Frequency Measurements of 9- and 10-μm N_2O Laser Transitions

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***Abstract*— We have measured frequencies of N_2O transitions by heterodyning sub-Doppler fluorescence-stabilized N_2O laser radiation with that from a reference CO_2 laser. A high-resolution cavity incorporates a ribbed tube and a highly reflective grating, permitting the CW oscillation of both the 10^00-02^00 9-μm and the 10^00-00^01 10-μm regular bands. This is the first sub-Doppler frequency measurement of the 9-μm band. The accuracy in the determination of the rotational constants for both bands has been improved by an order of magnitude, and calculated transition frequencies are presented.**

I. Introduction

The N_2O laser is a powerful source of 10-μm infrared radiation. Although its gain is lower than that of the CO_2 laser, its higher spectral density and slightly lower oscillation frequencies are helpful to spectroscopic investigations, covering the frequencies which are not accessible with CO_2 lasers [1]. The N_2O laser has been used for laser Stark spectroscopy [2], infrared double-resonance spectroscopy [3], and optical pumping of far-infrared lasers [4]. In addition, the absorption spectrum of N_2O is useful for frequency and wavenumber calibration [1]. In these applications, it is important to know the transition frequencies to high accuracy.

Center frequencies of Doppler-broadened absorption spectra in the 10^00-00^01 10-μm regular band and the 10^00-02^00 9-μm regular band had previously been measured by a tunable-diode-laser or Fourier-transform spectroscopy [5], [6]. These measurements have an absolute uncertainty of a few megahertz mainly because of the limited resolution of the apparatus. Whitford *et al.* [7] carried out sub-Doppler measurements with an accuracy of 60 kHz by heterodyning an N_2O laser and a reference CO_2 laser, each of which was set to its saturated-fluorescence line center. They measured frequencies of 33 lines in the 10-μm regular band and determined the rotational constants of the 10^00 and 00^01 states.

We report frequency measurements of the N_2O transitions, which can be used in sub-Doppler stabilization of the N_2O laser, based on the heterodyne difference frequency technique with fluorescence-stabilized CO_2 lasers. Major improvements of our method over the previous measurements [7] are summarized as follows.

1) The reference saturated-fluorescence absorption cells for the 9- and 10-μm bands of N_2O and CO_2 are located outside the laser cavities in order to avoid a systematic shift of the center of the saturated absorption signal due to the frequency pulling by the cavity modes.
2) Our novel design of the N_2O laser makes the 9-μm regular-band lines oscillate at well above 1 W, making stabilization to the saturation dips and the first measurement of their lasing frequencies possible. The lines of this band have a gain an order of magnitude smaller than those of the 10-μm regular band [1], and only Djeu and Wolga [8] had observed the CW-mode oscillation of this band with a 5-m-long laser cavity.
3) Frequencies of the P-branch high-J lines (up to $J = 47$) of the 10-μm regular band were also measured by using a $^{13}C^{16}O_2$ laser as a reference. This gives an accurate determination of the higher order molecular constants.

The least-squares fitting is carried out on the frequencies measured for 91 lines in the 10-μm regular band and 38 lines in the 9-μm regular band; the band centers and the rotational constants are determined with improved accuracy.

II. Experimental Aspects

The detailed experimental setup and procedures for heterodyne frequency measurements are described in [9]. In brief, the N_2O laser tube has no Brewster windows and is terminated by end blocks in which the end mirror and the grating are installed. The laser tube is made from a 19-mm inner-diameter Pyrex tube with 1.25-mm internal ribs squeezed into the wall with a spacing of 15 mm, resulting in an inside rib diameter of 16.5 mm. The ribbed laser tube was successfully used in achieving new lasing bands in CO_2 [10]. These ribs enhance the heat dissipation from the discharged gas to the tube wall since they promote turbulent flow, increasing the frequency of the wall collisions [11]. The ribs also contribute to increase the effective resolution of the grating-tuned laser cavity about three times by eliminating wall-bounce modes. The 2.7-m-long laser has a 2.38-m active discharge length. A gas mixture of 8% N_2O, 15% N_2, and 77% He flows through the laser tube at a total pressure of 4.4 kPa (33 torr) at the inlet. The discharge current is approximately 20 mA. The outside wall of the tube is cooled by a circulating alcohol coolant kept at a temperature of 253 K. The 163-line/mm grating provides 2% to 3% coupling in the zero order from 9 to 11 μm. The 10-m radius of curvature gold end mirror is 99% reflective. In this laser, we obtain CW-mode oscillation on 40 lines of the 9-μm regular band. The output power on the strongest line is 3.7 W.

