The Rotational Spectrum of Monothioformic Acid. II. *cis*- and *trans*-HC(:O)SD, DC(:O)SH, HC(:O)^{34}SH [1, 2]

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The rotational spectra of three isotopically substituted species of monothioformic acid, DCOSH, HCOSD, HCO^{34}SH, have been investigated. Transitions arising from two different isomeric forms have been observed in each instance. Rotational constants and quartic centrifugal distortion constants have been determined for all species using Watson's reduced Hamiltonian. It has been established that the two abundant isomers of monothioformic acid are the planar *cis* and *trans* thiol rotamers. The structure of *cis*-HC(:O)SH is found to be: r(C–H) = 1.100 Å, r(S–H) = 1.336 Å, r(C–S) = 1.771 Å, r(C=O) = 1.210 Å, ∢(OCS) = 122.4°, ∢(HSC) = 94.7° and ∢(HCS) = 114.6°; whereas for *trans*-HC(:O)SH: r(C–H) = 1.100 Å, r(S–H) = 1.351 Å, r(C–S) = 1.763 Å, r(C=O) = 1.218 Å, ∢(OCS) = 126.0°, ∢(HSC) = 92.7° and ∢(HCS) = 111.8°.

I. Introduction

The first paper in this series [1] (hereafter called I) presented our analysis of the ground state rotational spectra of the parent isotopic species of monothioformic acid, $H^{12}C^{16}O^{32}SH$. Two isomeric forms of this molecule were observed to be present in the gas phase at room temperature. These were identified in a preliminary communication [2] as the *cis* and *trans* rotamers of HC(:O)SH. In the present paper we report the results of our investigation of the rotational spectra of three isotopically substituted species of monothioformic acid: $H^{12}C^{16}O^{32}SD$, $D^{12}C^{16}O^{32}SH$ and $H^{12}C^{16}O^{34}SH$. For each isotope rotational transitions originating from the ground vibrational states of both isomeric forms have been assigned and measured. This additional isotopic data proves unequivocally that the abundant isomers of monothioformic acid are the *cis* and *trans* rotamers of HC(:O)SH. The molecular structure of each rotamer has been determined. The slight differences between the structures of the two rotamers are discussed in terms of nonbonded forces.

II. Experimental Procedures

The sample of monothioformic acid in which the labile hydrogen atom is replaced by a deuterium atom, HCOSD, was prepared by adding a deuterated (99% D) aqueous solution (50% D_2O) of orthophosphoric acid to solid sodium monothioformate, Na(HCOS). On the other hand, the sample in which the nonlabile hydrogen atom is replaced by a deuterium atom, DCOSH, was obtained by starting with formic-d acid, DCOOH, having 90% deuterium enrichment. Except for the use of the appropriate deuterium substituted acid, both preparations were performed following exactly the procedure described in Paper I for the preparation of the parent isotopic samples. The required deuterium enriched acids, orthophosphoric acid-d_3 and formic-d acid, were purchased from Merck Sharp and Dohme Canada Limited.

The samples of HCOSD and DCOSH were purified and handled following essentially the routines outlined for HCOSH in Paper I. However, it was necessary to deuterate the spectrometer cells before studing HCOSD in order to prevent serious reduction in the isotopic purity of the spectroscopic samples through acid proton exchange with water adsorbed on the cell walls. This was accomplished by repeatedly filling the cell with D_2O vapor. Nonetheless, the isotopic purity of the HCOSD samples was still degraded in the spectrometer cells from better than 90% to less than 60%. On the other hand, the DCOSH samples showed the expected deuterium enrichment of close to 90%. Both microwave and millimeter wave frequency measurements were made on each of the deuterium substituted isotopic species.

The sulfur-34 substituted rotamers, HC(:O)^{34}SH, were studied in natural isotopic abundance (4.22%). Because of the low intensity of the absorption lines, only microwave transitions were measured.

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[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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The microwave and millimeter wave spectrometers and their mode of operation were described in Paper I. The accuracy of the frequency measurements reported here is estimated to be better than ±30 kHz for the absorption lines of HC(:O)SD and DC(:O)SH and better than ±50 kHz for the weak lines of HC(:O)SH.

III. Rotational Spectra and Assignment

The rotational spectra of the three isotopically substituted species of monothioformic acid investigated in this work, HC(:O)SD, DC(:O)SH and HC(:O)^{34}SH, like that of HC(:O)SH, consist of only *a*- and *b*-type transitions. For the species studied using isotopically enriched samples, HC(:O)SD and DC(:O)SH, the analysis was straightforward and was carried through along the lines described in Paper I. More than 70 transitions have been measured and assigned for both the *cis* and *trans* rotamers of each of these two species. The measured transitions were selected from amongst the much larger number of observable lines in such a way as

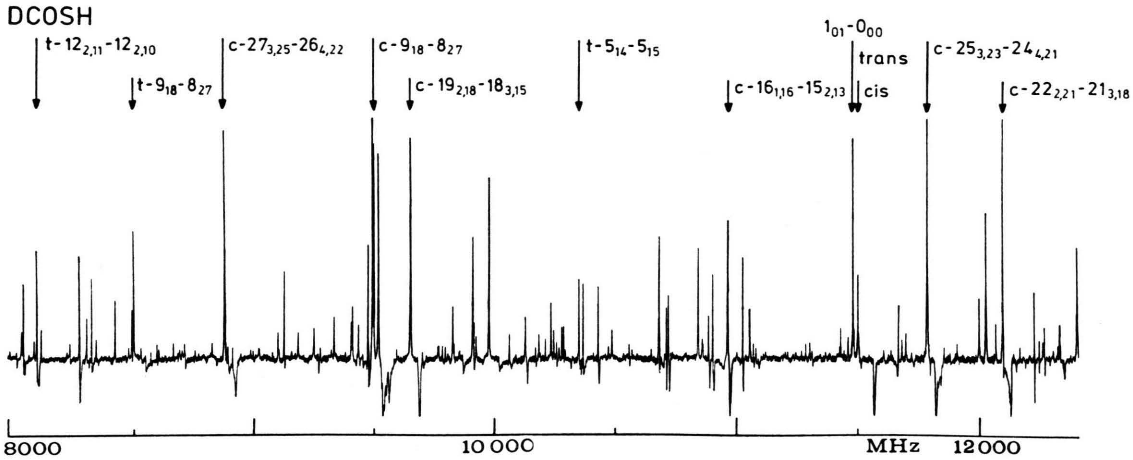


Fig. 1. Survey scan of the absorption spectrum of monothioformic-d acid, DCOSH, from 8 to 12.4 GHz.

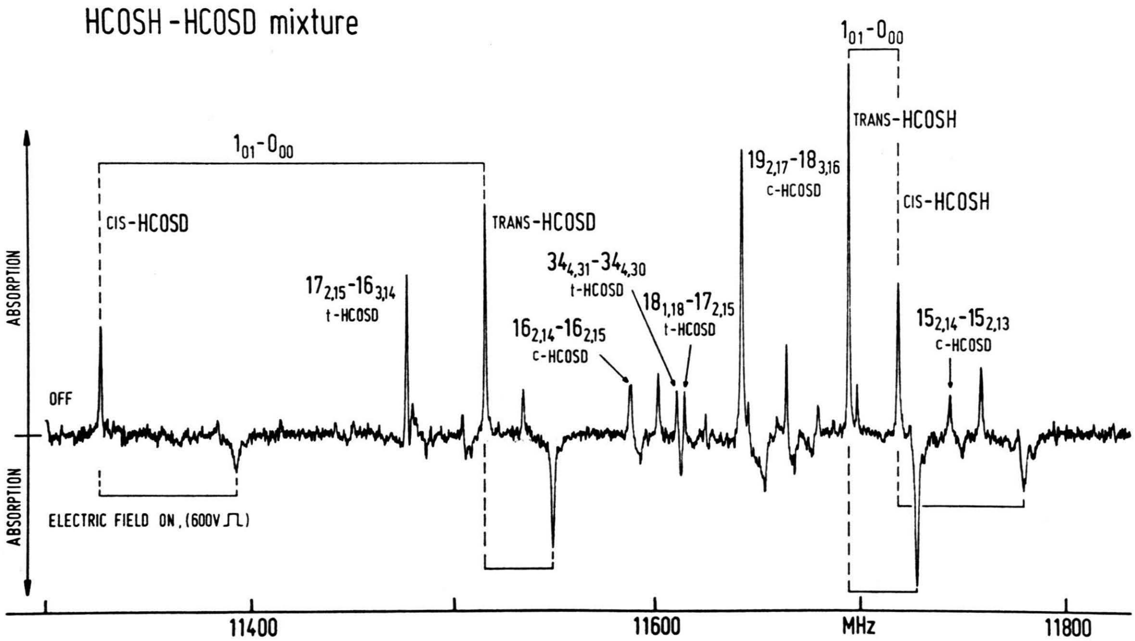


Fig. 2. The absorption spectrum of a mixed sample of HCOSH and HCOSD in the region 11.3—11.8 GHz.

