

THE ABSORPTION SPECTRUM OF NITROUS OXIDE IN THE 1- μm RANGE

G.A. Vandysheva and L.N. Sinitza

*Institute of Atmospheric Optics,
Siberian Branch of the USSR Academy of Sciences, Tomsk
Received January 19, 1989*

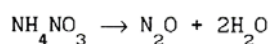
The absorption spectrum of N_2O in the region 9100–9500 cm^{-1} was studied using a highly sensitive intracavity laser spectrometer based on a neodymium glass laser. The threshold sensitivity and spectral resolution of the spectrometer are 10^{-8} cm^{-1} and 0.08 cm^{-1} , respectively. Two vibrational-rotational bands centered at 9219 and 9295 cm^{-1} were recorded; these bands are formed by transitions to the Fermi-resonance polyad 4002. The spectroscopic constants of the high vibrational-rotational states of nitrous oxide were determined.

Nitrous oxide is a minor component of the atmosphere, so that it is necessary to study its absorption spectrum in order to solve different atmospheric-optical problems. The absorption spectra of the asymmetric linear molecule N_2O have been studied in detail in the IR region of the spectrum. The band centers, the band intensities, and the rotational constants of the vibrational states, which make it possible to reproduce with an error of less than 0.01 cm^{-1} the energy spectrum of N_2O in the region 580–5000 cm^{-1} , are stored in a spectral-data bank.¹ Nitrous oxide was studied in the region 1800–8000 cm^{-1} using a high-resolution Fourier spectrometer with a resolution of $5 \cdot 10^{-3} \text{ cm}^{-1}$; 51 bands of the main isotope $^{14}\text{N}_2^{16}\text{O}$, (Ref. 2) as well as 233 bands of the isotopes $^{15}\text{N}_2^{16}\text{O}$, $^{14}\text{N}_2^{18}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ (Refs. 3 and 4) were recorded and the rotational structure of the bands was analyzed.

To determine the force field of the molecule it is especially important to determine the spectroscopic constants of the vibrational states at high frequencies. However nitrous oxide was studied in the photographic region 8000–12000 cm^{-1} only in 1950 using a diffraction spectrograph with a resolution of 0.1 cm^{-1} and a 4500 m path length in the cell.⁵ In this work the absorption spectrum of N_2O in the region 9100–9500 m^{-1} was recorded using a highly sensitive intracavity laser spectrometer.

The intracavity spectrometer is described in detail in Ref. 6. The threshold sensitivity of the spectrometer to absorption was equal to 10^{-8} cm^{-1} and the spectral resolution was $\sim 0.08 \text{ cm}^{-1}$.

Nitrous oxide was prepared by heating ammonium nitrate in a vacuum up to a temperature of 200°C:



The gas was not dried, and it contained water vapor; the absorption lines of H_2O were employed as references, relative to which the positions of the centers of the lines of N_2O were determined with an error of 0.03 cm^{-1} . The parallel band $4\nu_1 + \nu_3$ centered at $\nu_0 = 9295 \text{ cm}^{-1}$ was recorded in the

spectrum of nitrous oxide ($P = 200 \text{ torr}$); the positions of the centers of the lines in this band were measured with a higher accuracy than in Ref. 5. In addition, a previously not observed band centered at $\nu_0 = 9219 \text{ cm}^{-1}$ as well as a band at 9295 cm^{-1} , owing to transitions to the Fermi resonance polyad (4002), were recorded. The centers of the lines in the bands are presented in Table I.

TABLE I. The position of the centers of the absorption lines of N_2O , cm^{-1}

J	40021 \leftarrow 00001		40022 \leftarrow 00001	
	P(J)	R(J)	P(J)	R(J)
1	9294.13	9265.52	—	—
2	9293.27	9297.32	—	—
3	9292.80	9298.06	—	—
4	9291.47	9298.75	—	9222.82
5	9290.50	9299.43	9214.62	9223.54
6	9289.54	9300.07	9213.55	9224.23
7	9288.55	9300.73	9212.63	9224.90
8	9287.54	9301.34	9211.63	9225.60
9	9286.51	9301.92	9210.60	9226.14
10	9285.45	9302.48	9209.57	9226.79
11	9284.36	9303.03	9208.52	9227.29
12	9283.21	9303.49	9207.47	9227.87
13	9282.11	9303.98	9206.32	9228.38
14	9280.83	9304.47	9205.19	9228.81
15	9279.71	9304.91	9204.03	9229.29
16	9278.54	9305.31	9202.84	9229.77
17	9277.28	9305.68	9201.68	9230.18
18	9275.98	9306.06	9200.42	9230.57
19	9274.70	9306.37	9199.15	9230.94
20	9273.40	9306.68	9197.80	9231.28
21	9272.06	9306.95	9196.61	9231.64
22	9270.69	9307.20	9195.28	9231.97

TABLE I (continued)

23	9269.29	9307.42	9193.92	9232.22
24	9267.89	9307.63	9192.53	9232.46
25	9266.45	9307.83	9191.13	9232.73
26	9264.98		9189.81	9232.95
27	9263.46		9188.38	9233.17
28	9261.98		9186.91	

The rotational constant of the bands were determined with the help of the method of combination differences. The combination differences found for the lower states $\Delta_2 F(J) = R(J-1) - P(J+1)$ agree well with the combination differences of the 000 states,¹ and therefore the bands recorded at 9219 cm^{-1} and 9295 cm^{-1} are determined by transitions from the ground state. Using the values of J calculated by L. Teffo (private communication) the centers of the measured bands agree well with the energies of the levels in the polyad (9218.7 cm^{-1} and 9296.1 cm^{-1} respectively).

The spectroscopic constants of the upper vibrational states were determined with the help of the combination sums

$$R(J-1) + P(J) = 2\nu_0 + 2(B' - B'' + D'' - D')J^2 - 2(D' - D'')J^4,$$

where ν_0 is the center of the band; J is the rotational quantum number; and, B'' , D'' , B' and D' are the rotational constants of the lower and upper vibrational states, respectively.

Table II gives the spectroscopic constants of the recorded bands and their confidence intervals,

obtained by the method of least squares; the values of B'' and D'' are taken from Ref. 1.

TABLE II. The spectroscopic constants of N_2O , cm^{-1}

State	ν_0	B	$D \cdot 10^7$	Reference
40021	9294.99(2)	0.40637(8)	1.8(8)	(5)
40021	9295.04	0.4064	1.9	
40022	9219.01(1)	0.40751(7)	2.1(8)	

The information obtained will make it possible to determine more accurately the force field of the molecule and therefore to improve the accuracy of the calculation of the absorption by nitrous oxide at high frequencies.

REFERENCES

1. R.A. McClatchey, et al., "AFCRL Atmospheric Absorption Line Parameters Compilation". Environmental Research Paper 434. AFCRL-TR-73-0096, Air Force Cambridge Research Laboratories (1973).
2. G. Amiot and G. Guelashvili, J. Mol. Spectros., **51**, 475 (1974).
3. G. Amiot, **59**, 191 (1976).
4. G. Amiot, **59**, 380 (1976).
5. G. Herzberg and L. Herzberg, J. Chem. Phys., **18**, 1551 (1950).
6. L.N. Sinita, Kvant. Electron., **4**, 148 (1977).