_6 = 0$. The analysis was performed in the I^r axis representation so that the Hamiltonian may be written as follows:

$$\mathcal{H} = \mathcal{H}_r + \mathcal{H}_d + \mathcal{H}_{d'}, \tag{1}$$

$$\mathcal{H}_r = 1/2\,(\tilde{B}+\tilde{C})P^2 + [\tilde{A} - 1/2\,(\tilde{B}+\tilde{C})]\,P_a^2 + 1/2\,(\tilde{B}-\tilde{C})\,(P_b^2 - P_c^2)\,, \tag{2}$$

$$\mathcal{H}_d = -\Delta_J P^4 - \Delta_{JK} P^2 P_a^2 - \Delta_K P_a^4 - 2\,\delta_J P^2 (P_b^2 - P_c^2) - \delta_K [P_a^2 (P_b^2 - P_c^2) + (P_b^2 - P_c^2) P_a^2]\,, \tag{3}$$

$$\mathcal{H}_{d'} = H_J P^6 + H_{JK} P^4 P_a^2 + H_{KJ} P^2 P_a^4 + H_K P_a^6 + 2\,h_J P^4 (P_b^2 - P_c^2) + h_{JK} P^2 [P_a^2 (P_b^2 - P_c^2) + (P_b^2 - P_c^2) P_a^2] + h_K [P_a^4 (P_b^2 - P_c^2) + (P_b^2 - P_c^2) P_a^4] \tag{4}$$

where P, P_a, P_b and P_c are the operators for the total angular momentum and its components along the principal inertial axes. The constants $\tilde{A}$, $\tilde{B}$ and $\tilde{C}$ are Watson's reduced rotational constants which contain very small centrifugal distortion contributions [17]. The parameters in Eqs. (3) and (4) are the quartic and sextic centrifugal distortion constants respectively.

An iterative least squares procedure was used to determine values for the molecular constants which appear in the above Hamiltonian from the observed spectra. In each step of the iteration the energy matrix was diagonalized with the aid of the QR algorithm which diagonalizes tridiagonal matrices rapidly [18].

The observed and calculated transition frequencies of the *trans* rotamer have been listed in Table I; the frequencies of the *cis* rotamer are given in Table II. Several of the *a*-type R-branch lines whose *K*-type splitting is calculated to be larger than 10 kHz, but could not be resolved experimentally, were excluded from each fit. The K_a components with a calculated *K*-type splitting of less than 10 kHz were treated as single lines. A total of 164 transition frequencies with $J \leqq 45$ were included in the least squares analysis of the *trans* rotamer giving a standard deviation of the fit of 12.5 kHz. For the *cis* rotamer, 170 transition frequencies with $J \leqq 48$ were analyzed with a standard deviation of the fit of 17.2 kHz. The slight increase in the standard deviation of the fit on going from the *trans* to the *cis* rotamer is consistent with the observation that the absorption lines of the *cis* rotamer are significantly broader than those of the *trans*, and are therefore expected to be somewhat less accurately measured.

The molecular constants obtained in the least squares fits described above are collected in Table III. The rotational constants and the quartic centrifugal distortion constants are well determined. However, three of the sextic centrifugal distortion constants (H_{JK}, h_{JK}, h_K) are poorly determined.

The reduced Hamiltonian presented in Eqs. (1) – (4) is only one of an infinite set of effective Hamiltonians which may be obtained by applying a unitary transformation to the general rotational Hamiltonian [17]. Alternative reduced Hamiltonians [19, 20] and the use of different axis representations [21, 22] have in some instances been proposed. It is there-

Table III. Rotational constants and centrifugal distortion constants of monothioformic acid [a].

	cis-HC(:O)SH	*trans*-HC(:O)SH	
$\tilde{A}$	62927.7132 (21)	62036.0911 (17)	MHz
$\tilde{B}$	6134.26108 (19)	6125.30490 (14)	MHz
$\tilde{C}$	5584.75363 (19)	5569.64234 (14)	MHz
Δ_J	3.67858 (36)	3.42871 (27)	kHz
Δ_{JK}	−47.9619 (65)	−43.1667 (51)	kHz
Δ_K	1305.68 (18)	1250.74 (15)	kHz
δ_J	0.463122 (37)	0.434730 (32)	kHz
δ_K	17.653 (12)	16.5158 (84)	kHz
H_J	0.00279 (30)	0.00137 (24)	Hz
H_{JK}	−0.048 (13)	−0.002 (16)	Hz
H_{KJ}	−4.162 (51)	−4.737 (53)	Hz
H_K	80.6 (47)	88.1 (44)	Hz
h_J	0.001118 (18)	0.000737 (37)	Hz
h_{JK}	0.014 (16)	0.019 (18)	Hz
h_K	7.6 (19)	5.9 (20)	Hz
σ [b]	17.2	12.5	kHz
N [c]	170	164	

[a] The numbers in parentheses are standard errors.
[b] Standard deviation of the fit.
[c] The number of equally weighted transitions included in the fit.

fore desirable to check that the reduced Hamiltonian and axis representation used here are appropriate. Such a check is provided by a small ($<10^{-5}$) value of the coefficient of the unitary transformation[15,21,22], s_{111}. This coefficient was evaluated from the constants given in Table III using the procedure discussed by Yamada and Winnewisser[15], case 1. The results are $s_{111}=1.365\times10^{-7}$ for *trans*-HC(:O)SH and $s_{111}=1.429\times10^{-7}$ for *cis*-HC(:O)SH. These numbers indicate that the effective Hamiltonian given in Eqs. (1) – (4) is a suitable one for the analysis of the rotational spectrum of HC(:O)SH.