The N_2O laser is frequency-stabilized on the saturation dip of the 4.5-μm fluorescence from the 10^00 state by the tech-

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TABLE I
MEASURED LASER TRANSITIONS FOR THE 10^00-00^01 BAND OF N_2O

P-Branch					*R*-Branch				
J''	CO_2 Line	Freq. Diff. N_2O-CO_2 MHz	Measured Frequency MHz	Obs.-Calc. MHz	J''	CO_2 Line	Freq. Diff. N_2O-CO_2 MHz	Measured Frequency MHz	Obs.-Calc. MHz
0					0	10*P*(24)	-25 889.384(27)[a]	28 171 033.224	-0.013
1					1	10*P*(24)	-1 074.870(27)	28 195 847.737	-0.013
2	10*P*(28)	11 309.665(22)	28 095 979.464	-0.004	2	10*P*(22)	-31 381.330(5)	28 220 560.333	-0.013
3	10*P*(28)	-13 911.252(4)	28 070 758.547	-0.003	3	10*P*(22)	-6 770.775(5)	28 245 170.888	-0.006
4	10*P*(30)	18 004.460(2)	28 045 436.331	-0.004	4	10*P*(22)	17 737.600(7)	28 269 679.263	0.000
5	10*P*(30)	-7 418.937(3)	28 020 012.934	-0.008	5	10*P*(20)	-12 139.577(2)	28 294 085.312	-0.004
6	10*P*(32)	25 038.727(2)	27 994 488.486	0.000	6	10*P*(20)	12 164.020(4)	28 318 388.910	-0.008
7	10*P*(32)	-586.679(3)	27 968 863.080	-0.001	7	10*P*(18)	-17 183.875(6)	28 342 589.934	0.005
8	10*P*(32)	-26 312.917(4)	27 943 136.843	0.004	8	10*P*(18)	6 914.410(4)	28 366 688.220	0.011
9	10*P*(34)	6 589.083(2)	27 917 309.875	0.008	9	10*P*(16)	-21 906.098(4)	28 390 683.627	0.013
10	10*P*(34)	-19 338.512(4)	27 891 382.281	0.006	10	10*P*(16)	1 986.286(5)	28 414 576.010	0.011
11	10*P*(36)	14 112.115(2)	27 865 354.175	0.008	11	10*P*(16)	25 775.498(6)	28 438 365.223	0.007
12	10*P*(36)	-12 016.414(2)	27 839 225.645	0.000	12	10*P*(14)	-2 622.613(4)	28 462 051.106	-0.008
13	10*P*(36)	-38 245.243(3)	27 812 996.816	0.007	13	10*P*(14)	20 959.813(5)	28 485 633.532	-0.011
14	10*P*(38)	-4 342.635(2)	27 786 667.769	0.010	14	10*P*(12)	-6 914.314(4)	28 509 112.344	-0.003
15	10*R*(16)*[b]	1 738.230(2)	27 760 238.587	-0.001	15	10*P*(12)	16 460.708(3)	28 532 487.366	-0.004
16	10*R*(14)*	17 070.600(3)	27 733 709.392	0.000	16	10*P*(10)	-10 890.746(4)	28 555 758.448	-0.004
17	10*R*(14)*	-9 558.532(2)	27 707 080.260	0.000	17	10*P*(10)	12 276.234(4)	28 578 925.428	-0.004
18	10*R*(12)*	6 169.882(4)	27 680 351.279	-0.003	18	10*P*(8)	-14 553.624(3)	28 601 988.142	-0.003
19	10*R*(10)*	22 392.604(4)	27 653 522.540	-0.002	19	10*P*(8)	8 404.651(4)	28 624 946.417	-0.008
20	10*R*(10)*	-4 535.813(2)	27 626 594.122	-0.003	20	10*P*(6)	-17 904.504(3)	28 647 800.099	-0.003
21	10*R*(8)*	12 080.084(2)	27 599 566.106	-0.005	21	10*P*(6)	4 844.404(4)	28 670 549.007	0.002
