

NOTES

Heterodyne Frequency Measurements on SO₂ near 41 THz (1370 cm⁻¹)

In an effort to give frequency calibration data for the entire infrared region we have used heterodyne frequency measurement techniques to produce calibration tables based on absorption lines of N₂O between 1257 and 1340 cm⁻¹ (1) and CS₂ between 1460 and 1550 cm⁻¹ (2). To bridge the gap between 1340 and 1460 cm⁻¹, we have now made similar frequency measurements on the strong ν₃ band of SO₂ (sulfur dioxide) between 1349 and 1395 cm⁻¹. The experimental techniques used in these measurements were the same as those described in Refs. (1, 2).

The 001-000 transition of SO₂ has been measured by Guelachvili *et al.* (3) with a Fourier transform spectrometer, and their analysis gave excellent rovibrational constants for this band. With the exception of the band center all of the constants given by Guelachvili *et al.* were used in the present analysis. We had intended that the least-squares fit of the present measurements should only determine a new value for the band center. That was found to be ν₀ = 1362.06022 ± 0.00005 cm⁻¹, which was lower than the center given by Guelachvili *et al.* (3) by about 0.00047 cm⁻¹ (14 MHz). The direction and magnitude of the difference was what was expected from other comparisons with similar FTS measurements.

Although Guelachvili *et al.* implied that interactions affecting the frequencies of the 001-000 transitions are negligible (compared to experimental error), we found that the measurements could not be fit to within

TABLE I
Heterodyne Frequency Measurements on the ν₃ Band of Sulfur Dioxide

Transfer Oscillator		Freq. MHz	Sulfur Dioxide					Obs. Frequency* MHz	O-C MHz	
CO Trans. P _v (J ^a)	ν _{OSO} -ν _{CO} MHz		Transition J' K _a ' K _c ' J'' K _a '' K _c ''							
P ₃₀ (11)	40 458 311.6	-1291.8	17	6	11	18	6	12	40 457 019.8(50)	-2.5
		674.8	19	0	19	20	0	20	40 458 986.4(50)	9.6
		2463.9	15	10	5	16	10	6	40 460 775.5(90)	-7.1
		3051.3	16	8	9	17	8	10	40 461 362.9(50)	-6.9
		3882.0	18	2	17	19	2	18	40 462 193.6(50)	4.7
		4734.8	17	5	12	18	5	13	40 463 046.4(50)	-0.7
		6623.0	17	2	15	18	2	16	40 464 934.6(50)	-0.8
P ₃₀ (8)	40 737 592.1	-3055.5	21	12	9	21	12	10	40 734 536.6(40)	3.1
		-2593.0	4	2	3	5	2	4	40 734 999.1(40)	0.4
		-1665.7	20	12	9	20	12	8	40 735 926.4(40)	-0.3
		-342.4	19	12	7	19	12	8	40 737 249.7(40)	-3.9
		916.2	18	12	7	18	12	6	40 738 508.3(40)	-6.0
		3045.4	4	1	4	5	1	5	40 740 637.5(40)	4.4
		3236.9	16	12	5	16	12	4	40 740 829.0(40)	-7.9
		3904.7	25	11	14	25	11	15	40 741 496.8(40)	10.7
		4295.6	15	12	3	15	12	4	40 741 887.7(40)	-11.1
		6217.7	13	12	1	13	12	2	40 743 809.8(60)	-13.8
		7184.8	3	0	3	2	0	2	40 890 362.9(60)	15.5
P ₂₉ (14)	40 883 178.1	-2181.0	8	3	6	7	3	5	40 979 127.8(200)	-2.8
		403.8	9	6	3	8	6	2	40 981 712.6(100)	-8.0
		2587.1	10	8	3	9	8	2	40 983 895.9(90)	-8.8
P ₂₉ (12)	41 078 446.9	6857.0	9	5	4	8	5	3	40 988 165.8(150)	-8.9
		-3070.6	15	8	7	14	8	6	41 075 376.3(30)	-5.2
		150.5	17	11	6	16	11	5	41 078 597.4(60)	-3.9
		1508.3	14	1	14	13	1	13	41 079 955.2(50)	6.7
		1746.9	14	5	10	13	5	9	41 080 193.8(30)	-6.5
P ₂₉ (10)	41 269 727.9	-2149.5	27	10	17	26	10	16	41 267 578.4(50)	8.0
		1348.9	25	6	19	24	6	18	41 271 076.8(40)	-1.6
		1590.5	26	8	19	25	8	18	41 271 318.4(40)	2.3
		3051.2	28	11	18	27	11	17	41 272 779.1(40)	11.5
		5563.5	26	1	26	25	1	25	41 275 291.4(40)	11.6

