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Heterodyne Measurements on N_2O near 1635 cm^{-1}

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Heterodyne frequency measurements have been made on eight lines of the 10^00–01^10 band of N_2O between 1591 and 1673 cm^{-1}. These measurements were combined with other heterodyne frequency measurements to obtain improved frequency values for the 01^10–00^00 transitions from 520 to 660 cm^{-1}. © 1989 Academic Press, Inc.

In an earlier paper (*1*) heterodyne frequency measurements on the 01^11–00^00 (*2*) and 01^11–01^10 (*1*) bands of nitrous oxide (N_2O) were used to obtain frequencies for the 01^10–00^00 transition,[3] for which direct heterodyne measurements cannot be made in our laboratory. These measurements are part of a program designed to provide frequency measurements for frequency or wavenumber calibration tables throughout the infrared. The present heterodyne measurements were undertaken in order to provide an entirely different route for determining the frequencies of the 01^10–00^00 transitions. These measurements also provide calibration data in the region 1590 to 1675 cm^{-1}.

Heterodyne frequency measurements have been made on eight transitions of the 10^00–01^10 band of N_2O near 1635 cm^{-1}. These measurements used a CO laser as a local oscillator to transfer the frequency of combinations of two CO_2 lasers to the 1635 cm^{-1} region with a heterodyne technique that has been described in earlier publications (*1, 2*). The center of the N_2O absorption line was located by means of a first derivative lock of a tunable diode laser to the peak of the N_2O absorption. The measurements were made with a 1.7-m absorption cell containing up to 700 Pa (5 Torr) of N_2O.

The measurements are given in Table I along with an estimate of the accuracy of each measurement and the deviation of the measurement from the calculated frequency. The calculated frequency is given by the constants in Tables II and III. Table I also shows the frequency of the CO laser transition used as a local oscillator. The

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[3] The vibrational numbering system adopted by the IAU–IUPAP joint commission on spectroscopy (*3*) is used throughout this paper. Most other authors use a notation that interchanges ν_1 and ν_3.

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TABLE I

Heterodyne Measurements on the 10^00–01^10 Band of Nitrous Oxide

Transfer Oscillator		Nitrous Oxide		
Trans. Pv"(J")	Frequency, MHz	Trans.	Frequency, MHz	Obs. - Calc., MHz
P20(11)	47709947.3[a]	P(44)	47706760.3(100)[b]	-1.1
P19(13)	48233533.1	P(28)	48230503.8(100)	-8.7
P18(15)	48751484.0	P(10)	48754661.7(100)	0.8
P18(13)	48971682.3	Q(18)	48970527.3(50)	-1.2
P18(13)	48971682.3	Q(17)	48975279.7(50)	-6.0
P18(11)	49187918.6	R(6)	49185589.0(70)	3.3
P17(15)	49490058.3	R(20)	49493233.9(50)	-3.1
P17(9)	50145039.1	R(61)	50146501.0(100)	3.9

[a]We estimate that the CO frequency indicated represents the center of the transition to within ± 3 MHz. The uncertainty as a transfer oscillator is 0.2 MHz and this is included in the uncertainty in the frequency of the nitrous oxide transition.

[b]The estimated uncertainty in the last digits is given in parentheses. This is one-tenth of the TDL jitter linewidth plus one half of the Doppler width divided by the signal-to-noise ratio of the first derivative lock signal.

uncertainty in the CO laser frequency is determined by our estimate of the accuracy with which the center of the laser transition was located and has nothing to do with the accuracy of the N_2O measurements.

In the analysis the term values were given by

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

TABLE II

Band Centers Determined from Heterodyne Measurements on N_2O

Transition	Wavenumber (cm^{-1})	Frequency (MHz)
10^00-00^00	2223.756683(68)[a]	66666548.2(20)
01^11-00^00	1880.265709(85)	56368947.9(25)
10^00-01^10	1634.988914(100)	49015734.5(30)
01^11-01^10	1291.497940(73)	38718134.2(22)
00^01-00^00	1284.903279(68)	38520431.2(20)
10^00-00^01	938.8534038(10)	28146116.964(29)
01^10-00^00	588.767769(97)	17650813.7(29)

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

TABLE III

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

Vib. State	B_v	$D_v x 10^7$	$H_v x 10^{13}$
00^00	0.419011009(13)[a]	1.761014(122)	-0.1555(130)
01^10	0.4195735903(101)	1.788677(147)	-0.0895(212)
00^01[b]	0.417255074(12)	1.725808(156)	1.1474(251)
01^11[c]	0.417918445(26)	1.733586(271)	1.4070(672)
10^00	0.415559520(11)	1.754790(129)	-0.1242(134)
	$q_v x 10^4$	$q_{vJ} x 10^9$	$q_{vJJ} x 10^{13}$
01^10	7.9200568(37)	1.01272(715)	---
01^11	9.083898(265)	-2.8632(167)	1.1119(174)

a) The uncertainty in the last digits (twice the standard error) is given in parentheses.
b) For the 00^01 state L_v=4.392(149)x10^{-18} was also determined.
c) For the 01^11 state L_v=2.88(55)x10^{-18} was determined.

and the transition band center was given by

$$\nu_0 = G(v', l') - G(v'', l''). \qquad (2)$$

When $l = 1$ the l-type doubling was taken into account by substituting for B_v the expression

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

where the value of q_v is assumed to be positive and, for N_2O, the positive sign is needed for the f levels and the negative sign is needed for the e levels (that is, the e levels are lower in energy than the f levels).