22	10*R*(8)*	-15 047.449(2)	27 572 438.573	-0.005	22	10*P*(4)	-20 944.767(4)	28 693 192.953	-0.005
23	10*R*(6)*	1 960.476(3)	27 545 211.596	-0.005	23	10*P*(4)	1 594.059(4)	28 715 731.779	-0.006
24	10*R*(4)*	19 458.703(3)	27 517 885.246	-0.007	24	10*P*(4)	24 027.587(3)	28 738 165.308	0.003
25	10*R*(4)*	-7 966.938(3)	27 490 459.605	0.001	25	10*P*(2)	-1 347.595(5)	28 760 493.332	-0.004
26	10*R*(2)*	9 921.259(3)	27 462 934.718	-0.001	26	10*P*(2)	20 874.766(5)	28 782 715.693	0.003
27	10*R*(2)*	-17 702.801(3)	27 435 310.658	-0.005	27	10*P*(2)	42 991.261(3)	28 804 832.188	0.009
28	10*R*(2)*	-45 425.969(4)	27 407 587.490	-0.005	28	10*R*(2)	-51 059.820(4)	28 826 842.618	0.008
29					29	10*R*(2)	-29 155.645(4)	28 848 746.793	0.005
30					30	10*R*(2)	-7 357.917(3)	28 870 544.521	0.008
31	10*P*(4)*	34 377.296(2)	27 323 823.883	0.005	31	10*R*(2)	14 333.154(5)	28 892 235.592	0.008
32	10*P*(4)*	6 258.216(2)	27 295 704.804	0.002	32	10*R*(4)	-9 226.629(2)	28 913 819.802	0.008
33	10*P*(4)*	-21 959.721(2)	27 267 486.867	0.001	33	10*R*(4)	12 250.503(4)	28 935 296.933	0.000
34	10*P*(6)*	-2 225.633(2)	27 239 170.110	0.000	34	10*R*(6)	-10 790.275(4)	28 956 666.790	0.001
35	10*P*(6)*	-30 641.176(2)	27 210 754.567	-0.001	35	10*R*(6)	10 472.076(3)	28 977 929.142	-0.002
36	10*P*(8)*	-10 519.923(2)	27 182 240.273	0.000	36	10*R*(8)	-12 049.230(4)	28 999 083.775	-0.001
37	10*P*(10)*	10 087.088(2)	27 153 627.250	-0.001	37	10*R*(8)	8 997.450(3)	29 020 130.455	-0.006
38	10*P*(10)*	-18 624.636(3)	27 124 915.526	0.000	38	10*R*(10)	-13 003.736(4)	29 041 068.965	-0.003
39	10*P*(12)*	2 369.406(2)	27 096 105.113	-0.004	39	10*R*(10)	7 826.358(4)	29 061 899.059	-0.003
40	10*P*(12)*	-26 539.675(3)	27 067 196.033	-0.005	40	10*R*(12)	-13 653.892(3)	29 082 620.502	-0.004
41	10*P*(14)*	-5 158.444(4)	27 038 188.307	0.010	41	10*R*(12)	6 958.658(5)	29 103 233.052	-0.003
42	10*P*(16)*	16 708.854(3)	27 009 081.909	0.009	42	10*R*(14)	-13 999.655(3)	29 123 736.458	-0.004
43	10*P*(16)*	-12 496.198(5)	26 979 876.857	0.012	43	10*R*(14)	6 394.358(3)	29 144 130.471	0.000
44	10*P*(18)*	9 758.915(16)	26 950 573.150	0.022	44	10*R*(16)	-14 040.849(6)	29 164 414.827	0.002
45	10*P*(18)*	-19 643.470(27)	26 921 170.764	0.029	45	10*R*(16)	6 133.582(4)	29 184 589.258	-0.001
46	10*P*(20)*	2 999.945(25)	26 891 669.690	0.039	46	10*R*(18)	-13 777.166(28)	29 204 653.520	0.017
47					47	10*R*(18)	6 176.627(28)	29 224 607.312	0.032

