

Frequency Measurements of High- J Rotational Transitions of OCS and N₂O

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A metal-insulator-metal diode has been used to generate far-infrared radiation as the difference between two CO₂ lasers. With this technique rotational transitions of all the vibrational states below 2000 cm⁻¹ have been measured for the normal isotopic species of OCS with an accuracy of 200 kHz or better. Transitions were measured primarily in the range from $J = 65 \leftarrow 64$ to $J = 67 \leftarrow 66$ but some measurements were also made from $J = 91 \leftarrow 90$ to $J = 93 \leftarrow 92$. Measurements are also given for the lower vibrational states of ¹⁶O¹²C³⁴S in the range from $J = 67 \leftarrow 66$ to $J = 69 \leftarrow 68$ and for the normal isotopic species of N₂O for $J = 60 \leftarrow 59$.

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INTRODUCTION

As part of a project to develop absorption standards for frequency calibration throughout the infrared, we have been systematically measuring the relative energies of the lower rovibrational levels of carbonyl sulfide (OCS) (1, 2) and nitrous oxide (N₂O) (3, 4). For this project we have sought to obtain frequency measurements for high-, intermediate-, and low- J transitions for as many vibrational states as possible. Of course, there are many very good infrared measurements, based on wavelength measurement techniques, that cover the entire range of J values. However, such wavelength measurements are more prone to systematic errors and we prefer to base our standards on frequency measurements alone. There are also a number of studies of the microwave and sub-millimeter wave transitions of OCS and N₂O (5-9), but most are limited to fairly low J values (less than $J = 26$ except for the ground state of OCS).

Recently techniques have been developed to generate far-infrared radiation of accurately known and controlled frequencies for absorption studies (10, 11). These new techniques make it possible to extend accurate frequency measurements on OCS and N₂O rotational transitions to high- J values. The sensitivity is adequate to measure relatively high vibrational states for OCS. This paper presents measurements that exploit this technique to provide new data that are needed to verify and improve the accuracy of our calibration effort.

EXPERIMENTAL DETAILS

In our experiments, coherent, tunable far-infrared radiation was generated by non-linear mixing of the radiation from two CO₂ lasers in a metal-insulator-metal diode (10). Details of the spectrometer have been given elsewhere (11). The far-infrared radiation made a single pass through a glass absorption cell and was detected with a liquid helium-cooled bolometer. The cell was 2.3 cm i.d. and 75.0 cm long and is fitted with polyethylene windows. It was wrapped with an electrical heating tape for operation above room temperature. The far-infrared radiation was frequency modulated at a 1 kHz rate with an amplitude of 1 MHz. When tuned to an absorption line the frequency modulation results in a 1-kHz amplitude modulated signal which is then phase detected at the first harmonic. This produces a signal proportional to the first derivative of the line shape which is recorded.

In order to avoid the effects of pressure-induced frequency shifts the measurements were all made at pressures below 53 Pa (400 mTorr). Most of the measurements were made at temperatures in the range of 150–180°C.

ASSIGNMENT AND ANALYSIS OF THE DATA

Carbonyl Sulfide

The rotational constants are known well enough from earlier microwave (5–9) and infrared measurements (1, 2, 12–14) to predict all the transitions to within 10 MHz and in many cases to within 1 MHz. The assignments are unambiguous. The observed transitions and their assignments are given in Table I.

The constants given in Table II were determined by a least-squares fit that included the present data and all earlier frequency measurements made on OCS (1, 2, 14–19). In the least-squares fit the data were weighted by the inverse squares of their estimated uncertainties. The Hamiltonian used to fit the transitions included the effect of the *l*-type resonance but ignored the Fermi resonance term, which is not very important for OCS. The equations that were used are given in Ref. (14). Many of the higher-order terms, especially the H_v terms, were not determined very well, but they were usually retained in the fit or given the ground state value, on the assumption that this was better than setting them equal to zero. In the case of the Fermi resonant levels, 03¹0 and 01¹1, the *H* terms for the resonant levels 02⁰0 and 00⁰1, respectively, were used.