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-DCOSH 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)	11477.6250(1.0)	11477.6193(0.0005)	0.0057	0.383	0.000
2(0, 2) -	1(0, 1)	22946.7100(1.0)	22946.7048(0.0010)	0.0052	1.148	0.383
2(1, 2) -	1(1, 1)	22265.1200(1.0)	22265.1210(0.0009)	-0.0010	2.523	1.780
2(1, 1) -	1(1, 0)	23645.3800(1.0)	23645.3860(0.0010)	-0.0060	2.592	1.803
3(0, 3) -	2(0, 2)	34398.7350(1.0)	34398.7325(0.0014)	0.0025	2.296	1.148
3(1, 3) -	2(1, 2)	33392.2600(1.0)	33392.2675(0.0014)	-0.0075	3.637	2.523
3(1, 2) -	2(1, 1)	35462.5400(1.0)	35462.5415(0.0014)	-0.0015	3.775	2.592
3(2, 2) -	2(2, 1)	34433.1050(1.0)	34433.1008(0.0013)	0.0042	7.932	6.783
3(2, 1) -	2(2, 0)	34466.9050(1.0)	34466.9187(0.0013)	-0.0137	7.933	6.783
8(0, 8) -	7(0, 7)	91114.9300(1.0)	91114.9384(0.0030)	-0.0084	13.723	10.684
8(1, 8) -	7(1, 7)	88894.3220(1.0)	88894.3182(0.0028)	0.0038	14.764	11.798
8(1, 7) -	7(1, 6)	94397.2310(1.0)	94397.2268(0.0029)	0.0042	15.591	12.442
8(2, 7) -	7(2, 6)	91712.8530(1.0)	91712.8275(0.0026)	0.0255	19.409	16.350
8(2, 6) -	7(2, 5)	92412.2420(1.0)	92412.2493(0.0026)	-0.0073	19.468	16.385
8(3, 6) -	7(3, 5)	91911.2750(1.0)	91911.2727(0.0022)	0.0023	26.468	23.402
8(3, 5) -	7(3, 4)	91927.5330(1.0)	91927.5452(0.0022)	-0.0122	26.469	23.402
8(4, 5) -	7(4, 4)	91879.7390(0.0)	91879.6983(0.0021)	0.0407	36.322	33.258
8(4, 4) -	7(4, 3)	91879.7390(0.0)	91879.8338(0.0021)	-0.0948	36.322	33.258
8(5, 4) -	7(5, 3)	91864.9800(1.0)	91864.9822(0.0027)	-0.0022	48.992	45.928
8(5, 3) -	7(5, 2)	91864.9800(0.0)	91864.9827(0.0027)	-0.0027	48.992	45.928
8(6, 3) -	7(6, 2)	91859.5210(1.0)	91859.5179(0.0039)	0.0031	64.473	61.409
8(6, 2) -	7(6, 1)	91859.5210(0.0)	91859.5179(0.0039)	0.0031	64.473	61.409
8(7, 2) -	7(7, 1)	91858.6170(0.0)	91858.6433(0.0057)	-0.0263	82.764	79.700
8(7, 1) -	7(7, 0)	91858.6170(0.0)	91858.6433(0.0057)	-0.0263	82.764	79.700
13(0,13) -	12(0,12)	146383.7590(1.0)	146383.7524(0.0028)	0.0066	34.472	29.589
13(1,13) -	12(1,12)	144037.8760(1.0)	144037.8741(0.0028)	0.0019	35.113	30.309
13(1,12) -	12(1,11)	152810.0930(1.0)	152810.1083(0.0028)	-0.0153	37.190	32.093
13(2,12) -	12(2,11)	148698.1160(1.0)	148698.0666(0.0027)	0.0494	40.413	35.453
13(2,11) -	12(2,10)	151490.7110(1.0)	151490.7055(0.0027)	0.0055	40.776	35.723
13(3,11) -	12(3,10)	149499.3380(1.0)	149499.3343(0.0029)	0.0037	47.558	42.572
13(3,10) -	12(3, 9)	149690.3700(1.0)	149690.3711(0.0030)	-0.0011	47.575	42.582
13(4,10) -	12(4, 9)	149413.4080(1.0)	149413.3971(0.0040)	0.0109	57.402	52.418
13(4, 9) -	12(4, 8)	149418.0760(1.0)	149418.0684(0.0040)	0.0076	57.402	52.418
13(5, 9) -	12(5, 8)	149343.4410(0.0)	149343.4052(0.0059)	0.0358	70.064	65.083
13(5, 8) -	12(5, 7)	149343.4410(0.0)	149343.4623(0.0059)	-0.0213	70.064	65.083
13(6, 8) -	12(6, 7)	149309.3400(1.0)	149309.3604(0.0084)	-0.0204	85.542	80.562
13(6, 7) -	12(6, 6)	149309.3400(0.0)	149309.3608(0.0084)	-0.0208	85.542	80.562
13(7, 7) -	12(7, 6)	149293.0290(0.0)	149293.0686(0.0115)	-0.0396	103.831	98.852
13(7, 6) -	12(7, 5)	149293.0290(0.0)	149293.0686(0.0115)	-0.0396	103.831	98.852
14(0,14) -	13(0,13)	157253.9550(1.0)	157253.9443(0.0029)	0.0107	39.718	34.472
14(1,14) -	13(1,13)	155014.3430(1.0)	155014.3455(0.0028)	-0.0025	40.284	35.113
** A TYPE Q BRANCH **						
5(1, 4) -	5(1, 5)	10349.5300(1.0)	10349.5293(0.0013)	0.0007	7.322	6.977
6(1, 5) -	6(1, 6)	14485.9500(1.0)	14485.9500(0.0017)	0.0000	9.686	9.203
7(1, 6) -	7(1, 7)	19307.5100(1.0)	19307.4993(0.0022)	0.0107	12.442	11.798
9(1, 8) -	9(1, 9)	30989.1100(1.0)	30989.1008(0.0032)	0.0092	19.131	18.098
12(2,10) -	12(2,11)	8108.1200(1.0)	8108.1174(0.0016)	0.0026	35.723	35.453
13(2,11) -	13(2,12)	10900.7600(1.0)	10900.7563(0.0019)	0.0037	40.776	40.413
14(2,12) -	14(2,13)	14290.5700(1.0)	14290.5717(0.0023)	-0.0017	46.228	45.751
15(2,13) -	15(2,14)	18322.8400(1.0)	18322.8426(0.0026)	-0.0026	52.079	51.468
17(2,15) -	17(2,16)	28448.1200(1.0)	28448.1221(0.0032)	-0.0021	64.980	64.031
18(2,16) -	18(2,17)	34583.1400(1.0)	34583.1600(0.0036)	-0.0200	72.030	70.876
21(3,18) -	21(3,19)	8055.1500(1.0)	8055.1463(0.0027)	0.0037	101.560	101.292
22(3,19) -	22(3,20)	10429.1900(1.0)	10429.1842(0.0036)	0.0058	110.084	109.736
23(3,20) -	23(3,21)	13308.5400(1.0)	13308.5334(0.0046)	0.0066	119.006	118.562
24(3,21) -	24(3,22)	16752.2900(1.0)	16752.2636(0.0060)	0.0264	128.330	127.771
27(3,24) -	27(3,25)	30996.6100(0.0)	30996.5376(0.0130)	0.0724	158.718	157.684
** B TYPE R BRANCH **						
4(1, 4) -	3(0, 3)	84711.3600(1.0)	84711.3549(0.0032)	0.0051	5.121	2.296
5(1, 5) -	4(0, 4)	94511.4760(1.0)	94511.4906(0.0035)	-0.0146	6.977	3.824
11(1,11) -	10(0,10)	148453.5230(1.0)	148453.5158(0.0039)	0.0072	25.871	20.919
12(1,12) -	11(0,11)	157026.7420(1.0)	157026.7544(0.0038)	-0.0124	30.309	25.071

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-DCOSH (CONTINUED

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
** B TYPE Q BRANCH **						
14(1,13)	- 14(0,14)	88617.2640(1.0)	88617.2536(0.0036)	0.0104	42.673	39.718
20(1,19)	- 20(0,20)	145533.6910(1.0)	145533.6973(0.0067)	-0.0063	83.589	78.735
21(1,20)	- 21(0,21)	156971.8880(1.0)	156971.8669(0.0087)	0.0211	91.725	86.489
10(2, 9)	- 10(1,10)	146004.7640(1.0)	146004.7763(0.0042)	-0.0123	26.671	21.800
11(2,10)	- 11(1,11)	149923.8710(1.0)	149923.9003(0.0041)	-0.0293	30.872	25.871
12(2,11)	- 12(1,12)	154213.4090(1.0)	154213.4127(0.0041)	-0.0037	35.453	30.309
** B TYPE P BRANCH **						
1(1, 1)	- 2(0, 2)	18939.6800(1.0)	18939.6904(0.0015)	-0.0104	1.780	1.148
5(0, 5)	- 4(1, 4)	18331.7200(1.0)	18331.7057(0.0020)	0.0143	5.733	5.121
6(0, 6)	- 5(1, 5)	31274.8400(1.0)	31274.8605(0.0023)	-0.0205	8.020	6.977
10(0,10)	- 9(1, 9)	84580.3740(1.0)	84580.3564(0.0032)	0.0176	20.919	18.098
15(0,15)	- 14(1,14)	151092.5570(1.0)	151092.5834(0.0031)	-0.0264	45.324	40.284
7(2, 6)	- 8(1, 7)	22748.5600(1.0)	22748.5773(0.0041)	-0.0173	16.350	15.591
8(2, 7)	- 9(1, 8)	8326.4700(1.0)	8326.4798(0.0042)	-0.0098	19.409	19.131
11(1,10)	- 10(2, 9)	21366.3800(1.0)	21366.3771(0.0044)	0.0029	27.383	26.671
19(1,18)	- 18(2,17)	148385.7930(1.0)	148385.7837(0.0056)	0.0093	75.826	70.876
12(2,10)	- 13(1,13)	18283.6650(1.0)	18283.6560(0.0044)	0.0090	35.723	35.113
13(2,11)	- 14(1,14)	14760.0200(1.0)	14760.0160(0.0044)	0.0040	40.776	40.284
14(2,12)	- 15(1,15)	12221.0700(1.0)	12221.0626(0.0044)	0.0074	46.228	45.820
15(2,13)	- 16(1,16)	10709.5300(1.0)	10709.5326(0.0044)	-0.0026	52.079	51.722
16(2,14)	- 17(1,17)	10257.0500(1.0)	10257.0439(0.0043)	0.0061	58.329	57.987
17(2,15)	- 18(1,18)	10883.5400(1.0)	10883.5399(0.0045)	0.0001	64.980	64.617
18(2,16)	- 19(1,19)	12597.4400(1.0)	12597.4469(0.0054)	-0.0069	72.030	71.609
19(2,17)	- 20(1,20)	15396.3650(1.0)	15396.3744(0.0071)	-0.0094	79.479	78.965
14(3,12)	- 15(2,13)	25508.5600(1.0)	25508.5658(0.0046)	-0.0058	52.930	52.079
15(3,13)	- 16(2,14)	10678.6950(1.0)	10678.6856(0.0045)	0.0094	58.686	58.329
18(2,16)	- 17(3,15)	20351.8200(1.0)	20351.8358(0.0045)	-0.0158	72.030	71.351
22(2,20)	- 21(3,19)	87501.3190(1.0)	87501.3517(0.0081)	-0.0327	104.210	101.292
10(3, 7)	- 11(2,10)	86436.6770(1.0)	86436.6714(0.0057)	0.0056	33.755	30.872
17(3,14)	- 18(2,17)	16656.5500(1.0)	16656.5425(0.0039)	0.0075	71.432	70.876
18(3,15)	- 19(2,18)	8277.4100(1.0)	8277.4046(0.0042)	0.0054	78.372	78.096
23(2,22)	- 22(3,19)	18720.8900(1.0)	18720.8880(0.0086)	0.0020	110.708	110.084
26(2,25)	- 25(3,22)	30113.9200(0.0)	30113.9358(0.0177)	-0.0158	139.060	138.056
27(2,26)	- 26(3,23)	31874.1400(0.0)	31874.1709(0.0224)	-0.0309	149.248	148.185
22(4,19)	- 23(3,20)	17129.8300(1.0)	17129.8471(0.0083)	-0.0171	119.578	119.006
25(3,22)	- 24(4,21)	12560.4900(0.0)	12560.4277(0.0111)	0.0623	138.056	137.637
17(4,13)	- 18(3,16)	87713.0670(1.0)	87713.0518(0.0093)	0.0152	81.186	78.260
23(4,19)	- 24(3,22)	20153.0400(1.0)	20153.0564(0.0080)	-0.0164	128.443	127.771
24(4,20)	- 25(3,23)	9473.2400(0.0)	9473.2655(0.0090)	-0.0255	137.678	137.362
27(3,25)	- 26(4,22)	11024.2400(0.0)	11024.1918(0.0121)	0.0482	157.684	157.316
29(3,27)	- 28(4,24)	30017.1600(0.0)	30017.0965(0.0170)	0.0635	179.524	178.523

