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Absolute Frequency Measurements of the 00^02-00^00, 20^01-00^00, and 12^01-00^00 Bands of N_2O by Heterodyne Spectroscopy

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The absolute frequencies of 39 lines in the 00^02-00^00, 20^01-00^00, and 12^01-00^00 bands of N_2O in the range 4300–4800 cm^{-1} have been measured by heterodyne frequency techniques. The lines were each measured in Doppler-limited absorption, with a color-center laser as a tunable probe of the N_2O and two stabilized CO_2 lasers as reference frequencies. New rovibrational constants have been fitted to these measurements. Tables of calculated transition frequencies are given, with estimated absolute uncertainties as small as 10^{-4} cm^{-1}. The pressure shifts of four lines have been measured, and the values fall within the range of 0 to −2 MHz/kPa (0 to −0.2 MHz/Torr).

INTRODUCTION

Wavenumber values for the near-infrared rovibrational transitions of N_2O have been determined by Amiot and Guelachvili (*1*) using Fourier transform spectroscopy, and recently by Braund *et al.* (*2*) using a vacuum infrared monochromator. Both sets of measurements report uncertainties of 10^{-3} cm^{-1}. The latter measurements were calibrated against the 2-0 CO wavenumbers reported by Guelachvili (*3*), which were also determined by Fourier transform spectroscopy. In light of recent heterodyne spectroscopy measurements of the 2-0 CO frequencies (*4*), which were found to be in small but significant disagreement with those obtained by interferometry, it is valuable to confirm the wavelength measurements of important molecular species, such as N_2O, by direct frequency measurements.

In this present work, the absolute frequencies of 39 lines of the 00^02-00^00, 12^01-00^00, and 20^01-00^00 bands of N_2O were measured with a tunable color-center laser. In these measurements, the color-center laser was locked to the center of the N_2O line, and its frequency was measured by heterodyning in a metal–insulator–metal (MIM) diode with appropriate harmonics of two well-characterized CO_2 lasers. Measurements ranged approximately to $J = 50$ in both the R and P branches of each of the vibrational bands. Attempts to observe the transitions using Doppler-free saturated-

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absorption techniques were unsuccessful. Hence, the results reported here were derived from Doppler-limited spectra, with an estimated measurement uncertainty as low as 4 MHz on some lines. In addition, pressure-shift measurements were made on the 00^02-00^00 and 12^01-00^00 bands, which indicate that the pressure-induced shifts in the line centers lie in the 0 to −2 MHz/kPa range.

EXPERIMENTAL TECHNIQUE

A broadly tunable color-center laser was used to detect the N_2O transitions. The laser has been briefly described elsewhere (*5*); we note here that it used the $(F_2^+)_A$ center in KCl:Li and was tunable over the range 4200–4800 cm^{-1}, with cw single-mode powers ranging from 10 mW at the extremes to 200 mW at the peak of the tuning curve. The laser was actively stabilized by locking its frequency to the resonant frequency of a passively stabilized optical cavity to produce a residual linewidth of less than 10 kHz. Continuous tuning of the laser was accomplished by adjusting the optical length of the passive cavity with a galvo-driven Brewster plate.

A small portion of the color-center laser beam (5 mW) was sent through an 8-m cell filled with N_2O at pressures varying between 0.1 and 2 kPa (1 and 15 Torr). The transmitted radiation was monitored with a room-temperature InAs detector operated in the photovoltaic mode. The experimental setup is the same as in Ref. (*4*). We locked the laser onto an individual N_2O line by dithering its frequency 4 MHz peak-to-peak over the peak of the absorption feature and using the resultant first-derivative signal. The modulation frequency was 8 kHz, chosen to be well above the major noise spectrum of the laser (which followed the noise of the Nd:YAG pump laser and rolled off rapidly above 2 kHz) and yet low enough for the laser frequency to respond linearly to the sinusoidal dither signal from the lock-in amplifier. The derivative signal from the locking amplifier was used to control the length of the passive optical cavity to which the laser frequency was locked. Thus, the color-center laser was effectively locked to the peak of the N_2O absorption.

For each N_2O line a potential systematic error can occur because of offsets arising from background slope superimposed on the derivative signal. These offsets arise from atmospheric absorptions, interference effects from windows, etc. We found it impossible to entirely eliminate these effects in spite of attempts with ratio and difference schemes. Hence, prior to each measurement, we tuned the laser frequency across the absorption feature and carefully centered the derivative signal about zero using the offset adjustment of the lock-in amplifier. The observed signal-to-noise ratio (S/N) for most of the signals exceeded 100, which for the Doppler-limited width of about 300 MHz would, in principle, allow determination of the line center to within 3 MHz. Unfortunately, the background offsets often were of magnitudes larger than the noise and, hence, our line-center measurements were limited by how well these offsets could be zeroed, rather than by the S/N. The uncertainties, which ranged from ±4 to ±12 MHz, represent our best estimates of the errors in this adjustment. Since the offset error was probably different in magnitude and in sign for each measured transition, we assume that the offset errors will appear as random errors in the least-squares fit of the data.