The data given in Table I were combined in a least-squares fit with microwave measurements given in Refs. (*4–9*) for the 00^00, 01^10, 00^01, 01^11, and 10^00 states. Also included in the least-squares fit were infrared combination differences involving the 10^00, 00^01, 01^11, 01^10, and 00^00 states taken from Refs. (*10–12*). Finally, heterodyne measurements involving the 10^00–00^01 (*13*), 01^11–00^00 (*2*), 01^11–01^10 (*1*), and 00^01–00^00 (*1*) transitions were used in the fit. In these fits the data were weighted by the inverse square of our estimate of their uncertainties. Table II gives the band centers resulting from this fit while Table III gives the rotational constants. Table IV gives the transition wavenumbers calculated for the 01^10–00^00 band. The uncertainties given in Table IV were calculated by means of the variance–covariance matrix elements given by the least-squares fit.

Our measurements are in excellent agreement with the band center, 1634.988889(13) cm^{-1}, given by Toth (*12*). The present heterodyne value for the center of the 01^10–00^00 band is also in excellent agreement with the earlier heterodyne value (*1*) and with the various values that can be determined from Toth's measurements (*11, 12*). The transition wavenumbers given in Table IV are also in excellent agreement with those given by Guelachvili and Rao (*14*).

TABLE IV

Wavenumbers (cm^{-1}) Calculated for the $01^{1e}0$–00^00 Band of N_2O

P-Branch	J"	R-Branch	P-Branch	J"	P-Branch
---	0	589.60612(10)[a]	553.08300(10)	43	625.90244(10)
---	1	590.44481(10)	552.26262(10)	44	626.75049(10)
587.09206(10)	2	591.28382(10)	551.44271(10)	45	627.59862(10)
586.25472(10)	3	592.12315(10)	550.62327(10)	46	628.44683(10)
585.41773(10)	4	592.96280(10)	549.80431(10)	47	629.29512(11)
584.58108(10)	5	593.80276(10)	548.98582(11)	48	630.14348(11)
583.74480(10)	6	594.64302(10)	548.16781(11)	49	630.99189(11)
582.90886(10)	7	595.48359(10)	547.35027(11)	50	631.84036(11)
582.07329(10)	8	596.32446(10)	546.53322(11)	51	632.68888(12)
581.23809(10)	9	597.16562(10)	545.71665(11)	52	633.53744(12)
580.40326(10)	10	598.00707(10)	544.90056(12)	53	634.38604(12)
579.56880(10)	11	598.84880(10)	544.08496(12)	54	635.23466(13)
578.73472(10)	12	599.69082(10)	543.26984(12)	55	636.08330(13)
577.90102(10)	13	600.53310(10)	542.45521(13)	56	636.93195(13)
577.06770(10)	14	601.37566(10)	541.64107(13)	57	637.78060(14)
576.23477(10)	15	602.21848(10)	540.82742(14)	58	638.62926(14)
575.40224(10)	16	603.06155(10)	540.01426(14)	59	639.47790(15)
574.57010(10)	17	603.90489(10)	539.20160(15)	60	640.32653(16)
573.73835(10)	18	604.74847(10)	538.38943(15)	61	641.17514(16)
572.90701(10)	19	605.59229(10)	537.57776(16)	62	642.02371(17)
572.07607(10)	20	606.43635(10)	536.76658(17)	63	642.87224(18)
571.24555(10)	21	607.28064(10)	535.95590(17)	64	643.72073(18)
570.41543(10)	22	608.12517(10)	535.14572(18)	65	644.56917(19)
569.58573(10)	23	608.96991(10)	534.33603(19)	66	645.41754(20)
568.75644(10)	24	609.81487(10)	533.52685(20)	67	646.26584(21)
567.92758(10)	25	610.66004(10)	532.71817(21)	68	647.11407(22)
567.09913(10)	26	611.50541(10)	531.91000(21)	69	647.96221(23)
566.27112(10)	27	612.35099(10)	531.10232(22)	70	648.81025(24)
565.44353(10)	28	613.19675(10)	530.29515(23)	71	649.65820(25)
564.61638(10)	29	614.04271(10)	529.48849(25)	72	650.50604(27)
563.78966(10)	30	614.88885(10)	528.68233(26)	73	651.35377(28)
562.96338(10)	31	615.73516(10)	527.87667(27)	74	652.20136(29)
562.13753(10)	32	616.58164(10)	527.07153(28)	75	653.04883(31)
561.31213(10)	33	617.42829(10)	526.26689(30)	76	653.89616(33)
560.48718(10)	34	618.27510(10)	525.46275(32)	77	654.74334(35)
559.66267(10)	35	619.12206(10)	524.65913(33)	78	655.59036(37)
558.83861(10)	36	619.96916(10)	523.85601(35)	79	656.43722(39)
558.01501(10)	37	620.81640(10)	523.05341(37)	80	657.28391(41)
557.19186(10)	38	621.66378(10)	522.25131(39)	81	658.13041(43)
556.36916(10)	39	622.51128(10)	521.44973(41)	82	658.97673(46)
555.54693(10)	40	623.35891(10)	520.64865(44)	83	659.82285(49)
554.72515(10)	41	624.20665(10)	519.84808(47)	84	660.66876(52)
553.90384(10)	42	625.05450(10)	519.04803(49)	85	661.51446(55)

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

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