a) The uncertainty in the last digits of the frequency difference is given in parentheses.
b) The asterisks indicate that the $^{13}CO_2$ laser was used; all other measurements used the $^{12}CO_2$ laser.

nique developed by Freed and Javan [12]. The fluorescence cell is placed external to the laser cavity to avoid frequency pulling by the cavity modes. The reference N_2O gas pressure is 13.3 Pa (100 mtorr) for the 9-μm band, and 5.3 Pa (40 mtorr) for the 10-μm band. Even though the transition dipole matrix element of the 9-μm-band lines is relatively small (one-third that of the 10-μm band) [1], the saturation dip is observed with appreciable signal-to-noise ratio, and the laser is successfully locked to the fluorescence line center when the power in the fluorescence cell is more than 1.5 W. For the 10-μm band, the saturation dip is broadened dominantly by the saturation broadening, which is estimated about 1.1 MHz at the laser power of 2.0 W. The saturation broadening of the 9-μm lines is estimated to be 350 kHz at the same laser power and is comparable to the pressure broadening.

The radiations from the N_2O laser, a CO_2 laser stabilized to the line center by the same technique, and a microwave synthesizer are mixed in a metal-insulator-metal (MIM) tungsten–nickel point contact diode. The beat signal is displayed on a spectrum analyzer, and its frequency $|\nu_{N_2O} - \nu_{CO_2}| - m\nu_\mu$ is measured by comparison with a known marker frequency from a signal generator. ν_{N_2O}, ν_{CO_2}, and ν_μ are frequencies of the N_2O laser, the CO_2 laser, and the microwave, respectively, and m is an integer corresponding to the harmonic order. The intensity of the beat signal decreases as the harmonic order increases; hence, we generally select a suitable CO_2 reference line to satisfy $m = 1$ or 2. Typically, the spectrum of the beat signal has a width of about 200 kHz. The 1-σ uncertainty in the determination of the center frequency is estimated to be less than 5 kHz for most of the lines. In place of $^{12}C^{16}O_2$, the $^{13}C^{16}O_2$ isotopomer is used in the reference laser and the fluorescence cell for the measurements of the $P(J > 14)$ lines of the 10-μm band.

Each beat frequency is measured ten times, and the scatter of the data is used as a guide in estimating the uncertainty of the measurements. The frequencies of the N_2O transitions are

TABLE II
MEASURED LASER TRANSITIONS FOR THE 10^00-02^00 BAND OF N_2O

P-Branch					*R*-Branch				
J''	CO_2 Line	Freq. Diff. N_2O-CO_2 MHz	Measured Frequency MHz	Obs.-Calc. MHz	J''	CO_2 Line	Freq. Diff. N_2O-CO_2 MHz	Measured Frequency MHz	Obs.-Calc. MHz
8					8	9*P*(2)	18 718.228(61)[a]	31 861 652.780	0.058
9	9*P*(18)	-27 217.235(58)	31 410 842.940	0.050	9	9*P*(2)	41 282.059(13)	31 884 216.610	-0.027
10	9*P*(20)	-573.942(21)	31 383 326.461	0.018	10				
11	9*P*(22)	26 591.153(8)	31 355 552.650	0.004	11				
12	9*P*(22)	-1 439.314(7)	31 327 522.183	0.000	12	9*R*(2)	-8 648.407(4)	31 950 347.656	0.003
13	9*P*(24)	25 988.643(5)	31 299 235.791	0.002	13	9*R*(2)	12 876.461(5)	31 971 872.523	0.000
14	9*P*(24)	-2 552.904(4)	31 270 694.245	-0.002	14	9*R*(4)	-10 878.545(2)	31 993 138.838	0.002
15	9*P*(24)	-31 348.771(8)	31 241 898.378	-0.008	15	9*R*(4)	10 129.783(5)	32 014 147.165	-0.003
16	9*P*(26)	-3 912.231(7)	31 212 849.072	-0.013	16	9*R*(6)	-13 338.099(6)	32 034 898.151	0.006
17	9*P*(28)	24 039.090(5)	31 183 547.252	-0.014	17	9*R*(6)	7 156.192(7)	32 055 392.442	0.004
18	9*P*(28)	-5 514.266(10)	31 153 993.897	-0.005	18	9*R*(8)	-16 021.910(6)	32 075 630.752	-0.013
19	9*P*(30)	22 697.801(9)	31 124 189.984	-0.021	19	9*R*(8)	3 961.227(11)	32 095 613.889	0.002
20	9*P*(30)	-7 355.569(7)	31 094 136.614	-0.019	20	9*R*(10)	-18 924.294(7)	32 115 342.598	-0.012
21	9*P*(32)	21 116.819(5)	31 063 834.884	-0.003	21	9*R*(10)	550.869(7)	32 134 817.760	-0.021
22	9*P*(32)	-9 432.143(3)	31 033 285.922	0.013	22	9*R*(10)	19 773.380(8)	32 154 040.272	-0.018
23	9*P*(34)	19 300.143(5)	31 002 490.896	0.014	23	9*R*(12)	-3 068.420(7)	32 173 011.068	0.002
24	9*P*(34)	-11 739.712(8)	30 971 451.041	0.016	24	9*R*(12)	15 651.585(4)	32 191 731.072	-0.005
25	9*P*(36)	17 252.182(9)	30 940 167.613	0.015	25	9*R*(14)	-6 889.939(10)	32 210 201.333	0.004
26	9*P*(36)	-14 273.525(6)	30 908 641.906	0.014					
27	9*P*(38)	14 977.734(7)	30 876 875.249	0.012					
28	9*P*(38)	-17 028.531(3)	30 844 868.984	-0.007					
29	9*P*(40)	12 481.890(7)	30 812 624.541	-0.003					
30	9*P*(40)	-19 999.352(10)	30 780 143.299	-0.013					