The major portion of the color-center laser beam was reflected from a 70% reflectance beam splitter, and directed onto a W–Ni MIM point-contact diode. Coincident on the diode were about 200 mW of CO_2 laser radiation from two stabilized CO_2 lasers. For the 12^01-00^00 and 20^01-00^00 bands, $^{12}C^{16}O_2$ lasers were used. Except for the $P(61)$ and $P(56)$ lines, the 00^02-00^00 band required the use of $^{13}C^{16}O_2$ lasers. The two CO_2 laser frequencies ν_1 and ν_2 were chosen such that one of the harmonic combinations $5\nu_1$, $4\nu_1 + \nu_2$, or $3\nu_1 + 2\nu_2$ was approximately equal to the desired N_2O frequency (within 2 GHz). The difference, ν_B, between the color-center laser frequency and the synthesized frequency from the CO_2 lasers appeared as an rf beat on the point-contact diode. The beat signal was amplified and displayed on an rf spectrum analyzer. We measured N_2O lines for which a convenient combination of CO_2 lines would produce a beat frequency with the color-center laser which was within the pass band of our amplifiers. Each beat signal, typically with 10–20 db S/N, along with frequency markers on both sides from a Cs-referenced frequency synthesizer, was averaged for 30 sec. The averaged signal, typically 4 MHz wide, was plotted for later analysis. The line center of the beat signal could usually be found to within 200 kHz.

Knowledge of the CO_2 laser frequencies (*6, 7*), which have less than 200-kHz uncertainties, and of the beat frequency permitted the determination of the absolute frequency of the N_2O transitions. Thus,

$$\nu_{N_2O} = l\nu_1 + m\nu_2 \pm \nu_B,$$

where l and m are the harmonic numbers of the two CO_2 lasers. The frequency of the transition, ν_{N_2O}, from this measurement is absolute, and requires no further correction due to refractive index changes, diffraction effects, or other effects which often plague interferometric techniques.

HOW THE MEASUREMENTS WERE FIT

The measurements are given in Tables I, II, and III. These measurements were fit by a least-squares program to the usual equation for the rovibrational transitions of a linear molecule:

$$\nu_{obs} = \nu_0 + B_vJ'(J'+1) - D_v[J'(J'+1)]^2 + H_v[J'(J'+1)]^3 - B_0J''(J''+1) + D_0[J''(J''+1)]^2 - H_0[J''(J''+1)]^3. \quad (1)$$

In fitting the data, we took advantage of the very accurate ground state constants that could be determined from infrared measurements reported elsewhere (*1, 8–11*) and from microwave measurements (*12–17*). Ground state combination-differences from the infrared measurements were combined with the microwave measurements on the ground state to obtain the ground state constants given in Table IV. A total of 278 combination-differences extending to $J = 76$ and 19 microwave transitions from $J = 0$ to $J = 22$ were used in this least-squares fit.

The combination-differences were weighted by the inverse square of the RMS deviation of each data set, and the microwave measurements were weighted by the inverse square of the uncertainty given in the source paper, or given in Ref. (*18*).

In a separate fit, the upper state constants were determined from a least-squares fit of the present measurements, in which the ground state constants were treated as measured quantities and weighted by the inverse square of their respective uncertainties. Before the data were fit, an approximate correction to zero pressure was made by

TABLE I

Heterodyne Frequency Measurements for the 00^02-00^00 Band of N_2O near 4417 cm^{-1}

Rotational Transition	Measured[a] Freq. (MHz)	Obs.-Calc. (MHz)	Uncertainty (MHz)
P(61)	130 144 127.3	4.5	8
P(56)	130 388 676.3	-1.1	6
P(43)	130 976 979.5	1.4	5
P(33)	131 382 600.4	-0.3	6
P(23)	131 747 249.2	-1.9	6
P(11)	132 130 537.2	0.5	5
P(2)	132 378 993.4	0.1	6
R(1)	132 478 656.9	-0.4	6
R(11)	132 698 779.5	2.2	7
R(20)	132 861 336.0	-0.8	5
R(31)	133 014 162.2	0.0	4
R(42)	133 116 414.5	0.0	5
R(51)	133 162 374.1	2.4	7
R(56)	133 173 209.6	-6.8	8

a) These measurements were made at an N_2O pressure of 0.13 kPa (1 Torr) except P(61) and P(56), which were measured at a pressure of 2.0 kPa (15 Torr). Consequently, these values are probably low by 0.1 to 0.2 MHz except for P(61) and P(56), which are probably too low by 2 to 3 MHz.