TABLE I—Continued

$P_{28}(15)$	41 497 826.6	-3670.9	39	8	31	38	8	30	41	494	155.7(60)	3.0
		-2362.5	42	12	31	41	12	30	41	495	464.1(80)	13.6
		-1160.0	38	6	33	37	6	32	41	496	666.6(40)	-9.0
		1562.9	38	4	35	37	4	34	41	499	389.5(40)	-11.9
		2426.8	37	3	34	36	3	33	41	500	253.4(40)	-17.2
		4405.6	38	5	34	37	5	33	41	502	232.2(40)	-12.7
		6354.3	41	0	41	40	0	40	41	504	180.9(60)	7.4
		6915.5	39	7	32	38	7	31	41	504	742.1(50)	-4.9
		7088.4	41	10	31	40	10	30	41	504	915.0(60)	9.5
		7542.6	39	2	37	38	2	36	41	505	369.2(40)	-5.1
$P_{28}(12)$	41 795 322.9	-2743.4	57	8	49	56	8	48	41	792	579.5(40)	13.5
		-1945.1	59	10	49	58	10	48	41	793	377.8(50)	31.3
		-563.9	60	11	50	59	11	49	41	794	759.0(40)	-15.7
		700.9	59	3	56	58	3	55	41	796	023.8(60)	15.2
		899.7	61	1	60	60	1	59	41	796	222.6(50)	22.4
		1537.1	58	5	54	57	5	53	41	796	860.0(50)	14.9
		rms deviation of 47 measurements	10.5 MHz									

a) The estimated uncertainty in the last digits is given in parentheses.

the error limits of the present measurements. To verify this point, some of the measurements with large deviations were remeasured without substantially changing the observed value.

We also found that the deviations of the fit of the infrared measurements became even greater when microwave measurements (4) for the 001 state were added to the fit and the ν_3 rotational constants were floated. That was so because the uncertainty of the microwave measurements was very much smaller than the uncertainty of the infrared measurements. Since the deviations in the fit were actually dictated by the inability of the Hamiltonian to account for weak perturbations, rather than by experimental errors, all the experimental data should have been weighted according to the likelihood that the transitions might be perturbed. In the final analysis we chose to fit only our new measurements and to accept the constants given by Guelachvili *et al.* (3), except for the band center.

The transitions that were measured in this work are given in Table I. Since we do not have a Hamiltonian for calculating the energy levels of this band of SO_2 to the accuracy of the present measurements, we can only recommend that the transitions that have actually been measured be used for calibration purposes.

REFERENCES

1. J. S. WELLS, A. HINZ, AND A. G. MAKI, *J. Mol. Spectrosc.* **114**, 84–96 (1985).
2. J. S. WELLS, M. SCHNEIDER, AND A. G. MAKI, *J. Mol. Spectrosc.* **132**, 422–428 (1988).
3. G. GUELACHVILI, O. N. ULENIKOV, AND G. A. USHAKOVA, *J. Mol. Spectrosc.* **108**, 1–5 (1984).
4. F. J. LOVAS, *J. Phys. Chem. Ref. Data* **7**, 1445–1750 (1978).

M. D. VANEK¹
J. S. WELLS

Time and Frequency Division
National Institute of Standards and Technology
Boulder, Colorado 80303

A. G. MAKI

Department of Chemistry
University of Washington
Seattle, Washington 98195

JAMES B. BURKHOLDER

National Oceanic and Atmospheric Administration and
Cooperative Institute for Research in Environmental Sciences
Boulder, Colorado 80303

Received February 27, 1990

¹ Present address: NASA Langley Research Center, Hampton, Virginia 23665.