Reprinted from JOURNAL OF MOLECULAR SPECTROSCOPY, Volume 44, No. 3, December 1972
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JOURNAL OF MOLECULAR SPECTROSCOPY **44**, 553–557 (1972)

Millimeter Wave Spectrum of Thioformaldehyde

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The rotational spectrum of $H_2{}^{12}C^{32}S$ has been investigated in the millimeter region from 100 to 250 GHz. Twenty-five new *R*-branch transitions have been measured and combined with earlier data in a centrifugal distortion analysis of the spectrum. A set of rotational parameters are presented representing the best fit of all available data on the molecule. These rotational parameters allow reliable predictions for all transitions of $H_2{}^{12}C^{32}S$ up to $J = 30$ and $\nu < 300$ GHz.

Thioformaldehyde (H_2CS) was first characterized in the gas phase from its microwave spectrum in the region below 35 GHz (*1*). In a more recent paper (*2*), the spectra of several isotopically substituted forms of thioformaldehyde were investigated and an r_s structure was reported for the molecule. In that same paper a detailed centrifugal distortion analysis was presented for the most abundant isotopic form, $H_2{}^{12}C^{32}S$.

In October of 1971, the 2_{12}–2_{11} transition of thioformaldehyde was detected in absorption from the direction of the galactic center radio source Sgr B2 (*3*). With H_2CS thus established as a constituent of the interstellar medium, it is now important that the microwave spectrum of this molecule be thoroughly cataloged so that all transitions within the range of the radio telescopes can be identified. The most abundant isotopic form of thioformaldehyde, $H_2{}^{12}C^{32}S$, produces more than 130 transitions in the range from 100 MHz to 300 GHz between states with total rotational energies of less than 1000 cm^{-1}. It is clearly impractical to attempt a direct measurement of each of these transitions. A more reasonable approach is to measure a set of key transitions from which parameters can be determined which will allow a reliable prediction of the remainder of the spectrum (*4*). The centrifugal distortion analysis reported in Ref. (*2*) predicted the *Q*-branch transitions of $H_{25}{}^{12}C^{32}S$ well. However, the set of observed transitions available for that analysis included only four of the lowest lying R-branch transitions. As a result, the higher frequency R-branch transitions were predicted with such large uncertainties that positive identification of an observed telescope signal was unlikely. The purpose of the present paper is to extend the measurements to R-branch transitions of higher rotational energies in order to obtain more accurate predictions of the millimeter wave spectrum of $H_{25}{}^{12}C^{32}S$.

Gas phase H_2CS was generated on a continuous basis by direct pyrolysis of the trimer in the manner described in Ref. (*2*). All measurements were made in a 12-in. long parallel plate absorption cell fitted with Teflon lenses. Millimeter wave power was provided by frequency multiplication with harmonic generators of standard design. Stark modulation was employed for the majority of the measurements. Direct modulation of the multiplier diode was used as an alternate modulation method for checking all frequencies and for observing those transitions for which the Stark effect was unfavorable.

Twenty-five new R-branch transitions were measured and combined with data from the previous papers in the simultaneous fit of the entire observed spectrum of $H_2{}^{12}C^{32}S$ shown in Table I. These transitions were fit to a centrifugal distortion model described by Watson (*5*) using techniques described by Kirchhoff (*6*). All five fourth-order constants were included in the fit as well as one sixth-order constant h_{JK}. Each transition was weighted by the inverse square of its measurement uncertainty. The rotational constants are given in Table II. The number of significant figures given for each constant is necessary for recalculation of the microwave spectrum with round-off errors less than the standard deviations of the calculated frequencies.

Because H_2CS is a near prolate rotor with a-type transitions only, a great deal of correlation exists between the terms contributing to the calculation of the microwave transition frequencies. As a result the standard deviations of A'' and τ_{aaaa} were greater than 600 MHz. In addition, when both A'' and τ_{aaaa} were allowed to vary, convergence of the iteration procedure was very slow. From an analysis of the high resolution infrared spectrum plus the microwave data, Johns and Olson (*7*) were able to obtain greater accuracy for A'' and τ_{aaaa}, although the remaining constants were better determined from the microwave data reported in Table I. In order to take advantage of this better determination of A'' and τ_{aaaa} from the infrared spectrum, the value of τ_{aaaa}, viz., -141 MHz, was included in the least squares fit as a datum point weighted by the inverse square of its reported standard deviation, 18 MHz. This resulted in a rapid convergence of the iteration procedure and a better determination of A''. The value of τ_{aaaa} given by the fit differed negligibly from the input value. Had the microwave data been such that A'' and τ_{aaaa} could have been individually well determined, the τ_{aaaa} datum point would have been overwhelmed by the microwave data. The remaining constants and their standard deviations (except for τ_3 which is derived in part from τ_{aaaa}) were only slightly affected by the inclusion of τ_{aaaa} as a datum point.