TABLE II

Heterodyne Frequency Measurements for the 12^01-00^00 Band of N_2O near 4630 cm^{-1}

Rotational Transition	Measured[a] Freq. (MHz)	Pressure (kPa)	Obs.-Calc. (MHz)	Uncertainty (MHz)
P(41)	137 566 318.6	1.60	-4.4	7
P(30)	137 943 360.0	0.80	3.1	6
P(20)	138 257 759.1	0.80	-2.7	4
P(11)	138 518 373.4	0.80	-2.2	4
P(5)	138 680 576.9	0.80	2.6	6
P(1)	138 783 619.3	2.67	8.9	5
R(5)	138 954 117.1	0.80	-1.7	7
R(10)	139 068 215.3	0.80	-3.7	4
R(19)	139 257 195.6	0.80	-2.5	4
R(26)	139 389 267.0	0.40	1.2	4
R(30)	139 458 720.6	0.80	5.1	4
R(40)	139 612 588.2	0.80	-7.3	7
R(48)	139 714 734.6	0.80	2.6	7

a) We recommend that the zero pressure frequency be estimated by adding 1.2 x P(kPa) to the measured frequency in MHz.

TABLE III

Heterodyne Frequency Measurements for the 20^01-00^00 Band of N_2O near 4731 cm^{-1}

Rotational Transition	Measured[a] Freq. (MHz)	Obs.-Calc. (MHz)	Uncertainly (MHz)
P(50)	140 069 592.4	0.8	12
P(40)	140 501 736.7	-1.3	5
P(30)	140 894 004.2	2.9	5
P(26)	141 039 605.3	-0.6	4
P(19)	141 278 748.7	-2.0	5
P(10)	141 556 758.8	-0.5	6
P (3)	141 749 952.9	-1.7	6
R (0)	141 851 276.2	2.6	6
R(10)	142 075 625.7	1.2	6
R(20)	142 258 587.3	-0.2	6
R(30)	142 400 214.2	0.1	7
R(40)	142 500 689.5	0.8	9

a) These measurements were all made at an N_2O pressure of 0.133 kPa (1 Torr). Consequently, these frequencies are probably uniformly lower than the zero-pressure frequencies by about 0.1 to 0.2 MHz.

using the factor $\Delta_s = -1.2$ MHz/kPa (-0.16 MHz/Torr), which was determined as described in the next section.

PRESSURE-SHIFT MEASUREMENTS

Since these N_2O absorption bands are weak, some of the present measurements were made at relatively high pressures, and it is important to estimate the shift in

TABLE IV

Rovibrational Constants Determined for N_2O and Used to Calculate Tables VI, VII, and VIII

Band	ν_0 (MHz)
00^02-00^00	132 429 654.1 (25)
12^01-00^00	138 808 736.8 (55)
20^01-00^00	141 826 563.6 (23)

Vib. State	B (MHz)	D (kHz)	H (Hz)
00^02	12 354.452 61(802)	5.243 97(607)	-0.000 183(1188)
12^01	12 434.287 57(2789)	7.3008(329)	0.106 78(965)
20^01	12 355.010 15(1051)	4.861 30(1212)	0.018 17(370)
00^00	12 561.633 60(34)	5.278 421(567)	-0.000 5152(919)

the line centers due to the pressure-shift effect. We assume that the pressure shift takes the form:

$$\nu_{\text{obs}} = \nu + P\Delta_s, \tag{2}$$

where ν is the transition frequency at zero pressure, P is the pressure, and Δ_s is the pressure-shift coefficient. This is the form found for the pressure shift of the rotational transitions of other molecules by Belov *et al.* (*19*). It is also the form used for the pressure shift of CO by Bouanich (*20*).

Experiments were made here to determine the self-induced pressure shift for four transitions in the pressure range from 0.13 to 4.0 kPa (1 to 30 Torr), and the results are given in Table V. A calibrated capacitance manometer was used to measure the pressure.

While the uncertainty in the pressure shift for most of these measurements is nearly the same size and order of magnitude as the pressure shift itself, the sign and order of magnitude of the different measurements are consistent. The large uncertainty is easily understood since the line position was not reproducible to much better than ±2 MHz, and the measurement error increased significantly for higher pressures because of the line broadening.

The pressure shift for N_2O has the same sign and order of magnitude as that found for CO (*1*, *20*), as one might expect since both molecules have small dipole moments. We are not aware of any other measurements of the shift in the rovibrational transitions of N_2O. Wensink *et al.* (*21*) attempted to measure the pressure shift of the rotational transition $J = 1 \leftarrow 0$ in the ground vibrational state of $^{15}N_2O$. They could only suggest that the shift is less than 0.75 MHz/kPa (0.1 MHz/Torr), which agreed with some theoretical calculations they made.