TABLE II. OBSERVED AND CALCULATED FREQUENCIES OF CIS-DCOSH 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)	11497.9300(1.0)	11497.9146(0.0006)	0.0154	0.384	0.000
2(0, 2)	- 1(0, 1)	22987.4750(1.0)	22987.4772(0.0012)	-0.0022	1.150	0.384
2(1, 2)	- 1(1, 1)	22310.0050(1.0)	22309.9880(0.0011)	0.0170	2.539	1.795
2(1, 1)	- 1(1, 0)	23681.7000(1.0)	23681.7120(0.0012)	-0.0120	2.608	1.818
3(0, 3)	- 2(0, 2)	34460.3200(1.0)	34460.3452(0.0017)	-0.0252	2.300	1.150
3(1, 3)	- 2(1, 2)	33459.6600(1.0)	33459.6726(0.0017)	-0.0126	3.655	2.539
3(1, 2)	- 2(1, 1)	35517.1400(1.0)	35517.1336(0.0017)	0.0064	3.792	2.608
3(2, 2)	- 2(2, 1)	34494.0400(1.0)	34494.0327(0.0015)	0.0073	7.992	6.841
3(2, 1)	- 2(2, 0)	34527.0950(1.0)	34527.1025(0.0015)	-0.0075	7.993	6.842
8(0, 8)	- 7(0, 7)	91292.0500(1.0)	91292.0446(0.0036)	0.0054	13.749	10.704
8(1, 8)	- 7(1, 7)	89076.8980(1.0)	89076.8761(0.0035)	0.0219	14.805	11.834
8(1, 7)	- 7(1, 6)	94546.1030(1.0)	94546.1060(0.0035)	-0.0030	15.627	12.474
8(2, 7)	- 7(2, 6)	91877.1900(1.0)	91877.2170(0.0031)	-0.0270	19.490	16.425
8(2, 6)	- 7(2, 5)	92561.4660(1.0)	92561.4554(0.0031)	0.0106	19.547	16.460
8(3, 6)	- 7(3, 5)	92071.6670(1.0)	92071.6494(0.0027)	0.0176	26.619	23.548
8(3, 5)	- 7(3, 4)	92087.2990(1.0)	92087.3064(0.0027)	-0.0074	26.620	23.548
8(4, 5)	- 7(4, 4)	92041.0800(0.0)	92041.0199(0.0025)	0.0601	36.572	33.502
8(4, 4)	- 7(4, 3)	92041.0800(0.0)	92041.1482(0.0025)	-0.0682	36.572	33.502
8(5, 4)	- 7(5, 3)	92027.1120(1.0)	92027.1007(0.0032)	0.0113	49.368	46.298
8(5, 3)	- 7(5, 2)	92027.1120(0.0)	92027.1012(0.0032)	0.0108	49.368	46.298
8(6, 3)	- 7(6, 2)	92022.3120(1.0)	92022.3353(0.0048)	-0.0233	65.004	61.935
8(6, 2)	- 7(6, 1)	92022.3120(0.0)	92022.3353(0.0048)	-0.0233	65.004	61.935
13(0,13)	- 12(0,12)	146700.4210(1.0)	146700.4183(0.0035)	0.0027	34.541	29.648
13(1,13)	- 12(1,12)	144341.2940(1.0)	144341.2890(0.0034)	0.0050	35.197	30.382
13(1,12)	- 12(1,11)	153064.5730(1.0)	153064.5924(0.0034)	-0.0194	37.261	32.156
13(2,12)	- 12(2,11)	148971.0620(1.0)	148971.0438(0.0033)	0.0182	40.532	35.563
13(2,11)	- 12(2,10)	151709.1670(1.0)	151709.1683(0.0033)	-0.0013	40.888	35.827
13(3,11)	- 12(3,10)	149756.3290(1.0)	149756.3342(0.0036)	-0.0052	47.746	42.750
13(3,10)	- 12(3, 9)	149940.1930(1.0)	149940.2070(0.0036)	-0.0140	47.762	42.761
13(4,10)	- 12(4, 9)	149671.6220(1.0)	149671.5988(0.0049)	0.0232	57.688	52.696
13(4, 9)	- 12(4, 8)	149676.0360(1.0)	149676.0208(0.0049)	0.0152	57.688	52.696
13(5, 9)	- 12(5, 8)	149603.8970(0.0)	149603.8691(0.0071)	0.0279	70.477	65.487
13(5, 8)	- 12(5, 7)	149603.8970(0.0)	149603.9223(0.0071)	-0.0253	70.477	65.487
13(6, 8)	- 12(6, 7)	149571.5230(1.0)	149571.5208(0.0102)	0.0022	86.110	81.121
13(6, 7)	- 12(6, 6)	149571.5230(0.0)	149571.5212(0.0102)	0.0018	86.110	81.121
13(7, 7)	- 12(7, 6)	149556.6540(0.0)	149556.7017(0.0139)	-0.0477	104.582	99.593
13(7, 6)	- 12(7, 5)	149556.6540(0.0)	149556.7017(0.0139)	-0.0477	104.582	99.593
14(0,14)	- 13(0,13)	157599.8420(1.0)	157599.8327(0.0035)	0.0093	39.798	34.541
14(1,14)	- 13(1,13)	155342.5890(1.0)	155342.5754(0.0034)	0.0136	40.379	35.197
** A TYPE Q BRANCH **						
5(1, 4)	- 5(1, 5)	10285.5150(1.0)	10285.4958(0.0016)	0.0192	7.345	7.002
6(1, 5)	- 6(1, 6)	14396.3950(1.0)	14396.3786(0.0021)	0.0164	9.713	9.232
7(1, 6)	- 7(1, 7)	19188.2700(1.0)	19188.2572(0.0027)	0.0128	12.474	11.834
9(1, 8)	- 9(1, 9)	30798.7000(1.0)	30798.6835(0.0039)	0.0165	19.173	18.146
13(2,11)	- 13(2,12)	10676.3100(1.0)	10676.3052(0.0024)	0.0048	40.888	40.532
14(2,12)	- 14(2,13)	14002.3550(1.0)	14002.3683(0.0028)	-0.0133	46.347	45.880
15(2,13)	- 15(2,14)	17961.9500(1.0)	17961.9597(0.0032)	-0.0097	52.206	51.607
17(2,15)	- 17(2,16)	27917.8000(1.0)	27917.8128(0.0039)	-0.0128	65.125	64.194
18(2,16)	- 18(2,17)	33957.9500(1.0)	33957.9783(0.0043)	-0.0283	72.185	71.052
22(3,19)	- 22(3,20)	10061.3600(1.0)	10061.3516(0.0042)	0.0084	110.365	110.029
23(3,20)	- 23(3,21)	12846.5500(1.0)	12846.5506(0.0054)	-0.0006	119.300	118.871
24(3,21)	- 24(3,22)	16181.3100(1.0)	16181.2996(0.0071)	0.0104	128.636	128.096
27(3,24)	- 27(3,25)	30011.8400(0.0)	30011.7481(0.0154)	0.0919	159.063	158.062
** B TYPE R BRANCH **						
4(1, 4)	- 3(0, 3)	85235.7180(1.0)	85235.6949(0.0040)	0.0231	5.143	2.300
5(1, 5)	- 4(0, 4)	95065.7040(1.0)	95065.7182(0.0043)	-0.0142	7.002	3.831
11(1,11)	- 10(0,10)	149180.0180(1.0)	149180.0035(0.0048)	0.0145	25.935	20.959
12(1,12)	- 11(0,11)	157773.3610(1.0)	157773.3680(0.0046)	-0.0070	30.382	25.120
** B TYPE Q BRANCH **						
14(1,13)	- 14(0,14)	88623.8050(1.0)	88623.7999(0.0045)	0.0051	42.754	39.798
20(1,19)	- 20(0,20)	145114.1930(1.0)	145114.2064(0.0082)	-0.0134	83.744	78.904
21(1,20)	- 21(0,21)	156498.6190(1.0)	156498.5904(0.0107)	0.0286	91.896	86.676

TABLE II. OBSERVED AND CALCULATED FREQUENCIES OF CIS-DCOSH (CONTINUED

TRANSITION UPPER STATE	LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	LOWER STATE
10(2, 9) -	10(1,10)	147147.7680(1.0)	147147.7778(0.0053)	-0.0098	26.764	21.856
11(2,10) -	11(1,11)	151041.2370(1.0)	151041.2630(0.0052)	-0.0260	30.973	25.935
12(2,11) -	12(1,12)	155302.6840(1.0)	155302.6949(0.0052)	-0.0109	35.563	30.382
** B TYPE P BRANCH **						
1(1, 1) -	2(0, 2)	19323.2900(1.0)	19323.3056(0.0019)	-0.0156	1.795	1.150
5(0, 5) -	4(1, 4)	17995.4700(1.0)	17995.4551(0.0024)	0.0149	5.743	5.143
6(0, 6) -	5(1, 5)	30953.8000(1.0)	30953.7920(0.0028)	0.0080	8.035	7.002
10(0,10) -	9(1, 9)	84338.4520(1.0)	84338.4333(0.0038)	0.0187	20.959	18.146
15(0,15) -	14(1,14)	151039.1430(1.0)	151039.1770(0.0036)	-0.0340	45.417	40.379
7(2, 5) -	8(1, 7)	23923.8900(1.0)	23923.9135(0.0049)	-0.0235	16.425	15.627
8(2, 7) -	9(1, 8)	9497.4300(1.0)	9497.4510(0.0050)	-0.0210	19.490	19.173
11(1,10) -	10(2, 9)	20202.0900(1.0)	20202.0793(0.0051)	0.0107	27.438	26.764
12(1,11) -	11(2,10)	35445.1500(1.0)	35445.1377(0.0052)	0.0123	32.156	30.973
19(1,18) -	18(2,17)	147309.0040(1.0)	147309.0225(0.0064)	-0.0185	75.966	71.052
13(2,11) -	14(1,14)	15266.1900(1.0)	15266.1795(0.0058)	0.0105	40.888	40.379
14(2,12) -	15(1,15)	12605.8400(1.0)	12605.8343(0.0057)	0.0057	46.347	45.927
15(2,13) -	16(1,16)	10961.8150(1.0)	10961.8062(0.0056)	0.0088	52.206	51.841
16(2,14) -	17(1,17)	10366.6000(1.0)	10366.5891(0.0054)	0.0109	58.466	58.120
17(2,15) -	18(1,18)	10841.3000(1.0)	10841.2870(0.0056)	0.0130	65.125	64.763
18(2,16) -	19(1,19)	12395.6900(1.0)	12395.6874(0.0065)	0.0026	72.185	71.771
19(2,17) -	20(1,20)	15028.8500(1.0)	15028.8813(0.0085)	-0.0313	79.644	79.143
14(3,12) -	15(2,13)	27579.7800(1.0)	27579.7746(0.0051)	0.0054	53.126	52.206
15(3,13) -	16(2,14)	12784.5300(1.0)	12784.5197(0.0050)	0.0103	58.892	58.466
18(2,16) -	17(3,15)	18168.5600(1.0)	18168.5772(0.0051)	-0.0172	72.185	71.579
19(2,17) -	18(3,16)	34311.0400(1.0)	34311.0554(0.0056)	-0.0154	79.644	78.500
22(2,20) -	21(3,19)	85165.1040(1.0)	85165.1042(0.0096)	-0.0002	104.412	101.571
10(3, 7) -	11(2,10)	88290.9550(1.0)	88290.9487(0.0064)	0.0063	33.918	30.973
17(3,14) -	18(2,17)	18124.7700(1.0)	18124.7639(0.0047)	0.0061	71.657	71.052
18(3,15) -	19(2,18)	9651.6700(1.0)	9651.6632(0.0050)	0.0068	78.608	78.286
22(2,21) -	21(3,18)	12092.4100(1.0)	12092.4073(0.0080)	0.0027	102.233	101.830
23(2,22) -	22(3,19)	17878.1100(1.0)	17878.1144(0.0100)	-0.0044	110.961	110.365
25(2,24) -	24(3,21)	26828.5800(0.0)	26828.5901(0.0163)	-0.0101	129.531	128.636
27(2,25) -	26(3,23)	31855.3700(0.0)	31855.4156(0.0265)	-0.0456	149.579	148.516
17(4,14) -	18(3,15)	86995.2090(1.0)	86995.2030(0.0097)	0.0060	81.510	78.608
22(4,19) -	23(3,20)	20052.1650(1.0)	20052.2094(0.0105)	-0.0444	119.969	119.300
17(4,13) -	18(3,16)	90315.8710(1.0)	90315.8512(0.0098)	0.0198	81.513	78.500
24(4,20) -	25(3,23)	11782.8500(0.0)	11782.9103(0.0123)	-0.0603	138.096	137.703
27(3,25) -	26(4,22)	8876.9700(0.0)	8876.8667(0.0161)	0.1033	158.062	157.765

