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Heterodyne Frequency Measurements on N_2O near 930 cm^{-1}

A. G. MAKI

Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland 80899

AND

J. S. WELLS AND M. D. VANEK

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

Heterodyne frequency measurements have been made on the first hot band accompanying the N_2O laser transitions in the region from 896 to 955 cm^{-1}. These measurements tie the upper state energy level at 2798 cm^{-1} to the other low-lying energy levels of N_2O by measurements referred to the cesium frequency standard and thereby provide frequency calibration in the 2740 to 2840 cm^{-1} region.

INTRODUCTION

Whitford *et al.* (*1*) have measured the frequencies of 33 nitrous oxide (N_2O) laser transitions from 925 to 970 cm^{-1}. Measurement accuracies of 60 kHz were achieved through the use of saturated absorption techniques. Those measurements were later combined with other heterodyne measurements (*2–4*) to provide a chain of frequency measurements that would tie the upper energy level (10^00)[1] at 2224 cm^{-1} to the other energy levels of N_2O by measurements referable to the cesium frequency standard.

We have recently been involved in improving the accuracy of calibration data available throughout the infrared and have been particularly concerned with tying together all the lower rovibrational states of N_2O by measurements referred to the cesium frequency standard. We now have 12 heterodyne frequency measurements of the 11^10–01^11 transition of N_2O near 930 cm^{-1}. These new measurements have been combined with other frequency measurements (*4*, *6*) to give calibration frequencies for the 11^10–00^00 transition near 2798 cm^{-1}.

EXPERIMENTAL DETAILS

The technique used for the 12 new heterodyne measurements is essentially that described at the inception of this measurement program (*7*). The radiation from a tunable diode laser (TDL) whose frequency was locked to the N_2O feature of interest was heterodyned with the output of a CO_2 laser frequency standard, which was stabilized by the Freed–Javan technique (*8*). We list in Table I the difference frequency for each

[1] The vibrational numbering system adopted by the IAU–IUPAP joint commission on spectroscopy (*5*) is used throughout this paper. Most other authors use a notation that interchanges ν_1 and ν_3.

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measurement and the corresponding CO_2 laser transition. Both $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ lasers were used. The $^{12}C^{16}O_2$ laser frequencies were taken from the latest work by Petersen *et al.* (*9*) and the $^{13}C^{16}O_2$ values came from the most recent work at Massachusetts Institute of Technology (*10*). Combining the heterodyne difference frequency with the appropriate CO_2 laser frequency produced the values for the measured N_2O transition frequencies given in Table I. New heterodyne frequency measurements on the 10^00–00^01 band (designated the A band) are also given in Table I. The Obs. − Calc. (observed minus calculated) column in Table I shows that all residuals fall within our specified uncertainty.

The measurements were made at a pressure of 667 Pa (5 Torr) of N_2O in a 1.7 m long absorption cell. The cell was elevated to a temperature of 377 K.

ANALYSIS OF THE DATA

The upper state constants given by Amiot and Guelachvili (*11*) and the lower state constants given by Vanek *et al.* (*4*) were used to calculate and assign the 11^10–01^11 transitions. In addition the 10^00–00^01 transitions were assigned by using the tables given by Whitford *et al.* (*1*).

Both the 11^10–01^11 and 10^00–00^01 transitions were fitted by using the usual energy level expression,

$$E(v, l, J) = G(v, l) + B_vJ(J+1) - D_v[J(J+1) - l^2]^2 + H_v[J(J+1) - l^2]^3 + L_v[J(J+1) - l^2]^4 + \cdots , \quad (1)$$

TABLE I

Heterodyne Frequency Measurements on N_2O near 930 cm^{-1}

CO_2 Laser Trans.	$\nu_{NNO}-\nu_{OCO}$ (MHz)	Trans.[a]	Nitrous Oxide Frequency (MHz)	Obs.-Calc. (MHz)
$^3P_I(20)$[b]	1065.6	P(24)F	26889735.4(60)[c]	4.7
	3003.3	P(46)A	26891673.1(50)	3.5
	4583.6	P(24)E	26893253.4(50)	1.3
$^3P_I(6)$	-2223.2	P(34)A	27239172.6(50)	2.6
	-1571.9	P(11)F	27239823.9(80)	2.0
	-538.4	P(11)E	27240857.4(50)	1.7
$P_I(34)$	-2590.7	R(15)F	27908130.1(30)	0.6
	-2383.9	R(15)E	27908336.9(30)	1.2
$^3R_I(32)$	-3490.0	R(22)F	28068189.7(30)	-1.3
	-2537.6	R(22)E	28069142.1(30)	-1.2
	-921.7	P(3)A	28070758.0(30)	-0.6
$^3R_I(42)$	-3099.8	R(30)F	28244287.3(40)	-3.8
	-2217.5	R(3)A	28245169.6(40)	-1.3
	-768.9	R(30)E	28246618.2(40)	0.5
$P_I(16)$	383.8	R(38)F	28412973.5(70)	0.6
	1981.5	R(10)A	28414571.2(70)	-4.8
$P_I(8)$	-3412.0	R(48)F	28613129.8(90)	-1.3
$R_I(44)$	655.5	R(71)A	29669511.3(100)	-2.3

a) The band definitions are as follows; A ≡ 10^00-00^01, E ≡ $11^{1e}0$-$01^{1e}1$, and F ≡ $11^{1f}0$-$01^{1f}1$.

b) The left 3 superscript indicates the $^{13}C^{16}O_2$ isotope, otherwise $^{12}C^{16}O_2$ is used.

c) The uncertainty in the last digits is given in parentheses.