Because of the large uncertainties in the pressure-shift measurements, the m-dependence (where $m = -J$ for P-branch transitions and $m = J + 1$ for R-branch transitions) of the pressure shift is not clear. The pressure shift measured for the $R(42)$ transition, −1.2 MHz/kPa (−0.16 MHz/Torr), is almost certainly not as reliable as the statistical uncertainty indicates, but it is probably a good value to use for estimating the pressure shift (within a factor of 2) for all transitions of N_2O in the range 4000–5000 cm^{-1}. This pressure shift was used to correct the present measurements to zero pressure before they were used to determine the constants of Table IV.

THE FREQUENCY TABLES

Tables VI, VII, and VIII give the calculated frequencies and their estimated uncertainties for all the transitions within the range of measured J values in the three bands that we have investigated. The frequencies were calculated from the constants in Table IV. The estimated uncertainties in the frequencies were determined by adding in quadrature the statistically determined standard error, the estimated error from the pressure-shift uncertainty, and an estimated 0.9-MHz uncertainty in the calibration frequency. For the weaker $12^01\text{-}00^00$ band given in Table VII, the pressure shift was estimated to contribute an uncertainty of ±1 MHz. For the other two bands, the pressure shift contributed an uncertainty of only ±0.2 MHz.

The standard error was estimated by combining the variance–covariance matrix for the ground state constants (given by the least-squares fit of the microwave mea-

TABLE V

Measured Pressure-Shift Coefficients, Δ_s, for N_2O

Band	Line	Δ_s (MHz/kPa)
$00^{0}2-00^{0}0$	P(43)	-1.6 ± 0.4
$00^{0}2-00^{0}0$	P(2)	-0.83 ± 0.90
$00^{0}2-00^{0}0$	R(42)	-1.21 ± 0.06
$12^{0}1-00^{0}0$	R(26)	-0.7 ± 0.6

TABLE VI

Frequencies and Wavenumbers Calculated for the $00^{0}2$-$00^{0}0$ Band of N_2O (The uncertainty in the last digits (twice the estimated standard error) is given in parentheses.)