TABLE III. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-HCOSD 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)	11516.3100(1.0)	11516.3042(0.0036)	0.0058	0.384	0.000
2(0, 2) -	1(0, 1)	23025.3650(1.0)	23025.3616(0.0012)	0.0034	1.152	0.384
2(1, 2) -	1(1, 1)	22376.5400(1.0)	22376.5326(0.0011)	0.0074	2.622	1.876
2(1, 1) -	1(1, 0)	23688.6900(1.0)	23688.6966(0.0012)	-0.0066	2.688	1.898
3(0, 3) -	2(0, 2)	34519.9500(1.0)	34519.9326(0.0017)	0.0174	2.304	1.152
3(1, 3) -	2(1, 2)	33560.1600(1.0)	33560.1714(0.0016)	-0.0114	3.742	2.622
3(1, 2) -	2(1, 1)	35528.2800(1.0)	35528.3102(0.0017)	-0.0302	3.873	2.688
3(2, 2) -	2(2, 1)	34549.1000(1.0)	34549.1142(0.0015)	-0.0142	8.316	7.163
3(2, 1) -	2(2, 0)	34577.7800(1.0)	34577.7652(0.0015)	0.0148	8.317	7.163
5(0, 5) -	4(0, 4)	57436.8870(1.0)	57436.8731(0.0027)	0.0139	5.754	3.838
5(1, 4) -	4(1, 3)	59188.2580(1.0)	59188.2592(0.0026)	-0.0012	7.427	5.453
5(2, 4) -	4(2, 3)	57564.8600(1.0)	57564.8649(0.0022)	-0.0049	11.772	9.852
5(2, 3) -	4(2, 2)	57707.8700(1.0)	57707.8659(0.0022)	0.0041	11.781	9.856
5(3, 3) -	4(3, 2)	57605.9670(1.0)	57605.9803(0.0019)	-0.0133	19.287	17.365
5(3, 2) -	4(3, 1)	57606.9770(1.0)	57607.0064(0.0019)	-0.0294	19.287	17.365
5(4, 2) -	4(4, 1)	57599.2870(1.0)	57599.3088(0.0021)	-0.0218	29.802	27.881
5(4, 1) -	4(4, 0)	57599.2870(0.0)	57599.3110(0.0021)	-0.0240	29.802	27.881
8(0, 8) -	7(0, 7)	91529.1120(1.0)	91529.1060(0.0035)	0.0060	13.779	10.726
8(1, 8) -	7(1, 7)	89363.4190(1.0)	89363.4186(0.0033)	0.0004	14.926	11.946
8(1, 7) -	7(1, 6)	94597.9210(1.0)	94597.9168(0.0034)	0.0042	15.713	12.558
8(2, 7) -	7(2, 6)	92037.5930(1.0)	92037.5815(0.0030)	0.0115	19.833	16.763
8(2, 6) -	7(2, 5)	92631.9090(1.0)	92631.9106(0.0030)	-0.0016	19.883	16.793
8(3, 6) -	7(3, 5)	92206.6600(1.0)	92206.6393(0.0030)	0.0207	27.360	24.284
8(3, 5) -	7(3, 4)	92218.9330(1.0)	92218.9283(0.0030)	0.0047	27.360	24.284
8(4, 5) -	7(4, 4)	92179.5140(0.0)	92179.4636(0.0039)	0.0504	37.873	34.798
8(4, 4) -	7(4, 3)	92179.5140(0.0)	92179.5547(0.0039)	-0.0407	37.873	34.798
8(5, 4) -	7(5, 3)	92167.3710(1.0)	92167.3631(0.0059)	0.0079	51.390	48.315
8(5, 3) -	7(5, 2)	92167.3710(0.0)	92167.3635(0.0059)	0.0075	51.390	48.315
8(6, 3) -	7(6, 2)	92163.1930(1.0)	92163.1950(0.0087)	-0.0020	67.907	64.832
8(6, 2) -	7(6, 1)	92163.1930(0.0)	92163.1950(0.0087)	-0.0020	67.907	64.832
8(7, 2) -	7(7, 1)	92162.9670(0.0)	92162.9988(0.0122)	-0.0318	87.421	84.347
8(7, 1) -	7(7, 0)	92162.9670(0.0)	92162.9988(0.0122)	-0.0318	87.421	84.347
10(1, 9) -	9(1, 8)	118122.6730(1.0)	118122.6635(0.0037)	0.0095	23.202	19.261
** A TYPE Q BRANCH **						
5(1, 4) -	5(1, 5)	9839.2300(1.0)	9839.2197(0.0014)	0.0103	7.427	7.099
6(1, 5) -	6(1, 6)	13772.2450(1.0)	13772.2291(0.0018)	0.0159	9.796	9.336
8(1, 7) -	8(1, 8)	23591.9250(1.0)	23591.9248(0.0028)	0.0002	15.713	14.926
10(1, 9) -	10(1,10)	35990.0400(1.0)	35990.0383(0.0037)	0.0017	23.202	22.001
13(2,11) -	13(2,12)	9335.0000(1.0)	9335.0021(0.0019)	-0.0021	41.226	40.915
14(2,12) -	14(2,13)	12274.0850(1.0)	12274.0859(0.0022)	-0.0009	46.684	46.275
15(2,13) -	15(2,14)	15789.4700(1.0)	15789.4710(0.0026)	-0.0010	52.541	52.014
17(2,15) -	17(2,16)	24698.1000(1.0)	24698.1104(0.0033)	-0.0104	65.454	64.630
22(3,19) -	22(3,20)	8026.1400(1.0)	8026.1383(0.0034)	0.0017	111.154	110.886
23(3,20) -	23(3,21)	10282.0800(1.0)	10282.0677(0.0044)	0.0123	120.084	119.741
24(3,21) -	24(3,22)	12999.9500(1.0)	12999.9256(0.0058)	0.0244	129.414	128.981
25(3,22) -	25(3,23)	16233.2750(0.0)	16233.2327(0.0076)	0.0423	139.145	138.603
29(3,26) -	29(3,27)	35278.0800(0.0)	35277.9266(0.0212)	0.1534	182.095	180.918
** B TYPE Q BRANCH **						
8(1, 7) -	8(0, 8)	57996.8450(1.0)	57996.8571(0.0028)	-0.0121	15.713	13.779
14(1,13) -	14(0,14)	88297.3480(1.0)	88297.3489(0.0041)	-0.0009	42.865	39.920
** B TYPE P BRANCH **						
1(1, 1) -	2(0, 2)	21697.6900(1.0)	21697.7037(0.0021)	-0.0137	1.876	1.152
2(1, 2) -	3(0, 3)	9554.3000(1.0)	9554.3037(0.0019)	-0.0037	2.622	2.304
5(0, 5) -	4(1, 4)	15576.8850(1.0)	15576.8808(0.0021)	0.0042	5.754	5.234
7(2, 6) -	8(1, 7)	31465.4100(1.0)	31465.4221(0.0051)	-0.0121	16.763	15.713
8(2, 7) -	9(1, 8)	17132.7550(1.0)	17132.7600(0.0049)	-0.0050	19.833	19.261
11(1,10) -	10(2, 9)	12361.4800(1.0)	12361.4744(0.0045)	0.0056	27.533	27.121
14(1,13) -	13(2,12)	58470.7940(1.0)	58470.7923(0.0041)	0.0017	42.865	40.915
16(1,15) -	15(2,14)	90239.8800(1.0)	90239.8977(0.0046)	-0.0177	55.024	52.014
10(2, 8) -	11(1,11)	34261.3600(1.0)	34261.3482(0.0046)	0.0118	27.237	26.094
14(2,12) -	15(1,15)	15790.0700(1.0)	15790.0751(0.0046)	-0.0051	46.684	46.157
15(2,13) -	16(1,16)	13408.9800(1.0)	13408.9851(0.0044)	-0.0051	52.541	52.093

TABLE III. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-HCOSD (CONTINUED

TRANSITION UPPER STATE	LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	LOWER STATE
16(2,14) -	17(1,17)	12007.9800(1.0)	12007.9854(0.0043)	-0.0054	58.797	58.397
17(2,15) -	18(1,18)	11614.3300(1.0)	11614.3135(0.0042)	0.0165	65.454	65.066
18(2,16) -	19(1,19)	12245.3100(1.0)	12245.3038(0.0046)	0.0062	72.510	72.102
19(2,17) -	20(1,20)	13908.5350(1.0)	13908.5420(0.0059)	-0.0070	79.967	79.503
20(2,18) -	21(1,21)	16602.4300(1.0)	16602.4259(0.0084)	0.0041	87.823	87.269
15(3,13) -	16(2,14)	26386.7700(1.0)	26386.7632(0.0044)	0.0068	59.677	58.797
16(3,14) -	17(2,15)	11477.6400(1.0)	11477.6428(0.0042)	-0.0028	65.836	65.454
19(2,17) -	18(3,16)	19642.7700(1.0)	19642.7798(0.0052)	-0.0098	79.967	79.312
20(2,18) -	19(3,17)	35838.6000(1.0)	35838.6065(0.0067)	-0.0065	87.823	86.628
19(3,15) -	20(2,19)	10754.8200(1.0)	10754.8222(0.0046)	-0.0022	86.744	86.385
23(2,22) -	22(3,19)	11049.9450(1.0)	11049.9392(0.0066)	0.0058	111.522	111.154
24(2,23) -	23(3,20)	16929.3200(1.0)	16929.3106(0.0079)	0.0094	120.649	120.084
28(2,27) -	27(3,24)	31805.4400(0.0)	31805.5014(0.0202)	-0.0614	160.874	159.813
29(2,28) -	28(3,25)	33088.1800(0.0)	33088.3162(0.0258)	-0.1362	171.855	170.752
18(4,15) -	19(3,16)	91643.7390(1.0)	91643.7404(0.0110)	-0.0014	89.801	86.744
24(4,21) -	25(3,22)	10242.4250(0.0)	10242.5325(0.0163)	-0.1075	139.487	139.145
28(3,25) -	27(4,24)	35925.3600(0.0)	35925.0898(0.0286)	0.2702	170.752	169.553
25(4,21) -	26(3,24)	16496.8250(0.0)	16496.9057(0.0136)	-0.0807	149.159	148.609
29(3,27) -	28(4,24)	14317.1000(0.0)	14316.9588(0.0186)	0.1412	180.918	180.441