a) The uncertainty in the last digits of the frequency difference is given in parentheses.

TABLE III
CONSTANTS FOR THE REGULAR LASER TRANSITIONS OF N_2O

	10^00	00^01	02^00	02^20
E_v(GHz)	66 666.550 664(215)[a] {1500}[b]	38 520.433 729(215){1500}	35 019.728 820(215){1500}	35 307.890 899(1390){1500}
$\nu_0(10^00$-$00^01)$ (MHz)		28 146 116.935 1(14){100}		
$\nu_0(10^00$-$02^00)$ (MHz)			31 646 821.843 7(100){100}	
B_v (MHz)	12 458.161 366(41)	12 508.992 421(41)	12 588.877 251(78)	12 595.021 478(448)
D_v(kHz)	5.260 968(39)	5.173 721(40)	5.610 501(560)	5.433 318(912)
H_v(mHz)	-0.382 1(117)	3.346 8(137)	6.176 7(7282)	-12.461 1(7730)
L_v(μHz)	----	0.137 261(919)	----	----
q_v(MHz)	----	----	----	22.764 26(421)
q_{Jv}(Hz)	----	----	----	12.17(518)
Jmax	90	90	74	70
rms deviation of 0.009 MHz for 91 measured lines of 10^00-00^01				
rms deviation of 0.017 MHz for 38 measured lines of 10^00-02^00				

a) The uncertainty (twice the standard deviation) in the last digits is given in parentheses.
b) The estimated absolute uncertainty in the last digits (twice the standard deviation) is given in curly brackets.

calculated using the measured beat frequencies and the CO_2 transition frequencies reported in [13].

The pressure shift for N_2O is estimated to be -8 kHz for the 9-μm lines and -3 kHz for the 10-μm lines, based on the pressure-shift coefficient of self-broadened N_2O [6]. Here, we have assumed that the coefficient is not critically dependent on either the vibrational or rotational quantum number. Cavity misalignment of either of the two lasers causes a systematic shift of the measured laser frequency. As a test of reliability of our laser system, we measured the beat frequency between two CO_2 laser lines, $9R(32)$ and $9R(34)$, switching the roles of the two lasers. Deviation between the two measurements was less than 3 kHz. The systematic error due to cavity misalignment depends on such parameters as the pressure and the laser intensity in the fluorescence cell. We estimate it to be less than 10 kHz (2σ) for these measurements. The frequency accuracy of the microwave synthesizer and the signal generator has been checked by a frequency counter calibrated with a Cs standard. The uncertainty in the microwave and marker frequencies is well under 1 kHz.

III. ANALYSIS OF THE MEASUREMENTS

Tables I and II give the observed frequency differences between the N_2O laser transitions and the CO_2 laser transitions. These tables also give the derived frequencies of the N_2O laser transitions and the observed-calculated (obs.-calc.) differences given by the constants in Table III, found from our least-squares analysis of the data.

The constants given in Table III were determined from a least-squares analysis of the present measurements combined with infrared [5], [6], [14]–[17], microwave [18], and millimeter-wave [19]–[21] measurements reported for the three vibrational states involved in the laser transitions and other related states of N_2O. This analysis also included the earlier heterodyne measurements of these same laser transitions [5], [7]. In the analysis, the measurements were weighted by the inverse square of the estimated uncertainties of the measurements. The accuracy in the determination of the rotational constants for the lasing bands has been improved by an order of magnitude compared with the previous analysis