The constants determined from the least-squares fit are given in Table II. In order to use the constants for levels with $v_2 > 1$ it is essential that the *l*-type resonance be taken into account; otherwise the effective centrifugal distortion will be incorrect.

Fewer microwave and infrared measurements are available for the analysis of the measurements of ¹⁶O¹²C³⁴S, but the assignments are not in doubt. In addition to the measurements given in Table I, the analysis included measurements taken from Refs. (5–7, 9, 14, 15, 18–20). The same Hamiltonian was used for both isotopic species of OCS, although there were not enough data for the sulfur-34 species to determine some of the higher-order constants. Whenever an *H* constant could not be determined for the sulfur-34 species, it was set equal to the ground state value, except for the 00⁰1 state, where the *H* term for the sulfur-34 species was set equal to that for the normal species.

TABLE I
Rotational Transitions Measured for Carbonyl Sulfide (OCS) and Nitrous Oxide (N₂O)

Frequency (unc) (MHz)	o-c ^a (MHz)	Rot. Trans. J'←J''	Vib. State	Vib. Energy (cm ⁻¹)
¹⁶O¹²C³²S				
789163.801(200)	-0.014	65-64	00 ⁰ 0	0
789814.147(200)	-0.005	65-64	02 ^{2f} 1	1887
790105.845(200)	-0.046	65-64	01 ^{1e} 0	520
798834.732(200)	-0.053	66-65	00 ⁰ 1	859
801584.243(200)	-0.268	66-65	02 ^{2e} 1	1887
801901.657(200)	-0.098	66-65	02 ⁰ 1	1892
803050.609(200)	0.012	66-65	01 ^{1f} 0	520
803724.281(200)	0.145	66-65	02 ^{2e} 0	1041
803969.157(200)	0.095	66-65	02 ⁰ 0	1047
803993.512(200)	0.140	66-65	02 ^{2f} 0	1041
804115.917(200)	-0.116	66-65	03 ^{1e} 0	1573
805214.913(200)	0.076	66-65	03 ^{3e} 0	1562
805244.142(200)	-0.081	66-65	03 ^{3f} 0	1562
805718.448(200)	-0.095	66-65	03 ^{1f} 0	1573
808378.994(200)	-0.184	67-66	00 ⁰ 2	1710
812932.683(200)	0.011	67-66	01 ^{1f} 1	1372
1102905.314(200)	-0.010	91-90	00 ⁰ 0	0
1105951.322(200)	0.022	91-90	02 ^{2e} 0	1041
1106896.674(200)	-0.100	91-90	02 ⁰ 0	1047
1116241.324(200)	0.055	92-91	01 ^{1e} 0	520
1117399.237(200)	-0.050	92-91	01 ^{1f} 0	520
1118684.910(200)	-0.075	92-91	02 ^{2f} 0	1041
1123508.720(200)	-0.049	93-92	00 ⁰ 1	859
1126966.568(200)	0.063	93-92	00 ⁰ 0	0
¹⁶O¹²C³⁴S				
791107.050(200)	0.017	67-66	00 ⁰ 1	848
805302.973(200)	-0.057	68-67	00 ⁰ 0	0
807763.668(200)	-0.021	68-67	02 ^{2e} 0	1040
808049.576(200)	0.026	68-67	02 ^{2f} 0	1040
808062.907(200)	0.003	68-67	02 ⁰ 0	1045
818081.708(200)	-0.145	69-68	01 ^{1e} 0	520
818914.201(200)	0.005	69-68	01 ^{1f} 0	520
¹⁴N¹⁴N¹⁶O				
1502832.222(200)	-0.365	60-59	00 ⁰ 0	0
1503374.990(200)	-0.343	60-59	01 ^{1e} 0	589
1506198.421(200)	-0.112	60-59	01 ^{1f} 0	589

a) Observed - calculated transition frequency based on the constants given in Table II.