TABLE IV. OBSERVED AND CALCULATED FREQUENCIES OF CIS-HCOSD IN MHz

TRANSITION UPPER STATE	LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	LOWER STATE
** A TYPE R BRANCH **						
1(0, 1) -	0(0, 0)	11325.1550(1.0)	11325.1513(0.0008)	0.0037	0.378	0.000
2(0, 2) -	1(0, 1)	22645.0200(1.0)	22645.0216(0.0015)	-0.0016	1.133	0.378
2(1, 2) -	1(1, 1)	22064.9400(1.0)	22064.9254(0.0014)	0.0146	2.751	2.015
2(1, 1) -	1(1, 0)	23235.7000(1.0)	23235.7151(0.0015)	-0.0151	2.810	2.035
3(0, 3) -	2(0, 2)	33954.3500(1.0)	33954.3339(0.0022)	0.0161	2.266	1.133
3(1, 3) -	2(1, 2)	33093.9900(1.0)	33093.9850(0.0021)	0.0050	3.855	2.751
3(1, 2) -	2(1, 1)	34850.0600(1.0)	34850.0914(0.0022)	-0.0314	3.972	2.810
3(2, 2) -	2(2, 1)	33975.7400(1.0)	33975.7132(0.0019)	0.0268	8.854	7.721
3(2, 1) -	2(2, 0)	33996.4900(1.0)	33996.5272(0.0019)	-0.0372	8.855	7.721
5(0, 5) -	4(0, 4)	56520.2750(1.0)	56520.2828(0.0034)	-0.0078	5.660	3.775
5(1, 4) -	4(1, 3)	58064.7380(1.0)	58064.7186(0.0033)	0.0194	7.459	5.522
5(2, 4) -	4(2, 3)	56613.6200(1.0)	56613.6223(0.0029)	-0.0023	12.254	10.365
5(2, 3) -	4(2, 2)	56717.5580(1.0)	56717.5652(0.0029)	-0.0072	12.260	10.368
5(3, 3) -	4(3, 2)	56643.9440(1.0)	56643.9323(0.0027)	0.0117	20.489	18.599
5(3, 2) -	4(3, 1)	56644.5600(1.0)	56644.5393(0.0027)	0.0207	20.489	18.599
5(4, 2) -	4(4, 1)	56639.5590(1.0)	56639.5419(0.0030)	0.0171	32.013	30.124
5(4, 1) -	4(4, 0)	56639.5590(0.0)	56639.5429(0.0030)	0.0161	32.013	30.124
8(0, 8) -	7(0, 7)	90161.2710(1.0)	90161.2715(0.0046)	-0.0005	13.563	10.555
8(1, 8) -	7(1, 7)	88153.9810(1.0)	88153.9955(0.0044)	-0.0145	14.887	11.946
8(1, 7) -	7(1, 6)	92828.2980(1.0)	92828.3023(0.0045)	-0.0043	15.589	12.493
8(2, 7) -	7(2, 6)	90532.8240(1.0)	90532.8261(0.0041)	-0.0021	20.182	17.162
8(2, 6) -	7(2, 5)	90966.2990(1.0)	90966.2968(0.0041)	0.0022	20.218	17.184
8(3, 6) -	7(3, 5)	90657.0580(1.0)	90657.0524(0.0041)	0.0056	28.426	25.402
8(3, 5) -	7(3, 4)	90664.3140(1.0)	90664.3246(0.0041)	-0.0106	28.426	25.402
8(4, 5) -	7(4, 4)	90637.3660(0.0)	90637.3495(0.0052)	0.0165	39.949	36.925
8(4, 4) -	7(4, 3)	90637.3660(0.0)	90637.3934(0.0052)	-0.0274	39.949	36.925
8(5, 4) -	7(5, 3)	90629.6380(1.0)	90629.6281(0.0076)	0.0099	54.762	51.739
8(5, 3) -	7(5, 2)	90629.6380(0.0)	90629.6282(0.0076)	0.0098	54.762	51.739
8(6, 3) -	7(6, 2)	90627.9160(1.0)	90627.9186(0.0111)	-0.0026	72.862	69.839
8(6, 2) -	7(6, 1)	90627.9160(0.0)	90627.9186(0.0111)	-0.0026	72.862	69.839
8(7, 2) -	7(7, 1)	90629.3070(0.0)	90629.3341(0.0154)	-0.0271	94.246	91.222
8(7, 1) -	7(7, 0)	90629.3070(0.0)	90629.3341(0.0154)	-0.0271	94.246	91.222

TABLE IV. OBSERVED AND CALCULATED FREQUENCIES OF CIS-HCOSD (CONTINUED

TRANSITION UPPER STATE	LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	LOWER STATE
** A TYPE Q BRANCH **						
5(1, 4) -	5(1, 5)	8779.5750(1.0)	8779.5706(0.0019)	0.0044	7.459	7.166
6(1, 5) -	6(1, 6)	12289.7050(1.0)	12289.6900(0.0026)	0.0150	9.782	9.372
7(1, 6) -	7(1, 7)	16382.7950(1.0)	16382.7787(0.0034)	0.0163	12.493	11.946
10(1, 9) -	10(1,10)	32138.0400(1.0)	32138.0199(0.0056)	0.0201	22.939	21.867
14(2,12) -	14(2,13)	9085.9250(1.0)	9085.9335(0.0030)	-0.0085	46.504	46.201
15(2,13) -	15(2,14)	11744.2800(1.0)	11744.2848(0.0036)	-0.0048	52.242	51.850
16(2,14) -	16(2,15)	14896.1400(1.0)	14896.1563(0.0042)	-0.0163	58.371	57.874
20(2,18) -	20(2,19)	33052.1400(1.0)	33052.1058(0.0077)	0.0342	86.802	85.700
25(3,22) -	25(3,23)	10016.0200(0.0)	10016.0150(0.0104)	0.0050	138.120	137.786
26(3,23) -	26(3,24)	12451.4900(0.0)	12451.4804(0.0131)	0.0096	148.041	147.626
27(3,24) -	27(3,25)	15318.5750(0.0)	15318.5366(0.0166)	0.0384	158.354	157.843
** B TYPE R BRANCH **						
4(1, 4) -	3(0, 3)	91760.8050(1.0)	91760.7937(0.0055)	0.0113	5.327	2.266
** B TYPE Q BRANCH **						
7(1, 6) -	7(0, 7)	58074.9480(1.0)	58074.9357(0.0036)	0.0123	12.493	10.555
8(1, 7) -	8(0, 8)	60741.9540(1.0)	60741.9666(0.0038)	-0.0126	15.589	13.563
15(1,14) -	15(0,15)	92949.8970(1.0)	92949.8998(0.0070)	-0.0028	48.034	44.934
** B TYPE P BRANCH **						
1(1, 1) -	2(0, 2)	26437.1900(1.0)	26437.2151(0.0025)	-0.0251	2.015	1.133
2(1, 2) -	3(0, 3)	14547.8500(1.0)	14547.8066(0.0024)	0.0434	2.751	2.266
5(0, 5) -	4(1, 4)	10007.3200(1.0)	10007.3156(0.0027)	0.0044	5.660	5.327
7(0, 7) -	6(1, 6)	35465.1200(1.0)	35465.1457(0.0035)	-0.0257	10.555	9.372
11(0,11) -	10(1,10)	88201.7090(1.0)	88201.7092(0.0045)	-0.0002	24.809	21.867
8(2, 7) -	9(1, 8)	33305.8100(1.0)	33305.8143(0.0060)	-0.0043	20.182	19.071
9(2, 8) -	10(1, 9)	19185.9500(1.0)	19185.9643(0.0059)	-0.0143	23.579	22.939
12(1,11) -	11(2,10)	9797.5000(1.0)	9797.4948(0.0059)	0.0052	31.827	31.501
13(1,12) -	12(2,11)	24641.4900(1.0)	24641.4902(0.0058)	-0.0002	36.847	36.025
19(1,18) -	18(2,17)	117749.2130(1.0)	117749.2302(0.0094)	-0.0172	74.969	71.042
12(2,10) -	13(1,13)	33460.6400(1.0)	33460.6585(0.0069)	-0.0185	36.195	35.079
16(2,14) -	17(1,17)	17226.5400(1.0)	17226.5409(0.0067)	-0.0009	58.371	57.796
17(2,15) -	18(1,18)	15211.6550(1.0)	15211.6528(0.0063)	0.0022	64.891	64.384
18(2,16) -	19(1,19)	14077.5200(1.0)	14077.5198(0.0061)	0.0002	71.803	71.333
19(2,17) -	20(1,20)	13844.1100(1.0)	13844.1084(0.0066)	0.0016	79.106	78.645
20(2,18) -	21(1,21)	14524.1800(1.0)	14524.1840(0.0084)	-0.0040	86.802	86.318
21(2,19) -	22(1,22)	16123.4600(1.0)	16123.4591(0.0117)	0.0009	94.890	94.352
25(2,23) -	26(1,26)	31604.8000(0.0)	31604.7366(0.0397)	0.0634	131.146	130.092
12(3,10) -	13(2,11)	94493.3340(1.0)	94493.3201(0.0084)	0.0139	44.307	41.155
17(3,15) -	18(2,16)	26376.8750(1.0)	26376.8815(0.0055)	-0.0065	72.683	71.803
18(3,16) -	19(2,17)	11642.4900(1.0)	11642.4678(0.0057)	0.0222	79.495	79.106
21(2,19) -	20(3,18)	18987.0000(1.0)	18987.0168(0.0079)	-0.0168	94.890	94.256
22(2,20) -	21(3,19)	34869.7700(1.0)	34869.7501(0.0101)	0.0199	103.368	102.205
13(3,10) -	14(2,13)	90872.9600(1.0)	90872.9727(0.0075)	-0.0127	49.232	46.201
19(3,16) -	20(2,19)	31667.6600(1.0)	31667.6505(0.0081)	0.0095	86.756	85.700
21(3,18) -	22(2,21)	14582.9400(1.0)	14582.9572(0.0118)	-0.0172	102.330	101.843
26(2,25) -	25(3,22)	13435.0200(0.0)	13434.9425(0.0256)	0.0775	138.568	138.120
21(4,18) -	22(3,19)	90075.3650(1.0)	90075.3655(0.0144)	-0.0005	113.700	110.695
27(4,24) -	28(3,25)	9059.4750(0.0)	9059.7167(0.0245)	-0.2417	169.362	169.059