TABLE IV
CALCULATED FREQUENCIES FOR THE 10^00-00^01 BAND OF N_2O

Line	Frequency MHz	Uncertainty[a] MHz	Line	Frequency MHz	Uncertainty MHz
			R(0)	28 171 033.2368	0.0015
P(1)	28 121 098.9710	0.0015	R(1)	28 195 847.7498	0.0015
P(2)	28 095 979.4685	0.0015	R(2)	28 220 560.3457	0.0015
P(3)	28 070 758.5499	0.0014	R(3)	28 245 170.8940	0.0015
P(4)	28 045 436.3350	0.0014	R(4)	28 269 679.2623	0.0015
P(5)	28 020 012.9417	0.0013	R(5)	28 294 085.3157	0.0015
P(6)	27 994 488.4857	0.0013	R(6)	28 318 388.9177	0.0014
P(7)	27 968 863.0807	0.0012	R(7)	28 342 589.9291	0.0014
P(8)	27 943 136.8382	0.0011	R(8)	28 366 688.2089	0.0014
P(9)	27 917 309.8673	0.0011	R(9)	28 390 683.6140	0.0014
P(10)	27 891 382.2752	0.0010	R(10)	28 414 575.9987	0.0014
P(11)	27 865 354.1668	0.0010	R(11)	28 438 365.2154	0.0014
P(12)	27 839 225.6447	0.0010	R(12)	28 462 051.1143	0.0014
P(13)	27 812 996.8092	0.0010	R(13)	28 485 633.5431	0.0014
P(14)	27 786 667.7585	0.0010	R(14)	28 509 112.3473	0.0014
P(15)	27 760 238.5883	0.0010	R(15)	28 532 487.3701	0.0014
P(16)	27 733 709.3919	0.0010	R(16)	28 555 758.4521	0.0014
P(17)	27 707 080.2601	0.0011	R(17)	28 578 925.4318	0.0015
P(18)	27 680 351.2815	0.0011	R(18)	28 601 988.1448	0.0015
P(19)	27 653 522.5420	0.0011	R(19)	28 624 946.4246	0.0015
P(20)	27 626 594.1248	0.0011	R(20)	28 647 800.1018	0.0015
P(21)	27 599 566.1107	0.0011	R(21)	28 670 549.0045	0.0015
P(22)	27 572 438.5777	0.0011	R(22)	28 693 192.9581	0.0015
P(23)	27 545 211.6011	0.0011	R(23)	28 715 731.7851	0.0015
P(24)	27 517 885.2532	0.0011	R(24)	28 738 165.3054	0.0015
P(25)	27 490 459.6036	0.0011	R(25)	28 760 493.3357	0.0015
P(26)	27 462 934.7188	0.0011	R(26)	28 782 715.6898	0.0014
P(27)	27 435 310.6624	0.0011	R(27)	28 804 832.1787	0.0014
P(28)	27 407 587.4947	0.0011	R(28)	28 826 842.6098	0.0015
P(29)	27 379 765.2727	0.0011	R(29)	28 848 746.7876	0.0015
P(30)	27 351 844.0503	0.0011	R(30)	28 870 544.5130	0.0015
P(31)	27 323 823.8779	0.0012	R(31)	28 892 235.5838	0.0016
P(32)	27 295 704.8021	0.0012	R(32)	28 913 819.7938	0.0017
P(33)	27 267 486.8663	0.0012	R(33)	28 935 296.9334	0.0017
P(34)	27 239 170.1098	0.0012	R(34)	28 956 666.7893	0.0018
P(35)	27 210 754.5682	0.0012	R(35)	28 977 929.1441	0.0018
P(36)	27 182 240.2729	0.0012	R(36)	28 999 083.7765	0.0019
P(37)	27 153 627.2513	0.0012	R(37)	29 020 130.4609	0.0019
P(38)	27 124 915.5266	0.0013	R(38)	29 041 068.9676	0.0019
P(39)	27 096 105.1174	0.0015	R(39)	29 061 899.0622	0.0019
P(40)	27 067 196.0378	0.0018	R(40)	29 082 620.5060	0.0020
P(41)	27 038 188.2971	0.0022	R(41)	29 103 233.0553	0.0023
P(42)	27 009 081.8998	0.0029	R(42)	29 123 736.4616	0.0026
P(43)	26 979 876.8451	0.0037	R(43)	29 144 130.4712	0.0032
P(44)	26 950 573.1273	0.0047	R(44)	29 164 414.8251	0.0041
P(45)	26 921 170.7350	0.0060	R(45)	29 184 589.2589	0.0051
P(46)	26 891 669.6511	0.0075	R(46)	29 204 653.5026	0.0065
P(47)	26 862 069.8528	0.0092	R(47)	29 224 607.2802	0.0080
P(48)	26 832 371.3112	0.0112	R(48)	29 244 450.3097	0.0099
P(49)	26 802 573.9911	0.0135	R(49)	29 264 182.3027	0.0121
P(50)	26 772 677.8508	0.0161	R(50)	29 283 802.9643	0.0146