ROT. TRANS.	FREQUENCY(UNC) (MHz)	WAVENUMBER(UNC) (CM^{-1})	ROT. TRANS.	FREQUENCY(UNC) (MHz)	WAVENUMBER(UNC) (CM^{-1})
P(61)	130144125.2(38)	4341.14074(12)	R(0)	132454363.0(30)	4418.20197(10)
P(60)	130193846.8(28)	4342.79927(9)	R(1)	132478657.4(30)	4419.01235(10)
P(59)	130243163.2(21)	4344.44429(7)	R(2)	132502537.2(30)	4419.80889(10)
P(58)	130292074.3(18)	4346.07579(6)	R(3)	132526002.2(30)	4420.59160(10)
P(57)	130340579.9(19)	4347.69376(6)	R(4)	132549052.4(29)	4421.36047(9)
P(56)	130388679.8(22)	4349.29820(7)	R(5)	132571687.6(29)	4422.11550(9)
P(55)	130436373.8(24)	4350.88910(8)	R(6)	132593907.7(28)	4422.85669(9)
P(54)	130483661.7(27)	4352.46646(9)	R(7)	132615712.6(28)	4423.58402(9)
P(53)	130530543.4(29)	4354.03026(9)	R(8)	132637102.1(27)	4424.29750(9)
P(52)	130577018.6(30)	4355.58051(10)	R(9)	132658076.2(26)	4424.99711(8)
P(51)	130623087.3(30)	4357.11719(10)	R(10)	132678634.6(26)	4425.68287(8)
P(50)	130668749.2(31)	4358.64031(10)	R(11)	132698777.4(25)	4426.35476(8)
P(49)	130714004.1(31)	4360.14985(10)	R(12)	132718504.4(25)	4427.01278(8)
P(48)	130758851.9(30)	4361.64581(10)	R(13)	132737815.4(25)	4427.65693(8)
P(47)	130803292.4(29)	4363.12819(10)	R(14)	132756710.4(24)	4428.28720(8)
P(46)	130847325.5(29)	4364.59697(9)	R(15)	132775189.2(24)	4428.90359(8)
P(45)	130890950.9(28)	4366.05216(9)	R(16)	132793251.8(24)	4429.50609(8)
P(44)	130934168.5(27)	4367.49375(9)	R(17)	132810897.9(24)	4430.09470(8)
P(43)	130976978.2(27)	4368.92172(9)	R(18)	132828127.6(24)	4430.66942(8)
P(42)	131019379.7(26)	4370.33609(8)	R(19)	132844940.6(24)	4431.23024(8)
P(41)	131061373.0(26)	4371.73683(8)	R(20)	132861336.9(25)	4431.77716(8)
P(40)	131102957.8(26)	4373.12395(8)	R(21)	132877316.4(25)	4432.31018(8)
P(39)	131144133.9(26)	4374.49744(8)	R(22)	132892879.0(25)	4432.82929(8)
P(38)	131184901.3(26)	4375.85729(8)	R(23)	132908024.5(26)	4433.33449(8)
P(37)	131225259.7(26)	4377.20350(8)	R(24)	132922752.9(26)	4433.82578(8)
P(36)	131265209.1(26)	4378.53607(8)	R(25)	132937064.0(26)	4434.30315(8)
P(35)	131304749.1(26)	4379.85498(8)	R(26)	132950957.7(26)	4434.76659(8)
P(34)	131343879.8(26)	4381.16024(8)	R(27)	132964434.0(26)	4435.21611(8)
P(33)	131382600.8(26)	4382.45184(8)	R(28)	132977492.7(27)	4435.65170(9)
P(32)	131420912.2(26)	4383.72977(9)	R(29)	132990133.7(27)	4436.07336(9)
P(31)	131458813.6(27)	4384.99402(9)	R(30)	133002357.0(26)	4436.48109(8)
P(30)	131496305.1(27)	4386.24460(9)	R(31)	133014162.4(26)	4436.87487(8)