TABLE I

THE MICROWAVE SPECTRUM OF $\mathrm{H}_2{}^{12}\mathrm{C}^{32}\mathrm{S}$

Upper State			Lower State			Observed frequency (MHz)	Est. acc. (MHz)	Calculated frequency (MHz)	SD (MHz)	Obsd.-calcd. (MHz)	T
J	K_p	K_o	J	K_p	K_o						
1	0	1	0	0	0	34351.43	0.020	34351.417	0.010	0.013	0.8
2	1	1	2	1	2	3139.38	0.030	3139.406	0.001	−0.026	−0.9
2	0	2	1	0	1	68699.41	0.100	68699.370	0.019	0.040	0.4
2	1	2	1	1	1	67653.82	0.040	67653.814	0.019	0.006	0.2
2	1	1	1	1	0	69746.72	0.120	69746.731	0.019	−0.013	−0.1
3	1	2	3	1	3	6278.65	0.008	6278.631	0.002	0.019	2.6
3	0	3	2	0	2	103040.22	0.15	103040.398	0.027	−0.179	−1.2
3	1	3	2	1	2	101477.62	0.12	101477.751	0.025	−0.132	−1.1
3	1	2	2	1	1	104617.04	0.07	104616.977	0.025	0.063	1.0
3	2	2	2	2	1	103039.99	0.10	103039.845	0.027	0.145	1.5
3	2	1	2	2	0	103051.81	0.28	103051.785	0.027	0.024	0.1
4	1	3	4	1	4	10463.97	0.005	10463.967	0.003	0.003	0.9
4	0	4	3	0	3	137371.05	0.30	137371.041	0.038	0.009	0.0
4	1	4	3	1	3	135297.81	0.25	135298.131	0.034	−0.322	−1.3
4	1	3	3	1	2	139483.41	0.28	139483.467	0.034	−0.058	−0.2
4	2	3	3	2	2	137382.03	0.32	137381.955	0.029	0.072	0.2
4	2	2	3	2	1	137411.77	0.25	137411.803	0.029	−0.035	−0.1
4	3	2	3	3	1	137369.17	0.25	137369.314	0.045	−0.145	−0.6
4	3	1	3	3	0	137369.17	0.25	137369.346	0.045	−0.177	−0.7
5	1	4	5	1	5	15695.12	0.020	15695.127	0.004	−0.007	−0.3
5	0	5	4	0	4	171687.90	0.52	171687.842	0.065	0.058	0.1
5	1	5	4	1	4	169113.53	0.15	169113.783	0.058	−0.256	−1.9
5	1	4	4	1	3	174344.85	0.19	174344.943	0.058	−0.095	−0.5
5	2	4	4	2	3	171720.23	0.30	171720.207	0.044	0.022	0.1
5	2	3	4	2	2	171779.45	0.35	171799.893	0.044	−0.444	−1.3
5	3	3	4	3	2	171710.97	0.19	171710.885	0.047	0.084	0.5
5	3	2	4	3	1	171710.97	0.19	171710.996	0.047	−0.027	−0.2
5	4	2	4	4	1	171670.65	0.32	171670.730	0.090	−0.081	−0.3
5	4	1	4	4	0	171670.65	0.32	171670.730	0.090	−0.081	−0.3
6	1	5	6	1	6	21971.71	0.020	21971.712	0.005	−0.002	−0.1
7	1	6	7	1	7	29293.21	0.020	29293.187	0.006	0.023	1.2
7	0	7	6	0	6	240266.32	0.40	240266.145	0.184	0.175	0.5
7	1	7	6	1	6	236726.77	0.60	236726.271	0.173	0.497	0.9
7	1	6	6	1	5	244047.84	0.59	244047.746	0.173	0.092	0.2
7	2	6	6	2	5	240381.75	0.34	240381.277	0.149	0.472	1.6
7	4	4	6	4	3	240331.43	0.29	240331.437	0.121	−0.010	−0.0
7	4	3	6	4	2	240331.43	0.29	240331.439	0.121	−0.010	−0.0
7	5	3	6	5	2	240261.38	0.41	240261.330	0.182	0.050	0.1
7	5	2	6	5	1	240261.38	0.41	240261.330	0.182	0.050	0.1
8	1	7	8	1	8	37658.83	0.010	37658.845	0.007	−0.015	−2.2
9	1	8	9	1	9	47067.73	0.030	47067.775	0.010	−0.046	−1.7
10	1	9	10	1	10	57518.80	0.050	57518.817	0.017	−0.018	−0.4
11	1	10	11	1	11	69010.61	0.040	69010.514	0.027	0.096	3.4
15	2	13	15	2	14	7052.07	0.050	7052.044	0.018	0.026	0.6
16	2	14	16	2	15	9050.16	0.040	9050.123	0.018	0.037	1.1
17	2	15	17	2	16	11438.53	0.060	11438.524	0.018	0.006	0.1
18	2	16	18	2	17	14261.90	0.060	14261.873	0.017	0.027	0.5
19	2	17	19	2	18	17565.92	0.030	17565.967	0.014	−0.047	−1.9
20	2	18	20	2	19	21397.44	0.030	21397.406	0.012	0.034	1.3
21	2	19	21	2	20	25803.14	0.030	25803.196	0.011	−0.057	−2.1
22	2	20	22	2	21	30830.35	0.020	30830.326	0.011	0.024	1.5
23	2	21	23	2	22	36525.32	0.020	36525.324	0.013	−0.005	−0.3
24	2	22	24	2	23	42933.80	0.060	42933.814	0.015	−0.014	−0.3
25	2	23	25	2	24	50100.07	0.050	50100.063	0.018	0.007	0.1
26	2	24	26	2	25	58066.56	0.050	58066.557	0.024	0.003	0.1
27	2	25	27	2	26	66873.59	0.050	66873.593	0.041	−0.004	−0.1