a) The uncertainty given here is twice the statistically determined standard deviation. We believe that the total uncertainty (2σ) should be given by the square root of the sum of the square of the uncertainties given here and the square of the absolute uncertainty, 0.0100 MHz.

[1]. As we shall now describe, the analysis was carried out in the same way as described in [1].

For the 10^00 and 00^01 states, the energy levels were fitted by applying the equations

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

and

$$\nu_0 = G'_v - G''_v \quad (2)$$

with the prime ($'$) indicating the upper state and the double prime ($''$) indicating the lower state.

Because of the complication of l-type resonance, the analysis of the transitions involving the 02^00 state were handled differently from the other transitions. The energy levels for the 02^00 state were determined by finding the lowest eigenvalue for the 3×3 energy matrix [1]

$$\begin{vmatrix} E(02^20) & W & 0 \\ W & E(02^00) & W \\ 0 & W & E(02^{-2}0) \end{vmatrix}. \quad (3)$$

The coupling matrix element is given by [1]

$$W = 2^{-1/2}[q_v - q_{Jv}J(J+1)]\{J(J+1)[J(J+1)-2]\}^{1/2} \quad (4)$$

and the diagonal terms are given by (1). For N_2O, the other two eigenvalues correspond to the $02^{2f}0$ and $02^{2e}0$ levels, which were not measured in the present work but for which there are many measurements in the literature.

In this work, we have ignored the effect of Fermi resonance, which couples the 00^01 and 02^00 levels. The unusually large values for $H(00^01)$, $H(02^00)$, $H(02^20)$, and $L(00^01)$ are the result of the Fermi resonance. Since this resonance was not included in the analysis, the constants for the 02^00 and 02^20 levels should be considered as only effective constants which reproduce the observations. If new measurements were to extend to higher J values, the constants would likely change by more than the uncertainties given in Table III, and probably more constants would be needed.

The nuclear electric quadrupole of the two nitrogen nuclei results in a small quadrupole splitting of the transitions of N_2O [22], [23]. For the $R(0)$ transition, where the splitting is greatest, the strongest component will be displaced from the center of gravity of the hyperfine pattern by about 60 kHz and separated from the other components by about 300 kHz. The present measurements give the position of the center of gravity of the quadrupole hyperfine pattern, within experimental uncertainty, for all the transitions with the possible exception of $R(0)$, $R(1)$, $P(1)$, and $P(2)$. For those lowest J values, the error in the frequency measurement arising from the partially resolved hyperfine splitting is probably no greater than 20 kHz, which is slightly larger than the errors from other sources. Actually, the fit of the measurements indicates that the error is much less than that.

In Tables IV and V, we give the best estimate of the frequencies of the N_2O laser transitions and their uncertainties. These numbers are based on the constants given in Table III. The uncertainties in Tables IV and V are based on the uncertainties given by the variance-covariance matrix from the least-squares fit. Those uncertainties do not take into account the possibility of systematic error in the measurement process, which we believe to be no greater than 10 kHz (2σ). Tables IV and V should be taken as representing the frequencies for an N_2O pressure equal to that used in these measurements, 13.3 Pa (100 mtorr) for the 9-μm band and 5.3 Pa (40 mtorr) for the 10-μm band.

IV. CONCLUSION AND FUTURE PROSPECTS

We have measured frequencies of the 10^00-00^01 band and the 10^00-02^00 band of N_2O and determined the molecular constants of these vibrational states with improved accuracy. The frequency measurement of the 9-μm band has been carried out for the first time using sub-Doppler techniques. The measured frequencies agree with the calculated numbers within 10 kHz for the 10-μm lines and 20 kHz for the 9-μm lines except for the very weak lines. These numbers can be employed as secondary frequency standards in infrared laser Stark spectroscopy, laser magnetic resonance spectroscopy, and calibration in diode laser spectroscopy. The N_2O lines