P(29)	131533386.3(26)	4387.48150(8)	R(32)	133025549.8(26)	4437.25472(8)
P(28)	131570057.2(26)	4388.70471(8)	R(33)	133036519.2(26)	4437.62061(8)
P(27)	131606317.5(26)	4389.91422(8)	R(34)	133047070.4(26)	4437.97256(8)
P(26)	131642167.3(26)	4391.11004(8)	R(35)	133057203.3(26)	4438.31056(8)
P(25)	131677606.2(26)	4392.29216(8)	R(36)	133066917.9(25)	4438.63461(8)
P(24)	131712634.2(25)	4393.46057(8)	R(37)	133076214.0(25)	4438.94469(8)
P(23)	131747251.1(25)	4394.61526(8)	R(38)	133085091.6(25)	4439.24081(8)
P(22)	131781456.8(25)	4395.75624(8)	R(39)	133093550.5(26)	4439.52297(8)
P(21)	131815251.1(24)	4396.88350(8)	R(40)	133101590.7(26)	4439.79117(8)
P(20)	131848633.9(24)	4397.99703(8)	R(41)	133109212.1(26)	4440.04539(9)
P(19)	131881605.0(24)	4399.09682(8)	R(42)	133116414.6(27)	4440.28564(9)
P(18)	131914164.3(24)	4400.18289(8)	R(43)	133123198.1(28)	4440.51191(9)
P(17)	131946311.6(24)	4401.25521(8)	R(44)	133129562.5(29)	4440.72421(9)
P(16)	131978046.9(24)	4402.31378(8)	R(45)	133135507.7(29)	4440.92252(9)
P(15)	132009369.9(25)	4403.35860(8)	R(46)	133141033.7(30)	4441.10684(10)
P(14)	132040280.5(25)	4404.38967(8)	R(47)	133146140.3(30)	4441.27718(10)
P(13)	132070778.6(25)	4405.40698(8)	R(48)	133150827.6(30)	4441.43353(10)
P(12)	132100864.1(26)	4406.41052(8)	R(49)	133155095.3(30)	4441.57589(10)
P(11)	132130536.8(26)	4407.40029(8)	R(50)	133158943.4(30)	4441.70425(10)
P(10)	132159796.5(27)	4408.37630(9)	R(51)	133162371.9(29)	4441.81861(9)
P(9)	132188643.2(28)	4409.33852(9)	R(52)	133165380.6(27)	4441.91897(9)
P(8)	132217076.7(28)	4410.28696(9)	R(53)	133167969.5(25)	4442.00533(8)
P(7)	132245096.9(29)	4411.22161(9)	R(54)	133170138.5(23)	4442.07768(7)
P(6)	132272703.7(29)	4412.14247(9)	R(55)	133171887.6(21)	4442.13602(7)
P(5)	132299896.8(30)	4413.04954(10)	R(56)	133173216.5(20)	4442.18035(6)
P(4)	132326676.2(30)	4413.94280(10)	R(57)	133174125.4(23)	4442.21066(7)
P(3)	132353041.8(30)	4414.82226(10)	R(58)	133174614.1(30)	4442.22697(10)
P(2)	132378993.4(30)	4415.68791(10)	R(59)	133174682.5(40)	4442.22925(13)
P(1)	132404530.9(30)	4416.53975(10)	R(60)	133174330.6(54)	4442.21751(18)
			R(61)	133173558.3(70)	4442.19175(23)

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

TABLE VII

Frequencies and Wavenumbers Calculated for the $12^01\text{-}00^00$ Band of N_2O (The uncertainty in the last digits (twice the estimated standard error) is given in parentheses.)