TABLE II

THE ROTATIONAL CONSTANTS[a] OF THIOFORMALDEHYDE

$A'' = 291\ 660.05 \pm 50$ MHz

$B'' = 17\ 699.5551 \pm 0.0056$ MHz

$C'' = 16\ 653.0621 \pm 0.0056$ MHz

$\tau_1 = -2\ 321.202 \pm 2.4$ kHz

$\tau_2 = -184.5614 \pm 0.58$ kHz

$\tau_3 = 26.82 \pm 0.22$ MHz[b]

$\tau_{aaaa} = -139.81 \pm 17.6$ MHz[c]

$\tau_{bbbb} = -89.49296 \pm 0.64$ kHz

$\tau_{cccc} = -69.7911 \pm 0.63$ kHz

$h_{JK} = 13.18 \pm 5$ Hz

Assuming planarity, the following parameters were calculated from τ_1 , τ_2 , τ_{aaaa} and τ_{bbbb}

$\tau_{aabb} = 0.461 \pm 0.067$ MHz

$\tau_{abab} = -1.321 \pm 0.054$ MHz

$\tau_{bbcc} = -77.99 \pm 0.61$ kHz

$\tau_{ccaa} = -62.6 \pm 59$ kHz

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[a] The number of significant figures quoted are necessary to reproduce all of the calculated frequencies for $1 < J < 40$ and 100 MHz $< \nu <$ 300 GHz to within their standard deviations. The constants reported are those defined as "Watson's Determinable Parameters" in Ref. (*4*).

[b] The value of τ_3 is set using the planarity conditions and is not, strictly speaking, a determinable parameter.

[c] The value of τ_{aaaa} is determined primarily from the high resolution infrared spectrum. See text for details.

When more than one sixth order angular momentum (P^6) term was included in the least-squares fit, the standard deviations of the predicted (but unmeasured) transitions were five to ten times greater than those calculated using only one P^6 term. Experience with other molecules has indicated that ignoring contributions from all the P^6 terms causes the calculated transitions to be in error by no more than three standard deviations in the majority of cases. Thus, the most useful predictions of the unmeasured transitions are those obtained using a single P^6 term with the standard deviations of the calculated frequencies trebled.

In order to determine whether additional measurements would lead to an improvement in the values of the parameters, a calculation using synthetic data was performed. The synthetic data was generated by adding to a spectrum calculated from a fourth order model a set of random normal errors representative of presently attainable measurement accuracies (0.05 MHz for frequencies less than 50 GHz and an additional 0.05 MHz for every multiple of 50 GHz above 50 GHz). This synthetic data, consisting of 160 transitions with $J \leq 40$ and 100 MHz $< \nu <$ 300 GHz, was then fitted using a sixth-order model which included all seven P^6 terms. It was found that even with this extremely extensive microwave data τ_{aaaa} could not be obtained with better accuracy than that obtained from the infrared data. The sole sixth-order constant retained for the fit of the measured microwave data h_{JK} was chosen because it had the smallest correlation with the remaining parameters of all the sixth order parameters.

In conclusion, the rotational parameters obtained from the least-squares fit of the microwave data reported in Table I are of sufficient accuracy to predict all of the remaining transitions up to $J = 30$ and $\nu < 300$ GHz with standard deviations less than 0.5 MHz except for the $K_p = 3$, Q-branch series which has standard deviations less than 2 MHz. Above $J = 30$ the predictions become less accurate and the intensities become so weak that measurement of these transitions is not possible with existing equipment and techniques for the preparation of H_2CS. The predicted microwave spectrum for H_2CS along with information on line strengths and absolute rotational energies will be available soon (*4*).

RECEIVED: June 23, 1972

REFERENCES

1. D. R. JOHNSON AND F. X. POWELL, *Science* **169,** 679 (1970).
2. D. R. JOHNSON, F. X. POWELL, AND W. H. KIRCHHOFF, *J. Mol. Spectrosc.* **39,** 136 (1971).
3. M. W. SINCLAIR, J. C. RIBES, N. FOURIKIS, R. D. BROWN AND P. D. GODFREY, Int. Astron. Union Circ. No. 2362, Nov. 1971.
4. D. R. JOHNSON, F. J. LOVAS AND W. H. KIRCHHOFF, *J. Chem. Phys. Ref. Data,* (1972), in press.
5. J. K. G. WATSON, *J. Chem. Phys.* **48,** 4517 (1968).
6. W. H. KIRCHHOFF, *J. Mol. Spectrosc.* **41,** 333 (1972).
7. J. W. C. JOHNS AND W. B. OLSON, *J. Mol. Spectrosc.* **39,** 479 (1971).