Nitrous Oxide

Three transitions of N₂O were measured. They were easily assigned and fitted with the existing microwave and infrared measurements (5, 21). The constants resulting from this fit are given in Table II. Since the dipole moment of N₂O is weaker than that of OCS, the transitions of N₂O are 20 times weaker than those of OCS (ignoring all other factors).

DISCUSSION

We had two reasons for making these measurements; one was to test the accuracy of our estimates of the high rotational levels of many vibrational states which heretofore had depended (in some cases) on FTS measurements. The second reason was to obtain better guidance on where to truncate the Hamiltonian.

TABLE II
Rotational Constants for OCS and N₂O

Vib. State	B _v (MHz)/q (MHz)	D _v (kHz)/q _J (Hz)	H _v (mHz)/q _{JJ} (mHz)
¹⁶O¹²C³²S			
00 ⁰ 0	6081.492089(28) ^a	1.301266(87)	-0.1029(106)
01 ¹ 0	6092.077479(97)	1.322472(115)	-0.0833(130)
	6.3614150(28)	4.2993(278)	0.0230(115)
00 ⁰ 1	6063.357742(624)	1.329250(281)	0.0238(281)
02 ⁰ 0 ^b	6100.191874(750)	1.325349(343)	-0.1825(328)
	6.254800(102)	1.976(113)	---
02 ² 0	6102.559806(316)	1.344048(305)	-0.0411(262)
01 ¹ 1	6075.50658(145)	1.36273(143)	[0.02] ^c
	6.85079(287)	11.36(280)	---
03 ¹ 0 ^d	6108.653340(403)	1.336075(196)	[-0.18]
	6.188429(130)	0.804(156)	---
03 ³ 0	6112.935795(476)	1.364131(259)	[-0.0899]
00 ⁰ 2	6044.87603(116)	1.359193(391)	0.1197(350)
02 ⁰ 1 ^e	6084.392486(706)	1.365144(395)	[-0.0899]
	6.66292(467)	6.076(212)	---
02 ² 1	6087.232629(375)	1.389996(364)	[-0.0899]
¹⁶O¹²C³⁴S			
00 ⁰ 0	5932.833890(207)	1.241586(238)	-0.0918(165)
01 ¹ 0	5943.162107(388)	1.261634(239)	[-0.0918]
	6.0688126(29)	3.9215(270)	---
00 ⁰ 1	5915.15143(299)	1.266297(399)	{0.02}
02 ⁰ 0 ^f	5951.260644(556)	1.267062(442)	[-0.09]
	5.978822(182)	1.993(557)	---
02 ² 0	5953.389976(392)	1.281754(270)	[-0.09]
N₂O			
00 ⁰ 0	12561.633959(196)	5.279162(256)	-0.4912(290)
01 ¹ 0	12578.499656(359)	5.362132(518)	-0.3069(746)
	23.7437294(123)	30.147(122)	---

a) The uncertainty in the last digits (twice the standard error) is given in parentheses.

b) $\nu(02^00-02^20) = 5.74922(20) \text{ cm}^{-1}$

c) The values given in square brackets were fixed.

d) $\nu(03^10-03^30) = 10.75525(\text{fixed}) \text{ cm}^{-1}$

e) $\nu(02^01-02^21) = 5.28290(24) \text{ cm}^{-1}$

f) $\nu(02^00-02^20) = 5.37016(\text{fixed}) \text{ cm}^{-1}$

One of the problems with heterodyne infrared measurements is that they provide a rather small data base for fitting a relatively large number of rovibrational constants. The previous analysis of heterodyne measurements used microwave and sub-millimeter wave data to help determine the rotational constants, but the centrifugal distortion terms were poorly determined unless FTS measurements were also used. There are several ways in which small systematic errors might affect FTS measurements. Thus it was uncertain how reliable these measurements might be for determining the centrifugal distortion values. The present high-*J* frequency measurements show that the earlier determination of the centrifugal distortion terms was quite good, but they are now even more reliable.