TABLE II

Band Centers Determined from Heterodyne Measurements on N_2O

Vib. Transitions	ν_0 (cm^{-1})
11^10-01^11	918.026771(62)[a]
11^10-00^00	2798.292487(94)
01^11-00^00	1880.265717(70)
10^00-00^01	938.8534038(8)

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

with the band center given by

$$\nu_0 = G(v', l') - G(v'', l''). \tag{2}$$

When $l = 1$ the l-type doubling was taken into account by substituting for B_v in Eq. (1) the expression

$$B_v \pm 0.5[q_v - q_{vJ}J(J+1) + q_{vJJ}J^2(J+1)^2].$$

In this expression the upper sign (+) was used for the f levels while the lower sign (−) was used for the e levels.

Since the goal of this work was to provide the best estimate of the frequencies and uncertainties of N_2O transitions that might be used for calibration in many different frequency regions, the present frequency measurements were combined with many other frequency measurements in a large least-squares fit that gave the rovibrational constants needed to calculate the appropriate transitions and the variance–covariance matrix elements needed to calculate the uncertainties in the transitions. The resulting band centers are given in Table II and the rovibrational constants are given in Table III.

TABLE III

Rotational Constants (in cm^{-1}) Determined for N_2O

Vib. State	B_v (MHz)	D_v (kHz)	H_v (mHz)	L_v (μHz)
00^00	12561.63395(19)[a]	5.27915(24)	-0.4921(276)	---
00^01	12508.99224(28)	5.17354(33)	3.399(58)	0.1327(38)
01^11	12528.87971(70)	5.19709(75)	4.227(178)	0.0862(143)
10^00	12458.16082(24)	5.26046(26)	-0.400(29)	---
11^10	12476.13619(113)	5.34222(65)	-0.156(82)	---
	q_v (MHz)	q_{vJ} (kHz)	q_{vJJ} (mHz)	
01^11	27.23272(69)	-0.08613(46)	3.327(45)	
11^10	23.29882(66)	0.03603(26)	---	

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

DISCUSSION OF RESULTS

At the same time that measurements were made on the 11^10–01^11 transitions, measurements were also made on the 10^00–00^01 transitions even though they had already been measured more accurately by Whitford *et al.* (*1*). These measurements were considered to be primarily a test of our measurement techniques to ensure that there are no hidden systematic errors. In a preliminary test fit the present measurements on the 10^00–00^01 band were fitted to a different band center than the measurements of Whitford *et al.* (*1*), but the same rovibrational constants were used for the two sets of measurements. That test fit gave a band center that was 0.000004 cm^{-1} (0.11 MHz) lower than that given by the saturated absorption measurements of Whitford *et al.* The agreement with the earlier more accurate work is taken as evidence that the measurements on the 11^10–01^11 band are as accurate as the statistical analysis indicates. This also indicates that the pressure shift in the present measurements is at least as