ROT. TRANS.	FREQUENCY (UNC) (MHz)	WAVENUMBER(UNC) (CM^{-1})	ROT. TRANS.	FREQUENCY (UNC) (MHz)	WAVENUMBER(UNC) (CM^{-1})
P(53)	137116267.9(275)	4573.70638(91)	R(0)	138833605.3(57)	4630.99060(19)
P(52)	137155353.1(214)	4575.01012(71)	R(1)	138858219.0(56)	4631.81162(18)
P(51)	137194148.4(166)	4576.30420(55)	R(2)	138882577.6(55)	4632.62413(18)
P(50)	137232654.6(131)	4577.58863(43)	R(3)	138906680.8(53)	4633.42813(17)
P(49)	137270872.3(106)	4578.86343(35)	R(4)	138930528.3(52)	4634.22360(17)
P(48)	137308802.3(93)	4580.12864(31)	R(5)	138954119.7(50)	4635.01052(16)
P(47)	137346445.3(88)	4581.38428(29)	R(6)	138977454.7(48)	4635.78889(16)
P(46)	137383802.1(87)	4582.63036(29)	R(7)	139000532.8(46)	4636.55869(15)
P(45)	137420873.7(88)	4583.86694(29)	R(8)	139023353.4(44)	4637.31991(14)
P(44)	137457660.8(89)	4585.09402(29)	R(9)	139045916.0(42)	4638.07252(14)
P(43)	137494164.4(89)	4586.31165(29)	R(10)	139068220.0(40)	4638.81650(13)
P(42)	137530385.4(87)	4587.51986(29)	R(11)	139090264.7(39)	4639.55183(13)
P(41)	137566324.9(85)	4588.71867(28)	R(12)	139112049.6(38)	4640.27849(12)
P(40)	137601983.7(81)	4589.90812(27)	R(13)	139133573.7(38)	4640.99646(12)
P(39)	137637362.8(77)	4591.08824(25)	R(14)	139154836.5(38)	4641.70571(12)
P(38)	137672463.3(72)	4592.25907(24)	R(15)	139175837.0(39)	4642.40621(13)
P(37)	137707286.2(67)	4593.42063(22)	R(16)	139196574.4(40)	4643.09794(13)
P(36)	137741832.4(62)	4594.57297(20)	R(17)	139217047.9(41)	4643.78086(13)
P(35)	137776103.0(57)	4595.71612(19)	R(18)	139237256.4(42)	4644.45495(14)
P(34)	137810099.1(53)	4596.85010(17)	R(19)	139257199.1(43)	4645.12016(14)
P(33)	137843821.6(50)	4597.97496(16)	R(20)	139276874.9(44)	4645.77648(15)
P(32)	137877271.6(48)	4599.09073(16)	R(21)	139296282.9(45)	4646.42386(15)
P(31)	137910450.0(47)	4600.19745(15)	R(22)	139315421.9(46)	4647.06226(15)
P(30)	137943357.8(46)	4601.29513(15)	R(23)	139334290.8(46)	4647.69166(15)
P(29)	137975996.1(46)	4602.38383(15)	R(24)	139352888.7(46)	4648.31202(15)
P(28)	138008365.8(46)	4603.46357(15)	R(25)	139371214.2(46)	4648.92330(15)
P(27)	138040467.8(46)	4604.53437(15)	R(26)	139389266.3(46)	4649.52545(15)
P(26)	138072303.1(46)	4605.59629(15)	R(27)	139407043.8(46)	4650.11844(15)
P(25)	138103872.6(46)	4606.64933(15)	R(28)	139424545.4(46)	4650.70223(15)
P(24)	138135177.1(46)	4607.69354(15)	R(29)	139441770.0(47)	4651.27679(15)
P(23)	138166217.6(45)	4608.72894(15)	R(30)	139458716.4(48)	4651.84205(16)
P(22)	138196994.8(44)	4609.75555(14)	R(31)	139475383.1(50)	4652.39800(16)
P(21)	138227509.6(43)	4610.77342(14)	R(32)	139491769.1(54)	4652.94458(18)
P(20)	138257762.7(42)	4611.78255(14)	R(33)	139507873.1(58)	4653.48175(19)
P(19)	138287755.0(41)	4612.78299(13)	R(34)	139523693.7(62)	4654.00946(20)
P(18)	138317487.0(40)	4613.77474(13)	R(35)	139539229.7(67)	4654.52769(22)
P(17)	138346959.4(39)	4614.75783(13)	R(36)	139554479.9(72)	4655.03638(24)
P(16)	138376173.0(38)	4615.73229(12)	R(37)	139569442.9(77)	4655.53549(25)
P(15)	138405128.2(38)	4616.69814(12)	R(38)	139584117.4(82)	4656.02498(27)
P(14)	138433825.7(38)	4617.65538(12)	R(39)	139598502.4(85)	4656.50481(28)
P(13)	138462265.9(39)	4618.60405(13)	R(40)	139612596.4(88)	4656.97494(29)
P(12)	138490449.4(40)	4619.54415(13)	R(41)	139626398.3(89)	4657.43532(29)
P(11)	138518376.6(42)	4620.47569(14)	R(42)	139639906.8(90)	4657.88592(30)
P(10)	138546047.8(44)	4621.39871(14)	R(43)	139653120.8(89)	4658.32669(29)
P(9)	138573463.4(46)	4622.31319(15)	R(44)	139666039.1(88)	4658.75760(29)
P(8)	138600623.8(48)	4623.21917(16)	R(45)	139678660.6(89)	4659.17860(29)
P(7)	138627529.1(50)	4624.11663(16)	R(46)	139690984.1(95)	4659.58967(31)
P(6)	138654179.6(52)	4625.00560(17)	R(47)	139703008.6(108)	4659.99077(36)
P(5)	138680575.4(53)	4625.88606(17)	R(48)	139714733.0(132)	4660.38185(44)
P(4)	138706716.6(55)	4626.75804(18)	R(49)	139726156.4(168)	4660.76289(56)
P(3)	138732603.4(56)	4627.62153(18)	R(50)	139737277.8(215)	4661.13387(72)
P(2)	138758235.7(57)	4628.47654(19)	R(51)	139748096.4(276)	4661.49473(92)
P(1)	138783613.6(57)	4629.32305(19)			