TABLE V. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-HCO34SH 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)	11414.2900(1.0)	11414.2813(0.0019)	0.0087	0.381	0.000
2(0, 2) -	1(0, 1)	22824.7600(1.0)	22824.7503(0.0037)	0.0097	1.142	0.381
2(1, 2) -	1(1, 1)	22299.1900(1.0)	22299.1680(0.0035)	0.0220	2.994	2.250
2(1, 1) -	1(1, 0)	23358.1250(1.0)	23358.1333(0.0036)	-0.0083	3.047	2.268
3(0, 3) -	2(0, 2)	34227.6400(1.0)	34227.5967(0.0054)	0.0433	2.284	1.142
3(1, 2) -	2(1, 1)	35034.6500(1.0)	35034.6387(0.0053)	0.0113	4.215	3.047
3(1, 3) -	2(1, 2)	33446.2300(1.0)	33446.2557(0.0053)	-0.0257	4.110	2.994
3(2, 1) -	2(2, 0)	34258.4400(1.0)	34258.4619(0.0065)	-0.0219	9.797	8.654
3(2, 2) -	2(2, 1)	34243.5200(1.0)	34243.5292(0.0065)	-0.0092	9.797	8.654
** A TYPE Q BRANCH **						
6(1, 5) -	6(1, 6)	11116.6050(1.0)	11116.5998(0.0037)	0.0052	10.057	9.686
7(1, 6) -	7(1, 7)	14819.8850(1.0)	14819.8885(0.0045)	-0.0035	12.782	12.288
9(1, 8) -	9(1, 9)	23805.5650(1.0)	23805.5752(0.0059)	-0.0102	19.398	18.604
10(1, 9) -	10(1,10)	29084.2900(1.0)	29084.3063(0.0063)	-0.0163	23.288	22.318
11(1,10) -	11(1,11)	34883.3850(1.0)	34883.3674(0.0067)	0.0176	27.566	26.402
15(2,13) -	15(2,14)	8579.4300(1.0)	8579.4409(0.0039)	-0.0109	53.436	53.150
16(2,14) -	16(2,15)	10930.0950(1.0)	10930.1056(0.0045)	-0.0106	59.591	59.227
17(2,15) -	17(2,16)	13698.1200(1.0)	13698.1140(0.0051)	0.0060	66.138	65.681
18(2,16) -	18(2,17)	16914.8600(1.0)	16914.8771(0.0055)	-0.0171	73.077	72.512
19(2,17) -	19(2,18)	20608.2950(1.0)	20608.3067(0.0058)	-0.0117	80.408	79.721
21(2,19) -	21(2,20)	29516.5700(1.0)	29516.5570(0.0066)	0.0130	96.251	95.266
22(2,20) -	22(2,21)	34766.2400(1.0)	34766.2253(0.0078)	0.0147	104.762	103.603
28(3,25) -	28(3,26)	11128.1500(0.0)	11128.0978(0.0143)	0.0522	172.048	171.676
30(3,27) -	30(3,28)	16304.2200(0.0)	16304.1135(0.0214)	0.1065	194.714	194.170
** B TYPE P BRANCH **						
1(1, 1) -	2(0, 2)	33216.0200(1.0)	33216.0348(0.0058)	-0.0148	2.250	1.142
2(1, 2) -	3(0, 3)	21287.6000(1.0)	21287.6061(0.0043)	-0.0061	2.994	2.284
3(1, 3) -	4(0, 4)	9114.8350(1.0)	9114.8438(0.0034)	-0.0088	4.110	3.805
6(0, 6) -	5(1, 5)	15911.9750(1.0)	15911.9592(0.0043)	0.0158	7.987	7.456
7(0, 7) -	6(1, 6)	28733.2400(1.0)	28733.2299(0.0053)	0.0101	10.645	9.686
10(2, 9) -	11(1,10)	26305.6100(1.0)	26305.6144(0.0081)	-0.0044	28.443	27.566
11(2,10) -	12(1,11)	11875.1700(1.0)	11875.1730(0.0071)	-0.0030	32.627	32.231
14(1,13) -	13(2,12)	17644.7830(1.0)	17644.7804(0.0072)	0.0026	42.720	42.131
15(1,14) -	14(2,13)	32717.2900(1.0)	32717.3133(0.0091)	-0.0233	48.543	47.451
15(2,13) -	16(1,16)	32104.4300(1.0)	32104.4202(0.0088)	0.0098	53.436	52.365
16(2,14) -	17(1,17)	27801.7400(1.0)	27801.7174(0.0086)	0.0226	59.591	58.664
17(2,15) -	18(1,18)	24210.8600(1.0)	24210.8681(0.0080)	-0.0081	66.138	65.330
20(2,18) -	21(1,21)	17997.0900(1.0)	17997.0961(0.0093)	-0.0061	88.133	87.533
21(2,19) -	22(1,22)	17518.6150(1.0)	17518.6182(0.0128)	-0.0032	96.251	95.667
27(2,25) -	28(1,28)	31948.3700(0.0)	31948.2496(0.0646)	0.1204	153.212	152.146
19(3,17) -	20(2,18)	35220.6200(1.0)	35220.6219(0.0145)	-0.0019	89.308	88.133
23(2,21) -	22(3,20)	10060.4900(1.0)	10060.4954(0.0089)	-0.0054	113.667	113.332
24(2,22) -	23(3,21)	25847.0600(1.0)	25847.0571(0.0123)	0.0029	122.965	122.103
22(3,19) -	23(2,22)	33318.4000(1.0)	33318.4063(0.0123)	-0.0063	113.426	112.314
24(3,21) -	25(2,24)	16493.8950(0.0)	16493.8901(0.0188)	0.0049	131.410	130.860
25(3,22) -	26(2,25)	8728.7000(0.0)	8728.7037(0.0244)	-0.0037	140.985	140.694
29(2,28) -	28(3,25)	11487.7000(0.0)	11487.6846(0.0545)	0.0154	172.431	172.048
30(2,29) -	29(3,26)	17059.7250(0.0)	17059.7076(0.0697)	0.0174	183.753	183.184

TABLE VI. OBSERVED AND CALCULATED FREQUENCIES OF CIS-HCO34SH 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)	11449.8950(1.0)	11449.8959(0.0029)	-0.0009	0.382	0.000
2(0, 2) -	1(0, 1)	22896.0400(1.0)	22896.0618(0.0057)	-0.0218	1.146	0.382
2(1, 2) -	1(1, 1)	22373.5750(1.0)	22373.5758(0.0056)	-0.0008	3.020	2.274
2(1, 1) -	1(1, 0)	23426.1950(1.0)	23426.2136(0.0056)	-0.0186	3.073	2.292
3(0, 3) -	2(0, 2)	34334.7850(1.0)	34334.7701(0.0084)	0.0149	2.291	1.146
3(1, 3) -	2(1, 2)	33557.9000(1.0)	33557.9091(0.0084)	-0.0091	4.140	3.020
3(1, 2) -	2(1, 1)	35136.8100(1.0)	35136.7976(0.0084)	0.0124	4.245	3.073
3(2, 2) -	2(2, 1)	34350.5200(1.0)	34350.4751(0.0112)	0.0449	9.895	8.749
3(2, 1) -	2(2, 0)	34364.9300(0.0)	34365.0534(0.0111)	-0.1234	9.895	8.749
** A TYPE Q BRANCH **						
7(1, 6) -	7(1, 7)	14731.3260(1.0)	14731.2766(0.0085)	0.0494	12.837	12.345
10(1, 9) -	10(1,10)	28910.7500(1.0)	28910.7588(0.0112)	-0.0088	23.374	22.409
11(1,10) -	11(1,11)	34675.5700(1.0)	34675.5665(0.0114)	0.0035	27.664	26.507
16(2,14) -	16(2,15)	10684.1700(1.0)	10684.1782(0.0080)	-0.0082	59.836	59.480
17(2,15) -	17(2,16)	13393.9900(1.0)	13393.9779(0.0087)	0.0121	66.401	65.955
18(2,16) -	18(2,17)	16544.9450(1.0)	16544.9453(0.0094)	-0.0003	73.360	72.808
21(2,19) -	21(2,20)	28905.8600(1.0)	28905.8779(0.0152)	-0.0179	96.599	95.634
22(2,20) -	22(2,21)	34062.3700(0.0)	34062.2728(0.0209)	0.0972	105.134	103.997
** B TYPE P BRANCH **						
1(1, 1) -	2(0, 2)	33826.9900(1.0)	33827.0424(0.0088)	-0.0524	2.274	1.146
2(1, 2) -	3(0, 3)	21865.8350(1.0)	21865.8482(0.0065)	-0.0132	3.020	2.291
3(1, 3) -	4(0, 4)	9661.4450(1.0)	9661.4571(0.0053)	-0.0121	4.140	3.817
6(0, 6) -	5(1, 5)	15426.3670(1.0)	15426.3745(0.0068)	-0.0075	8.012	7.497
7(0, 7) -	6(1, 6)	28277.8100(1.0)	28277.7925(0.0081)	0.0175	10.678	9.735
10(2, 9) -	11(1,10)	28053.4200(1.0)	28053.4048(0.0150)	0.0152	28.600	27.664
11(2,10) -	12(1,11)	13603.4180(1.0)	13603.4082(0.0122)	0.0098	32.796	32.342
14(1,13) -	13(2,12)	15953.9950(1.0)	15954.0026(0.0110)	-0.0076	42.863	42.330
15(1,14) -	14(2,13)	31044.9200(1.0)	31044.9302(0.0169)	-0.0102	48.703	47.667
15(2,13) -	16(1,16)	33146.3100(0.0)	33146.3820(0.0134)	-0.0720	53.664	52.558
16(2,14) -	17(1,17)	28726.6500(1.0)	28726.6266(0.0132)	0.0234	59.836	58.878
17(2,15) -	18(1,18)	25009.3000(1.0)	25009.3333(0.0127)	-0.0333	66.401	65.567
18(2,16) -	19(1,19)	22025.4650(1.0)	22025.4545(0.0119)	0.0105	73.360	72.625
21(2,19) -	22(1,22)	17721.3800(1.0)	17721.3815(0.0135)	-0.0015	96.599	96.007
22(2,20) -	23(1,23)	17894.4850(1.0)	17894.4823(0.0186)	0.0027	105.134	104.537
27(2,25) -	28(1,28)	31059.3000(0.0)	31058.9564(0.0912)	0.3436	153.717	152.681
21(3,19) -	22(2,20)	8513.2200(1.0)	8513.2370(0.0200)	-0.0170	105.418	105.134
22(3,19) -	23(2,22)	35561.3800(1.0)	35561.3641(0.0152)	0.0159	113.923	112.737
23(3,20) -	24(2,23)	26840.5100(1.0)	26840.5177(0.0179)	-0.0077	122.747	121.852
25(3,22) -	26(2,25)	10620.1850(0.0)	10620.3108(0.0430)	-0.1258	141.562	141.208
29(2,28) -	28(3,25)	10061.7550(0.0)	10061.5601(0.1026)	0.1949	173.047	172.712
30(2,29) -	29(3,26)	15818.2400(0.0)	15818.0049(0.1281)	0.2351	184.407	183.879