TABLE IV

Wavenumbers (in cm^{-1}) Calculated for the $11^{1e}0$–00^00 Band of N_2O

P-Branch	J''	R-Branch	P-Branch	J''	R-Branch
---	0	2799.12403(09)[a]	2765.13406(09)	35	2824.10992(09)
---	1	2799.94908(09)	2764.07164(09)	36	2824.70506(09)
2796.60997(09)	2	2800.76765(09)	2763.00287(09)	37	2825.29354(09)
2795.75900(09)	3	2801.57973(09)	2761.92775(09)	38	2825.87534(09)
2794.90156(09)	4	2802.38530(09)	2760.84629(09)	39	2826.45048(10)
2794.03766(09)	5	2803.18438(09)	2759.75849(09)	40	2827.01894(10)
2793.16730(09)	6	2803.97695(09)	2758.66435(10)	41	2827.58071(10)
2792.29049(09)	7	2804.76301(09)	2757.56387(10)	42	2828.13580(10)
2791.40722(09)	8	2805.54255(09)	2756.45706(10)	43	2828.68419(10)
2790.51751(09)	9	2806.31557(09)	2755.34392(10)	44	2829.22588(10)
2789.62135(09)	10	2807.08207(09)	2754.22445(10)	45	2829.76086(10)
2788.71875(09)	11	2807.84204(09)	2753.09866(10)	46	2830.28913(10)
2787.80972(09)	12	2808.59547(09)	2751.96654(10)	47	2830.81068(10)
2786.89425(09)	13	2809.34237(09)	2750.82811(10)	48	2831.32551(10)
2785.97236(09)	14	2810.08272(09)	2749.68336(10)	49	2831.83361(11)
2785.04404(09)	15	2810.81653(09)	2748.53230(11)	50	2832.33497(11)
2784.10930(09)	16	2811.54378(09)	2747.37493(11)	51	2832.82959(11)
2783.16815(09)	17	2812.26448(09)	2746.21125(11)	52	2833.31746(11)
2782.22058(09)	18	2812.97861(09)	2745.04126(11)	53	2833.79858(12)
2781.26660(09)	19	2813.68618(09)	2743.86497(11)	54	2834.27295(12)
2780.30622(09)	20	2814.38717(09)	2742.68238(12)	55	2834.74054(12)
2779.33943(09)	21	2815.08158(09)	2741.49350(12)	56	2835.20137(13)
2778.36625(09)	22	2815.76942(09)	2740.29831(12)	57	2835.65541(13)
2777.38667(09)	23	2816.45066(09)	2739.09683(13)	58	2836.10268(13)
2776.40069(09)	24	2817.12532(09)	2737.88907(13)	59	2836.54315(14)
2775.40833(09)	25	2817.79337(09)	2736.67501(14)	60	2836.97683(14)
2774.40958(09)	26	2818.45483(09)	2735.45467(14)	61	2837.40370(15)
2773.40445(09)	27	2819.10967(09)	2734.22804(14)	62	2837.82377(15)
2772.39295(09)	28	2819.75791(09)	2732.99514(15)	63	2838.23702(16)
2771.37506(09)	29	2820.39952(09)	2731.75595(15)	64	2838.64346(16)
2770.35081(09)	30	2821.03451(09)	2730.51049(16)	65	2839.04306(17)
2769.32018(09)	31	2821.66287(09)	2729.25876(17)	66	2839.43584(18)
2768.28320(09)	32	2822.28460(09)	2728.00075(17)	67	2839.82177(18)
2767.23984(09)	33	2822.89969(09)	2726.73647(18)	68	2840.20086(19)
2766.19013(09)	34	2823.50813(09)	2725.46593(19)	69	2840.57310(20)

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

small as the uncertainty in the measurements. We expect that the pressure shift for N_2O at 667 Pa (5 Torr) is negative and on the order of 1 to 2 MHz.

The present results were used to calculate the transitions (given in Table IV) for the 2798 cm^{-1} band (11^10–00^00). The FTS values given by Guelachvili and Rao (*12*) for that band show a systematic difference of 0.0006 cm^{-1} (18 MHz) from the present results. The earlier FTS measurements were too high. This agrees with a trend that was observed earlier (*13, 14*) and probably arises from a systematic error in the CO calibration that was used for the FTS measurements.

The need for L_v terms for both the 00^01 and 01^11 states is not unexpected since those states exhibit a weak Fermi resonance with the 02^00 and 03^10 states respectively. The unusually large H_v terms (nearly ten times the ground state value) are another indication of the effect of the Fermi resonance.

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REFERENCES

1. B. G. WHITFORD, K. J. SIEMSEN, H. D. RICCIUS, AND G. R. HANES, *Opt. Commun.* **14,** 70–74 (1975).
2. J. S. WELLS, A. HINZ, AND A. G. MAKI, *J. Mol. Spectrosc.* **114,** 84–96 (1985).
3. L. R. ZINK, J. S. WELLS, AND A. G. MAKI, *J. Mol. Spectrosc.* **123,** 426–433 (1987).
4. M. D. VANEK, M. SCHNEIDER, J. S. WELLS, AND A. G. MAKI, *J. Mol. Spectrosc.* **134,** 154–158 (1989).
5. R. S. MULLIKEN, *J. Chem. Phys.* **23,** 1997–2011 (1955).
6. J. S. WELLS, D. A. JENNINGS, A. HINZ, J. S. MURRAY, AND A. G. MAKI, *J. Opt. Soc. Amer. B: Opt. Phys.* **2,** 857–861 (1985).
7. J. S. WELLS, F. R. PETERSEN, AND A. G. MAKI, *Appl. Opt.* **18,** 3567–3573 (1979).
8. C. FREED AND A. JAVAN, *Appl. Opt. Lett.* **17,** 53–56 (1970).
9. F. R. PETERSEN, E. C. BEATY, AND C. R. POLLOCK, *J. Mol. Spectrosc.* **102,** 112–122 (1983).
10. L. C. BRADLEY, K. L. SOOHOO, AND C. FREED, *IEEE J. Quant. Elect.* **OE-22,** 234–267 (1986).
11. C. AMIOT AND G. GUELACHVILI, *J. Mol. Spectrosc.* **59,** 171–190 (1976).
12. G. GUELACHVILI AND K. NARAHARI RAO, "Handbook of Infrared Standards," Academic Press, Orlando, FL, 1986.
13. C. R. POLLOCK, F. R. PETERSEN, D. A. JENNINGS, J. S. WELLS, AND A. G. MAKI, *J. Mol. Spectrosc.* **107,** 62–71 (1984).
14. L. R. BROWN AND R. TOTH, *J. Opt. Soc. Amer. B: Opt. Phys.* **2,** 842–856 (1985).