Watson has shown that there is one set of parameters which are invariant to a unitary transformation of the rotational Hamiltonian. These parameters, which are designated $\mathfrak{A}$, $\mathfrak{B}$, $\mathfrak{C}$, τ'_{aaaa}, τ'_{bbbb}, τ'_{cccc}, τ_1 and τ_2 may be calculated from the spectral parameters reported in Table III using equations given by Watson[17]. The results are presented in Table IV. Also reported in Table IV are values of

Table IV. Watson's determinable rotational constants and quartic centrifugal distortion constants for monothioformic acid [a, b].

	cis-HC(:O)SH	*trans*-HC(:O)SH	
$\tilde{\mathfrak{A}}$	62927.7206(21)	62036.0980(17)	MHz
$\tilde{\mathfrak{B}}$	6134.18424(19)	6125.23469(14)	MHz
$\tilde{\mathfrak{C}}$	5584.74926(19)	5569.63993(14)	MHz
τ'_{aaaa}	−5045.59(72)	−4844.01(60)	kHz
τ'_{bbbb}	−18.4193(15)	−17.1927(11)	kHz
τ'_{cccc}	−11.0093(15)	−10.2370(11)	kHz
τ_1	147.705(26)	131.522(21)	kHz
τ_2'	0.8784(25)	0.4900(20)	kHz
$\Delta\tau'_{cccc}$	−0.01447(55)	−0.01992(42)	kHz

[a] The numbers in parentheses are standard errors.
[b] $\tau_2'=\tau_2/(\alpha+\beta+\gamma)$; where α, β and γ are rotational constants defined by Kivelson and Wilson[25]. See also Ref.[15,23].

the quantity known as the τ-defect[23], $\Delta\tau'_{cccc}$. For a planar molecule, in its equilibrium configuration, the τ-defect should be zero. The small negative values of $\Delta\tau'_{cccc}$ given in Table IV are typical for a planar molecule in its ground vibrational state[23].

If a molecule is planar then there exist relations which reduce the number of linearly independent quartic distortion constants from five to four[17]. These relations are strictly valid only for the equilibrium rotational parameters, but also apply approximately to the ground vibrational state constants. The planarity constraints were applied to the HC(:O)SH ground state spectral constants following Yamada and Winnewisser[15,24] case 1, in order to determine values for the seven constants α', β', γ', τ_{aabb}, τ_{bbcc}, τ_{aacc} and τ_{abab}. The results are collected in Table V. The Kivelson and Wilson[25] rotational constants, α', β', γ', contain no centrifugal distortion contributions and hence are the appropriate constants to use in a structural determination.

Table V. Rotational constants and quartic centrifugal distortion constants derived from the planarity relations [a].

	cis-HC(:O)SH	*trans*-HC(:O)SH	
α'	62927.695	62036.075	MHz
β'	6134.2083	6125.2551	MHz
γ'	5584.8152	5569.7002	MHz
$\hbar^4\tau_{aabb}$	150.03	137.39	kHz
$\hbar^4\tau_{bbcc}$	−14.086	−13.108	kHz
$\hbar^4\tau_{aacc}$	84.617	74.555	kHz
$\hbar^4\tau_{abab}$	−36.428	−33.660	kHz

[a] Calculated using the planarity conditions as described in Ref.[15] case 1.

V. Interstellar Search

A preliminary search has been conducted for the $2_{12}-2_{11}$ transition of both rotamers of HC(:O)SH in the galactic radio sources W3, W3(OH) and Sgr B2 using the 100 m telescope of the Max Planck Institut für Radioastronomie. The results of this search were negative. Upper limits were obtained on the antenna temperature, T_A, of the $2_{12}-2_{11}$ transition. These are: $T_{AL}<0.027$ K in Sgr B2 and $T_{AL}<0.05$ K in W3 and W3(OH) for the *cis* rotamer, and $T_{AL}<0.05$ K in W3 and W3(OH) for the *trans* rotamer, where the limits represent three times the noise level. No reliable limits could be derived from the observations on the *trans* rotamer line in Sgr B2 because it is seriously blended with various Doppler shifted velocity components of the strong absorption spectrum of OH. The interstellar search for different rotational transitions of monothioformic acid is being continued.

Acknowledgements

The authors would like to express their thanks to Dr. Koichi Yamada for the use of his least squares centrifugal distortion fitting program. They also thank Dr. Brenda P. Winnewisser for commenting

on the manuscript and many stimulating discussions. The helpful criticism of Drs. Edwin Pearson, Robert Creswell and Manfred Winnewisser is acknowledged. One of us (W.H.H.) is grateful to the National Research Council of Canada for financial assistance in the form of a NATO Fellowship.

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