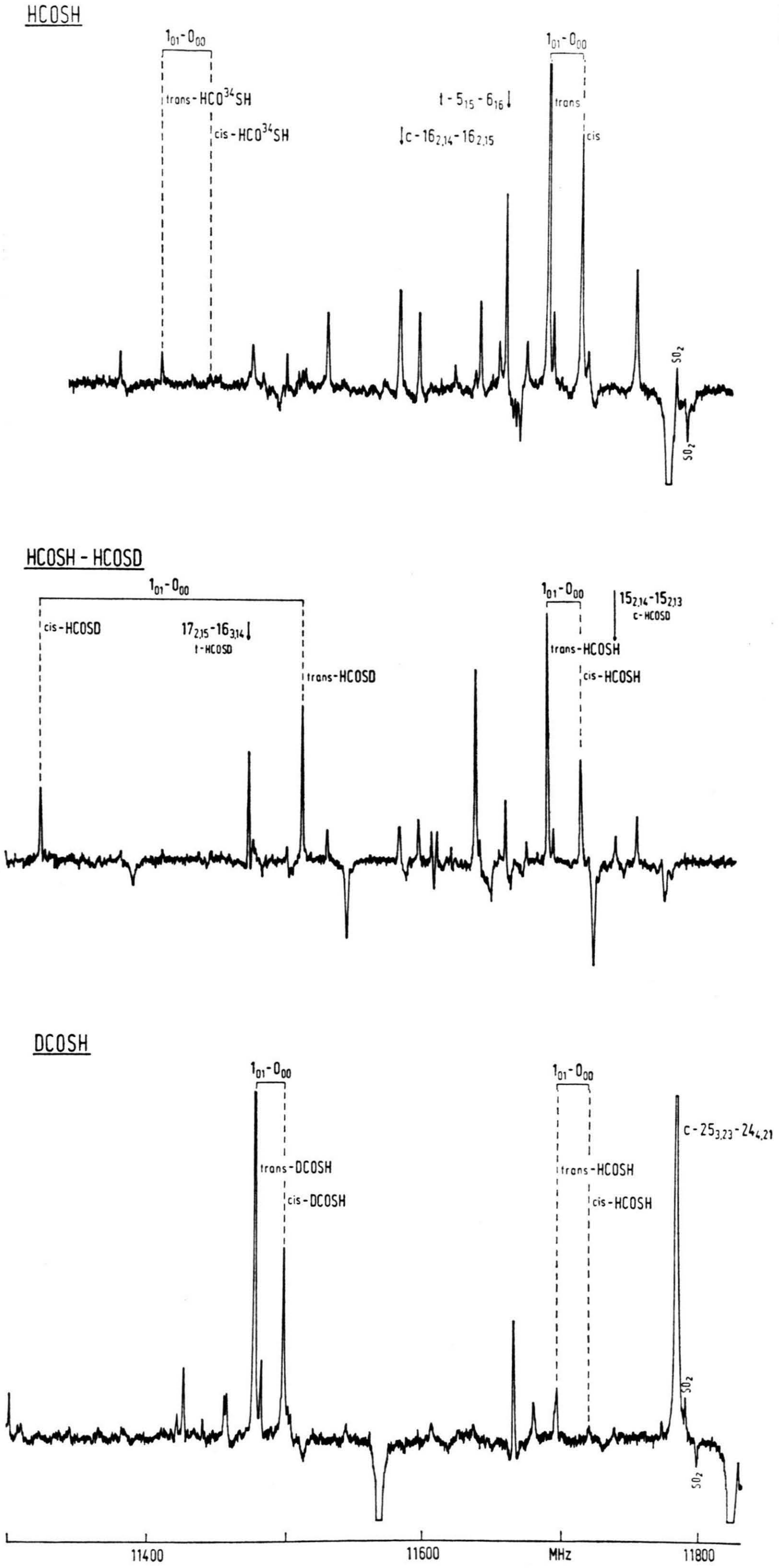


Fig. 3. Comparison of the absorption spectra of HCOSH, HCOSD and DCOSH in the region 11.3–11.8 GHz.

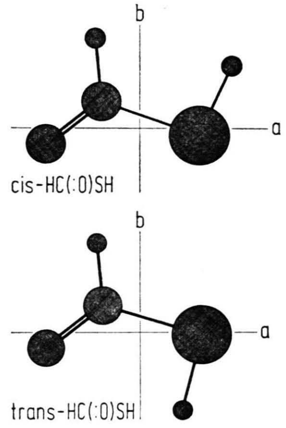


Fig. 4. Illustration of the molecular structures of the two abundant isomers of monothioformic acid.

to provide a nearly uniform sampling of the accessible branches, and hence to assure the accurate determination of rotational constants and quartic distortion constants.

The rotational spectrum of DCOSH in the frequency region 8 – 12.4 GHz is shown in Figure 1. It is similar in appearance to that of the parent isotopic species (see Fig. 1 of Paper I), but has a slightly higher density of lines. This is due primarily to the decrease in the A rotational constants of the two rotamers (from over 60 GHz to less than 50 GHz). The outstanding feature of this region is the pair of $1_{01} - 0_{00}$ transitions near 11.5 GHz. For DC(:O)SH, like HC(:O)SH and HC(:O)^{34}SH, the line belonging to the *cis* rotamer falls slightly (<40 MHz) to high frequency of that produced by the *trans* rotamer. The opposite is true in the case of HC(:O)SD where the *cis* line falls over 180 MHz to low frequency of the *trans* line. This latter situation is illustrated in Fig. 2 which shows the spectrum of a mixed sample of HCOSD and HCOSH in the 11.3 – 11.8 GHz frequency range. The four $1_{01} - 0_{00}$ transitions due to the *cis* and *trans* rotamers of HC(:O)SH and HC(:O)SD have been labelled in Figure 2. Both the zero field and corresponding Stark shifted absorption lines are identified in each case. The observed shifts in the frequencies of the $1_{01} - 0_{00}$ transitions upon substitution of the labile hydrogen atom with deuterium provided the basis for our initial identification of the abundant isomers of monothioformic acid as the *cis* and *trans* thiol rotamers. A comparison of the microwave spectra of HCOSH, HCOSD and DCOSH in the region of the $1_{01} - 0_{00}$ transitions is presented in Figure 3.

The analysis of the spectra of the sulfur-34 substituted species, *cis*- and *trans*-HC(:O)^{34}SH, was more difficult because of the low intensity of the absorption signals. In the spectrum of pure HCOSH shown in Fig. 3 the $1_{01} - 0_{00}$ transition belonging to the *trans* rotamer of HC(:O)^{34}SH in natural abundance is clearly visible, while that of the *cis* rotamer is just discernable. The bootstrap procedure outlined in Paper I was used to assign all of the measured HC(:O)^{34}SH transitions, starting with the low-*J* *a*-type lines. Initially the analysis was based on the centrifugal distortion constants obtained for the parent isotopic species. Some care was necessary in order to avoid confusing the sulfur-34 signals with weak lines belonging to the parent isotopic species in different excited vibrational states.

IV. Centrifugal Distortion Analysis

The measured rotational transition frequencies of the various isotopic species of monothioformic acid were analysed in the $\mathbf{I}^r$ axis representation using the reduced Hamiltonian derived by Watson [3]. Only rigid rotor and quartic centrifugal distortion terms were considered. The effective rotational Hamil-

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

	cis-HC(:O)SD	*trans*-HC(:O)SD	
$\tilde{A}$	55038.2202(35)	50809.8095(29)	MHz
$\tilde{B}$	5955.31696(39)	6086.24103(31)	MHz
$\tilde{C}$	5369.84705(39)	5430.07687(31)	MHz
Δ_J	3.1865(10)	3.42625(90)	kHz
Δ_{JK}	−23.553(22)	−22.105(18)	kHz
Δ_K	746.23(20)	582.53(13)	kHz
δ_J	0.411391(96)	0.486644(83)	kHz
δ_K	15.473(21)	16.642(10)	kHz
σ [b]	16.3	11.7	kHz
N [c]	63	63	
	cis-DC(:O)SH	*trans*-DC(:O)SH	
$\tilde{A}$	48403.2600(24)	47970.8473(19)	MHz
$\tilde{B}$	6091.93570(31)	6083.92022(25)	MHz
$\tilde{C}$	5405.99264(31)	5393.71191(25)	MHz
Δ_J	3.42549(68)	3.20376(55)	kHz
Δ_{JK}	−25.735(11)	−22.9348(95)	kHz
Δ_K	627.28(11)	609.78(11)	kHz
δ_J	0.523121(76)	0.489187(62)	kHz
δ_K	16.072(11)	15.0373(88)	kHz
σ [b]	16.4	13.4	kHz
N [c]	82	82	
	cis-HC(:O)^{34}SH	*trans*-HC(:O)SH	
$\tilde{A}$	62712.427(15)	62013.8403(92)	MHz
$\tilde{B}$	5988.1552(15)	5971.92667(95)	MHz
$\tilde{C}$	5461.7548(15)	5442.36776(95)	MHz
Δ_J	3.534(13)	3.2769(70)	kHz
Δ_{JK}	−46.95(36)	−41.66(20)	kHz
Δ_K	1297.3(43)	1245.1(23)	kHz
δ_J	0.43568(58)	0.40447(28)	kHz
δ_K	16.917(51)	15.823(28)	kHz
σ [b]	23.0	15.9	kHz
N [c]	32	39	

[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.

tonian and the general analysis procedure were described in detail in Paper I. To ensure that the results would not be seriously biased by the neglect of sextic and higher distortion terms, the data sets were restricted to include only transitions with J less than 25 and K_a less than 7. The observed and calculated transition frequencies have been collected in Tables I – VI; the spectroscopic constants are summarized in Table VII.

As a check on the correctness of the above analysis, the least squares fits were repeated using data sets restricted to include all measured transitions with J less than 20 and K_a less than 6. The resulting constants agree with those given in Table VII to within 2 standard errors.

Tables VIII and IX contain derived constants that were calculated from the spectroscopic constants given in Table VII. Watson's determinable parameters [3] which are invariant to a unitary transformation are listed in Table VIII. Application of the planarity constraints [4] yielded the constants collected in Table IX. For a discussion of the meaning and determination of these derived constants the reader is referred to Paper I.