If the contribution of *l*-type resonance were removed, the earlier work could not give values for the H_v terms (except for the ground state). In a preliminary fit, in which all the vibrational states were given the same value for the H_v term, the new measurements were not fitted to within our estimate of their uncertainty. In some

cases this prompted us to make new measurements, but the final conclusion was that in most cases each state requires a unique H_v term in the fit.

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REFERENCES

1. J. S. WELLS, M. D. VANEK, AND A. G. MAKI, *J. Mol. Spectrosc.* **135**, 84-88 (1989).
2. M. SCHNEIDER, A. G. MAKI, M. D. VANEK, AND J. S. WELLS, *J. Mol. Spectrosc.* **134**, 349-353 (1989).
3. L. R. ZINK, J. S. WELLS, AND A. G. MAKI, *J. Mol. Spectrosc.* **123**, 426-433 (1987).
4. A. HINZ, J. S. WELLS, AND A. G. MAKI, *Z. Phys. D*, **5**, 351-358 (1987).
5. F. J. LOVAS, *J. Phys. Chem. Ref. Data* **7**, 1445-1750 (1978).
6. J. G. SMITH, *J. Chem. Soc. Faraday Trans. 2* **72**, 2298-2300 (1976).
7. A. DUBRULLE, J. DEMAISON, J. BURIE, AND D. BOUCHER, *Z. Naturforsch. A* **35**, 471-474 (1980).
8. M. BOGEY AND A. BAUER, *J. Mol. Spectrosc.* **84**, 170-178 (1980).
9. K. TANAKA, H. ITO, AND T. TANAKA, *J. Mol. Spectrosc.* **107**, 324-332 (1984).
10. K. M. EVENSON, D. A. JENNINGS, AND F. R. PETERSEN, *J. Appl. Phys.* **46**, 576-578 (1984).
11. I. G. NOLT, J. V. RADOSTITZ, G. DILONARDO, K. M. EVENSON, D. A. JENNINGS, K. R. LEOPOLD, M. D. VANEK, L. R. ZINK, A. HINZ, AND K. V. CHANCE, *J. Mol. Spectrosc.* **125**, 274-287 (1987).
12. A. FAYT, R. VANDENHAUTE, AND J.-G. LAHAYE, *J. Mol. Spectrosc.* **119**, 233-266 (1986).
13. J.-G. LAHAYE, R. VANDENHAUTE, AND A. FAYT, *J. Mol. Spectrosc.* **123**, 48-83 (1987).
14. A. G. MAKI, WM. B. OLSON, J. S. WELLS, AND M. D. VANEK, *J. Mol. Spectrosc.* **130**, 69-80 (1988).
15. J. S. WELLS, F. R. PETERSEN, AND A. G. MAKI, *Appl. Opt.* **18**, 3567-3573 (1979).
16. J. S. WELLS, F. R. PETERSEN, A. G. MAKI, AND D. J. SUKLE, *Appl. Opt.* **20**, 1676-1684 (1981); *Appl. Opt.* **20**, 2874 (1981).
17. J. P. SATTTLER, T. L. WORCHESKY, A. G. MAKI, AND W. J. LAFFERTY, *J. Mol. Spectrosc.* **90**, 460-466 (1981).
18. J. S. WELLS, F. R. PETERSEN, AND A. G. MAKI, *J. Mol. Spectrosc.* **98**, 404-412 (1983).
19. A. G. MAKI, J. S. WELLS, AND A. HINZ, *Int. J. Infrared Millimeter Waves* **7**, 909-917 (1986).
20. J. S. WELLS, F. R. PETERSEN, A. G. MAKI, AND D. J. SUKLE, *J. Mol. Spectrosc.* **89**, 421-429 (1981).
21. J. S. WELLS, A. HINZ, AND A. G. MAKI, *J. Mol. Spectrosc.* **114**, 84-96 (1985).