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

surements and the infrared combination-differences) with the variance–covariance matrix from the fit of the upper state constants.

For the convenience of the many people preferring to work with wavenumber units, Tables VI, VII, and VIII contain such information obtained from the frequencies with $c = 299\,792\,458$ m/sec (*22*).

CONCLUSION

Despite the uncertainty in the pressure-shift coefficient, the present measurements provide a substantial improvement in the accuracy of the N_2O transition frequencies that can be used for calibration from 4340 to 4755 cm^{-1}. The present measurements

TABLE VIII

Frequencies and Wavenumbers Calculated for the 20^01-00^00 Band of N_2O (The uncertainty in the last digits (twice the estimated standard error) is given in parentheses.)

ROT. TRANS.	FREQUENCY(UNC) (MHz)	WAVENUMBER(UNC) (CM^{-1})	ROT. TRANS.	FREQUENCY(UNC) (MHz)	WAVENUMBER(UNC) (CM^{-1})
P(51)	140024211.2(98)	4670.70493(33)	R(0)	141851273.6(29)	4731.64917(9)
P(50)	140069591.6(80)	4672.21866(26)	R(1)	141875570.2(29)	4732.45962(9)
P(49)	140114580.7(66)	4673.71933(22)	R(2)	141899453.4(28)	4733.25628(9)
P(48)	140159177.6(56)	4675.20693(18)	R(3)	141922923.0(28)	4734.03914(9)
P(47)	140203381.5(48)	4676.68141(16)	R(4)	141945979.0(27)	4734.80820(9)
P(46)	140247191.6(43)	4678.14276(14)	R(5)	141968621.2(27)	4735.56347(9)
P(45)	140290607.0(39)	4679.59094(13)	R(6)	141990849.6(26)	4736.30493(8)
P(44)	140333627.1(37)	4681.02593(12)	R(7)	142012664.2(25)	4737.03258(8)
P(43)	140376250.9(36)	4682.44771(12)	R(8)	142034064.9(25)	4737.74643(8)
P(42)	140418477.8(35)	4683.85625(11)	R(9)	142055051.7(24)	4738.44648(8)
P(41)	140460307.0(33)	4685.25152(11)	R(10)	142075624.5(24)	4739.13271(8)
P(40)	140501738.0(32)	4686.63351(10)	R(11)	142095783.3(23)	4739.80514(7)
P(39)	140542769.9(31)	4688.00219(10)	R(12)	142115528.1(23)	4740.46376(7)
P(38)	140583402.2(30)	4689.35754(10)	R(13)	142134859.0(23)	4741.10857(7)
P(37)	140623634.2(29)	4690.69953(9)	R(14)	142153776.0(23)	4741.73957(7)
P(36)	140663465.3(27)	4692.02815(9)	R(15)	142172279.0(23)	4742.35676(7)
P(35)	140702894.9(26)	4693.34338(8)	R(16)	142190368.2(23)	4742.96015(7)
P(34)	140741922.5(26)	4694.64520(8)	R(17)	142208043.6(23)	4743.54974(7)
P(33)	140780547.5(25)	4695.93359(8)	R(18)	142225305.2(23)	4744.12552(7)
P(32)	140818769.3(25)	4697.20854(8)	R(19)	142242153.1(24)	4744.68751(8)
P(31)	140856587.4(24)	4698.47001(8)	R(20)	142258587.5(24)	4745.23570(8)
P(30)	140894001.4(24)	4699.71801(8)	R(21)	142274608.4(24)	4745.77010(8)
P(29)	140931010.6(24)	4700.95251(8)	R(22)	142290215.9(24)	4746.29071(8)
P(28)	140967614.8(24)	4702.17349(8)	R(23)	142305410.2(24)	4746.79754(8)
P(27)	141003813.4(24)	4703.38094(8)	R(24)	142320191.5(24)	4747.29059(8)
P(26)	141039605.9(24)	4704.57485(8)	R(25)	142334559.8(24)	4747.76986(8)
P(25)	141074992.0(24)	4705.75521(8)	R(26)	142348515.3(24)	4748.23537(8)
P(24)	141109971.2(24)	4706.92199(8)	R(27)	142362058.3(24)	4748.68712(8)
P(23)	141144543.1(24)	4708.07518(8)	R(28)	142375189.0(24)	4749.12511(8)
P(22)	141178707.4(24)	4709.21478(8)	R(29)	142387907.5(24)	4749.54935(8)
P(21)	141212463.7(24)	4710.34077(8)	R(30)	142400214.1(25)	4749.95986(8)
P(20)	141245811.5(23)	4711.45313(7)	R(31)	142412109.0(25)	4750.35663(8)
P(19)	141278750.7(23)	4712.55186(7)	R(32)	142423592.5(26)	4750.73968(8)
P(18)	141311280.7(23)	4713.63695(7)	R(33)	142434665.0(26)	4751.10901(8)
P(17)	141343401.5(23)	4714.70838(7)	R(34)	142445326.6(27)	4751.46465(9)
P(16)	141375112.5(23)	4715.76615(7)	R(35)	142455577.7(28)	4751.80659(9)
P(15)	141406413.5(23)	4716.81024(7)	R(36)	142465418.8(30)	4752.13485(10)
P(14)	141437304.3(23)	4717.84064(7)	R(37)	142474850.0(31)	4752.44944(10)
P(13)	141467784.5(23)	4718.85735(7)	R(38)	142483871.8(32)	4752.75038(10)
P(12)	141497853.9(24)	4719.86036(8)	R(39)	142492484.6(33)	4753.03767(11)
P(11)	141527512.3(24)	4720.84966(8)	R(40)	142500688.7(34)	4753.31133(11)
P(10)	141556759.3(25)	4721.82523(8)	R(41)	142508484.8(36)	4753.57138(12)
P(9)	141585594.9(25)	4722.78708(8)	R(42)	142515873.1(37)	4753.81783(12)
P(8)	141614018.7(26)	4723.73520(8)	R(43)	142522854.2(39)	4754.05069(13)
P(7)	141642030.5(27)	4724.66958(9)	R(44)	142529428.6(43)	4754.26999(14)
P(6)	141669630.2(27)	4725.59020(9)	R(45)	142535596.8(48)	4754.47574(16)
P(5)	141696817.6(28)	4726.49708(9)	R(46)	142541359.4(55)	4754.66796(18)
P(4)	141723592.5(28)	4727.39019(9)	R(47)	142546716.9(66)	4754.84666(22)
P(3)	141749954.6(29)	4728.26954(9)	R(48)	142551670.0(80)	4755.01188(26)
P(2)	141775904.0(29)	4729.13511(9)	R(49)	142556219.2(98)	4755.16363(32)
P(1)	141801440.4(29)	4729.98691(9)			

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

are systematically lower in frequency by about 15 MHz (0.0005 cm^{-1}) than the values given by Amiot and Guelachvili (*1*) as later corrected by them (*23*). The present measurements are also lower than the results of Braund *et al.* (*2*) by about the same amount. Since both of these previous measurements were based on calibrations provided by the 2-0 band of CO, this discrepancy is exactly what one would expect, since we have shown from similar frequency measurements (*4*) that the previously accepted wavenumbers for the 2-0 band are too high by about 15 MHz.

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