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

	cis-HC(:O)SD	*trans*-HC(:O)SD	
$\mathfrak{A}$	55038.2266(35)	50809.8164(29)	MHz
$\mathfrak{B}$	5955.26801(39)	6086.19152(31)	MHz
$\mathfrak{C}$	5369.86164(39)	5430.09588(31)	MHz
τ'_{aaaa}	−2903.45(80)	−2255.40(52)	kHz
τ'_{bbbb}	−16.0371(41)	−17.5982(37)	kHz
τ'_{cccc}	−9.4549(41)	−9.8118(37)	kHz
τ_1	55.974(89)	47.305(73)	kHz
τ_2'	−4.1467(85)	−4.8148(76)	kHz
$\Delta\tau'_{cccc}$	−0.0152(14)	−0.0228(11)	kHz
	cis-DC(:O)SH	*trans*-DC(:O)SH	
$\mathfrak{A}$	48403.2668(24)	47970.8537(19)	MHz
$\mathfrak{B}$	6091.88362(31)	6083.87264(25)	MHz
$\mathfrak{C}$	5406.00695(31)	5393.72643(25)	MHz
τ'_{aaaa}	−2419.88(44)	−2360.19(44)	kHz
τ'_{bbbb}	−17.8869(28)	−16.7285(22)	kHz
τ'_{cccc}	−9.5170(28)	−8.9015(22)	kHz
τ_1	61.834(45)	53.294(38)	kHz
τ_2'	−3.0623(50)	−3.2380(43)	kHz
$\Delta\tau'_{cccc}$	−0.0168(10)	−0.02255(83)	kHz
	cis-HC(:O)^{34}SH	*trans*-HC(:O)^{34}SH	
$\mathfrak{A}$	62712.434(15)	62013.8468(92)	MHz
$\mathfrak{B}$	5988.0806(15)	5971.85911(97)	MHz
$\mathfrak{C}$	5461.7496(15)	5442.36511(97)	MHz
τ'_{aaaa}	−5015.(17)	−4826.9(92)	kHz
τ'_{bbbb}	−17.621(52)	−16.343(28)	kHz
τ'_{cccc}	−10.650(52)	−9.872(28)	kHz
τ_1	145.4(14)	127.32(80)	kHz
τ_2'	0.85(12)	0.312(68)	kHz
$\Delta\tau'_{cccc}$	−0.013(11)	−0.0173(60)	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 [5].

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

	cis-HC(:O)SD	*trans*-HC(:O)SD	
α'	55038.203	50809.791	MHz
β'	5955.2739	6086.1956	MHz
γ'	5369.8985	5430.1314	MHz
$\hbar^4\,\tau_{aabb}$	91.096	89.841	kHz
$\hbar^4\,\tau_{bbcc}$	−12.172	−12.982	kHz
$\hbar^4\,\tau_{aacc}$	46.429	45.756	kHz
$\hbar^4\,\tau_{abab}$	−34.689	−37.655	kHz
	cis-DC(:O)SH	*trans*-DC(:O)SH	
α'	48403.242	47970.831	MHz
β'	6091.8895	6083.8766	MHz
γ'	5406.0475	5393.7635	MHz
$\hbar^4\,\tau_{aabb}$	99.379	91.101	kHz
$\hbar^4\,\tau_{bbcc}$	−12.846	−11.997	kHz
$\hbar^4\,\tau_{aacc}$	48.076	41.767	kHz
$\hbar^4\,\tau_{abab}$	−36.387	−33.788	kHz
	cis-HC(:O)^{34}SH	*trans*-HC(:O)^{34}SH	
α'	62712.410	62013.824	MHz
β'	5988.1047	5971.8792	MHz
γ'	5461.8136	5442.4230	MHz
$\hbar^4\,\tau_{aabb}$	145.3	132.0	kHz
$\hbar^4\,\tau_{bbcc}$	−13.56	−12.56	kHz
$\hbar^4\,\tau_{aacc}$	82.88	72.42	kHz
$\hbar^4\,\tau_{abab}$	−34.64	−32.25	kHz

[a] Calculated using the planarity conditions as described in Ref. [4], Case 1.

V. Molecular Structure

The moments of inertia and inertial defect, Δ, of each of the isotopic species of monothioformic acid studied so far were calculated from the Kivelson and Wilson [5] rotational constants, α', β', γ', reported in Table IX of this paper and Table V of

Paper I using the conversion factor[6] $(\beta' \cdot I_b) = 505379.0(38)$ MHz·uÅ². Since they do not contain any centrifugal distortion contributions, the α', β' and γ' constants are the appropriate rotational constants to use in a structural determination. The calculated inertial defect values are reported in Table X. They show that both isomers are planar in their equilibrium configuration.

Table X. Inertial defect[a] of monothioformic acid[b].

	cis	*trans*	
HC(:O)SH	0.07352	0.08325	uÅ²
HC(:O)SD	0.06856	0.08597	uÅ²
DC(:O)SH	0.08368	0.09320	uÅ²
HC(:O)^{34}SH	0.07369	0.08327	uÅ²

[a] $\Delta = I_c - I_b - I_a$.
[b] The errors in the inertial defect values are determined by the uncertainty in the conversion factor: $(I_b \cdot \beta') = 505379.0(38)$ MHz·uÅ².

The substitution coordinates[7] of the two hydrogen atoms and the sulfur atom were calculated for each isomer using Kraitchman's equations[8]

$$|a| = \left\{ \frac{\Delta I_b}{\mu} \left(1 + \frac{\Delta I_a}{I_a - I_b} \right) \right\}^{1/2}, \quad (1a)$$

$$|b| = \left\{ \frac{\Delta I_a}{\mu} \left(1 + \frac{\Delta I_b}{I_b - I_a} \right) \right\}^{1/2}, \quad (1b)$$

where $\Delta I_g = I_g' - I_g$ is the change in the gth moment of inertia on isotopic substitution and μ is the reduced mass. The carbon and oxygen atoms were then located by applying the center of mass and moment of inertia equations

$$\sum_i m_i a_i = 0, \quad \sum_i m_i b_i = 0; \quad (2)$$

$$\sum_i m_i a_i^2 = I_b, \quad \sum_i m_i b_i^2 = I_a. \quad (3)$$

Since Kraitchman's equations yield only the magnitude of a substitution coordinate there are 16 physically distinct possible ways of choosing the signs for the hydrogen and sulfur coordinates. Furthermore, for each choice of these signs there exist four solutions to Eqs. (2) and (3), giving a total of 64 different structural possibilities for each isomer of monothioformic acid. The product of inertia, $\sum_i m_i a_i b_i$, provides a useful criterion for selecting the two correct structures from amongst the 128 solutions of the inertial equations. This quantity is identically zero for an equilibrium structure. For structures calculated from ground state moments of inertia it is typically less than a few tenths of 1 uÅ². Most of the 128 solutions to Eqs. (1) – (3) could thus be easily eliminated because they yield too large a value for $\sum_i m_i a_i b_i$. The 20 solutions (10 for each isomer) which give values of $\sum_i m_i a_i b_i$ of less than 1 uÅ² were examined closely. For each isomer only one of these solutions is physically reasonable, i. e. the atoms are arranged in such a way that the bond lengths and angles are consistent with the known structures of related molecules. The two correct solutions, which correspond to the *cis* and *trans* rotamers of HC(:O)SH, are reported in Table XI as structures I.

Table XI. Alternative structures for monothioformic acid.

	trans-HC(:O)SH I	*trans*-HC(:O)SH II	*cis*-HC(:O)SH I	*cis*-HC(:O)SH II	
a(H)[a]	0.722	0.722	1.569	1.569	Å
a(S)	1.047	1.047	1.019	1.019	Å
a(H)[b]	−0.741	−0.741	−0.748	−0.748	Å
a(C)	−0.642	−0.642	−0.650	−0.650	Å
a(O)	−1.610	−1.610	−1.602	−1.602	Å
b(H)[a]	−1.353	−1.353	1.096	1.096	Å
b(S)	−0.039	−0.042	−0.121	−0.122	Å
b(H)[b]	1.559	1.559	1.566	1.566	Å
b(C)	0.461	0.463	0.469	0.470	Å
b(O)	−0.280	−0.277	−0.278	−0.276	Å
$\sum_i m_i a_i b_i$	0.188	0.000	0.071	0.000	uÅ²

[a] Labile hydrogen atom. [b] Nonlabile hydrogen atom.

A second structure (II) has also been reported in Table XI for each rotamer. It is the same as structure I except that the small sulfur b-coordinate was determined using the product of inertia relation ($\sum_i m_i a_i b_i = 0$) rather than Equation (1b). Since Kraitchman's equations normally yield inaccurate results for coordinates smaller than 0.15 Å, this is presumed to be the best method for calculating the sulfur b-coordinate[7]. The bond lengths and angles corresponding to the coordinates of structures II are presented in Table XII. The geometry of each rotamer and its orientation with respect to the principal axis system are illustrated in Figure 4.

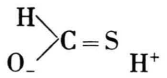
The uncertainty in the structural parameters reported in Table XII, due to zero point vibrational effects, is estimated to be ±0.01 Å for the bond

Table XII. The molecular structure of HC(:O)SH.

	trans	*cis*	Δ (c−t) [a]
r(C−H)	1.100	1.100	0.000 Å
r(C=O)	1.218	1.210	−0.008 Å
r(C−S)	1.763	1.771	0.008 Å
r(S−H)	1.351	1.336	−0.015 Å
∢(OCS)	126.0°	122.4°	−3.6°
∢(HSC)	92.7°	94.7°	2.0°
∢(HCS)	111.8°	114.6°	2.8°

[a] Change in the molecular structure on going from the *trans* to the *cis* rotamer.

lengths and $\pm 1°$ for the bond angles. Nonetheless, a comparison of the structures of the two rotamers with each other should be valid to a much higher accuracy, since the vibrational contributions are expected to be similar in each case. Thus the slight changes observed in the bond lengths and angles on going from the *trans* to the *cis* rotamer are believed to be real. The opening of the HCS and HSC angles and (in part) the closing of the OCS angle may be attributed to repulsion of the hydrogen atoms in the *cis* rotamer. Furthermore, the shortening of the CO and SH bond lengths, the lengthening of the CS bond length, and the closing of the OCS angle are all consistent with a weak attraction of the labile hydrogen atom by the electronegative oxygen atom in the *trans* rotamer. This latter effect may be represented by a small contribution to the structure of the *trans* rotamer by the resonance from



The corresponding ionic resonance form for the *cis* rotamer is expected to be less important since it is not stabilized by electrostatic attraction. A similar, but more pronounced example of this phenomenon has been observed by Cox et al. in *cis* and *trans* nitrous acid [9].

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1 W. H. Hocking and G. Winnewisser, Z. Naturforsch. **31 a**, 438 [1976]; Part I.
2 W. H. Hocking and G. Winnewisser, J. Chem. Soc. Chem. Comm. **63** [1975].
3 J. K. G. Watson, J. Chem. Phys. **46**, 1935 [1967].
4 K. Yamada and M. Winnewisser, Z. Naturforsch. **30 a**, 672 [1975]; erratum ibid. p. 1794.
5 D. Kivelson and E. B. Wilson, Jr., J. Chem. Phys. **20**, 1575 [1952].
6 E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data **2**, 663 [1973].
7 C. C. Costain, J. Chem. Phys. **29**, 864 [1958].
8 J. Kraitchman, Am. J. Phys. **21**, 17 [1953].
9 A. P. Cox, A. H. Brittain, and D. J. Finnigan, Trans. Faraday Soc. **67**, 2179 [1971].