TABLE V
CALCULATED FREQUENCIES FOR THE 10^00-02^00 BAND OF N_2O

Line	Frequency MHz	Uncertainty[a] MHz	Line	Frequency MHz	Uncertainty MHz
			R(0)	31 671 738.1454	0.0100
P(1)	31 621 644.1116	0.0099	R(1)	31 696 392.8904	0.0099
P(2)	31 596 205.1270	0.0096	R(2)	31 720 786.0041	0.0096
P(3)	31 570 505.1191	0.0093	R(3)	31 744 917.4632	0.0092
P(4)	31 544 544.3687	0.0088	R(4)	31 768 787.2960	0.0087
P(5)	31 518 323.2079	0.0082	R(5)	31 792 395.5820	0.0081
P(6)	31 491 842.0200	0.0075	R(6)	31 815 742.4519	0.0074
P(7)	31 465 101.2392	0.0068	R(7)	31 838 828.0876	0.0067
P(8)	31 438 101.3508	0.0060	R(8)	31 861 652.7215	0.0059
P(9)	31 410 842.8902	0.0052	R(9)	31 884 216.6369	0.0051
P(10)	31 383 326.4434	0.0045	R(10)	31 906 520.1669	0.0043
P(11)	31 355 552.6460	0.0038	R(11)	31 928 563.6947	0.0035
P(12)	31 327 522.1833	0.0031	R(12)	31 950 347.6529	0.0029
P(13)	31 299 235.7893	0.0026	R(13)	31 971 872.5232	0.0023
P(14)	31 270 694.2467	0.0023	R(14)	31 993 138.8355	0.0020
P(15)	31 241 898.3860	0.0022	R(15)	32 014 147.1678	0.0019
P(16)	31 212 849.0846	0.0022	R(16)	32 034 898.1449	0.0020
P(17)	31 183 547.2668	0.0023	R(17)	32 055 392.4384	0.0022
P(18)	31 153 993.9020	0.0025	R(18)	32 075 630.7653	0.0024
P(19)	31 124 190.0046	0.0026	R(19)	32 095 613.8873	0.0026
P(20)	31 094 136.6328	0.0027	R(20)	32 115 342.6098	0.0028
P(21)	31 063 834.8869	0.0028	R(21)	32 134 817.7808	0.0028
P(22)	31 033 285.9092	0.0028	R(22)	32 154 040.2896	0.0029
P(23)	31 002 490.8817	0.0027	R(23)	32 173 011.0657	0.0029
P(24)	30 971 451.0251	0.0027	R(24)	32 191 731.0773	0.0029
P(25)	30 940 167.5975	0.0028	R(25)	32 210 201.3295	0.0030
P(26)	30 908 641.8923	0.0029	R(26)	32 228 422.8633	0.0032
P(27)	30 876 875.2371	0.0033	R(27)	32 246 396.7534	0.0036
P(28)	30 844 868.9911	0.0041	R(28)	32 264 124.1062	0.0044
P(29)	30 812 624.5437	0.0054	R(29)	32 281 606.0586	0.0057
P(30)	30 780 143.3123	0.0073	R(30)	32 298 843.7750	0.0075
P(31)	30 747 426.7399	0.0098	R(31)	32 315 838.4458	0.0100
P(32)	30 714 476.2933	0.0131	R(32)	32 332 591.2849	0.0133
P(33)	30 681 293.4601	0.0173	R(33)	32 349 103.5272	0.0175
P(34)	30 647 879.7469	0.0225	R(34)	32 365 376.4263	0.0227
P(35)	30 614 236.6761	0.0289	R(35)	32 381 411.2520	0.0290
P(36)	30 580 365.7839	0.0365	R(36)	32 397 209.2875	0.0366
P(37)	30 546 268.6171	0.0455	R(37)	32 412 771.8266	0.0456
P(38)	30 511 946.7306	0.0561	R(38)	32 428 100.1715	0.0562
P(39)	30 477 401.6847	0.0684	R(39)	32 443 195.6295	0.0685
P(40)	30 442 635.0420	0.0826	R(40)	32 458 059.5102	0.0826

a) The uncertainty given here is twice the statistically determined standard deviation. We believe that the total uncertainty (2σ) should be given by the square root of the sum of the square of the uncertainties given here and the square of the absolute uncertainty, 0.0100 MHz.

are quite promising as pumping sources for new FIR lasers. In a preliminary experiment, more than ten new FIR lines have been observed from CH_3OH and N_2H_4 pumped by our N_2O laser.

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