

Heterodyne Frequency Measurements on the Nitric Oxide Fundamental Band

A. HINZ

Institut für Angewandte Physik, der Universität Bonn, Wegelestrasse 8, D-5300, Bonn 1, West Germany

J. S. WELLS

Time and Frequency Division, National Bureau of Standards, Boulder, Colorado 80303

AND

A. G. MAKI

Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland 20899

Heterodyne frequency measurements have been made on the fundamental band of nitric oxide from 1750 to 1931 cm^{-1} . Based on the analysis of these new measurements, minor changes are made in the band constants and an improved list of calculated energy levels for the $v = 0$ and $v = 1$ states is given. © 1986 Academic Press, Inc.

INTRODUCTION

We have used a tunable infrared diode laser and heterodyne measurement techniques to obtain accurate frequency values for the absorption features of nitric oxide (NO) in the spectral region from 1750 to 1960 cm^{-1} .

The most recent and accurate previous measurements of this band of NO were those reported in Refs. (1-3). In connection with measurements of the Λ -doublet splittings of the 2-0 band, Pine *et al.* (4) have given a consistent set of constants for the $v = 0, 1$, and 2 states of NO.

A number of papers have reported far-infrared, microwave, and radio frequency measurements of NO. A paper by Van Den Heuvel *et al.* (5) presents the constants resulting from a refit of the best available measurements of the $v = 0$ and $v = 1$ states. Improved Λ -doubling and hyperfine parameters from IR-rf double resonance measurements were then given by Lowe *et al.* (6).

The present measurements are in good agreement with those of Amiot *et al.* (1) although there seems to be a small skewing in their calibration. These heterodyne frequency measurements are also in excellent agreement with the constants given by Van Den Heuvel *et al.*, except for those constants that would have been affected by the small calibration error in the spectrum of Ref. (1). We suggest a small adjustment of the band constants of NO to give frequencies of the calculated absorption features that more exactly fit the present measurements. Based on our correction to the constants, a table of energy levels is given for the $v = 0$ and $v = 1$ states of NO.

EXPERIMENTAL DETAILS

In order to make measurements using our transfer oscillator technique (7), there must be a frequency overlap of 10 GHz or less between the NO absorption feature and the CO laser transition used for the transfer. This 10 GHz is near the upper frequency limit of our HgCdTe detector and also happens to be the upper frequency limit of our rf amplifiers. The number of such overlaps turns out to be rather small for the ${}^2\Pi_{1/2}$ - ${}^2\Pi_{1/2}$ transitions and even smaller for the ${}^2\Pi_{3/2}$ - ${}^2\Pi_{3/2}$ transitions; this does not permit a large number of constants to be fit using only frequency measurements of the type we describe.

Once the possible overlaps had been determined, the first step was to synthesize a frequency close to the CO laser frequency. This was done with a combination of frequencies, ν_1 and ν_2 , from two CO₂ lasers and a frequency, ν_M , from a microwave oscillator. The radiation from these oscillators was either focused on or coupled to a metal-insulator-metal (MIM) diode which generated combinations of harmonics of these frequencies as currents in the diode. These synthesized frequency currents combined with the current generated by the CO laser (when it was also focused on the MIM diode) to produce current at a beat frequency, ν_B , which propagated from the diode. This beat note was amplified and displayed on an rf spectrum analyzer, and the center of the beatnote was marked by a signal at frequency, ν_m , from an rf frequency synthesizer. The primary function of the CO laser was as a transfer oscillator; however, we also obtained the center frequency for each laser line that we used. To do this, the laser was tuned through its lasing bandwidth and the corresponding excursion of the beatnote, ν_{B1} , was centered on the spectrum analyzer display and the marker, ν_m , was adjusted to coincide with the center of the excursion. The CO laser was constrained to the frequency corresponding to the value, ν_m , for the measurement.

One of the combinations,

$$\nu_{\text{CO}} = \nu_{\text{xfer}} = \nu_1 + \nu_2 \pm \nu_M \text{ (or 0)} \pm \nu_m \quad (1)$$

or

$$\nu_{\text{CO}} = \nu_{\text{xfer}} = 3\nu_1 - \nu_2 \pm \nu_M \text{ (or 0)} \pm \nu_m, \quad (2)$$

indicated the frequency for the CO laser for each of the measurements in Table I.

The CO₂ laser standards were stabilized by the Freed-Javan technique (8) and the absolute frequencies and reproducibilities of our particular lasers are known to about one part in 10^9 (9, 10). We estimate that we can determine the CO laser line center to within ± 3 MHz and have indicated our values in Table I. Our ${}^{12}\text{C}^{16}\text{O}$ frequencies are on the average 6.5 MHz lower than the values calculated from the best available constants in the literature (11). The uncertainty in the CO laser frequency when the laser is used as a transfer oscillator was estimated to be ± 0.2 MHz. The frequency, ν_{xfer} , with this smaller uncertainty was the basis for the remainder of the measurement.

The second of the two simultaneous measurements was a difference frequency measurement between the transfer laser and a tunable diode laser (TDL) whose frequency was locked to the NO absorption feature of interest. A first derivative lock (with a nonzero correction to compensate for any power-frequency slope where necessary) was used for this purpose. The uncertainty in the lock point was taken to be one-half of the frequency difference between the derivative extrema, divided by the signal to

TABLE I
Frequency Measurements on Nitric Oxide with Respect to CO₂ Laser Standard Frequencies
Via a CO Laser^a Transfer Oscillator

CO Laser		NO molecule		Obs.-Ref.(1) MHz	Obs.-Calc. MHz
Transition	Frequency MHz	Transition	Frequency ^b MHz		
a) Transitions for the ${}^2\Pi_{1/2} - {}^2\Pi_{1/2}$ states.					
P ₁₃ (15)	52 469 724.4	P(32.5)	52 465 656.4(100)	15.9	-6.9
P ₁₂ (11) ^c	52 727 470.9	P(30.5)	52 728 472.6(40)	17.0	0.3
P ₁₂ (17)	52 984 209.4	P(28.5)	52 987 432.4(80)	10.3	-1.2
P ₁₁ (18)	53 614 910.9	P(23.5)	53 617 709.7(80)	15.4	3.0
			53 617 877.6(80)	-4.4	3.9
P ₉ (17)	55 246 237.3	P(9.5)	55 249 808.1(60)	-8.6	-1.8
			55 250 126.7(60)	-8.9	-3.6
P ₇ (20)	56 387 993.7	R(0.5)	56 392 005.4(60)	-9.1	-5.1
			56 392 368.3(60)	-1.5	3.6
P ₈ (13)	56 491 371.1	R(1.5)	56 489 691.6(50)	-6.4	-2.7
			56 490 049.9(50)	-1.6	3.6
P ₆ (20)	57 148 230.1	R(8.5)	57 144 652.8(50)	-6.3	-2.1
			57 144 967.9(50)	-8.4	-3.0
P ₆ (18)	57 403 402.3	R(11.5)	57 409 807.5(50)	0.6	6.9
			57 410 093.7(50)	-5.5	-0.3
P ₅ (20)	57 910 696.3	R(17.5)	57 911 619.8(80)	-14.5	1.5
			57 911 862.5(80)	-3.6	1.5
b) Transitions for the ${}^2\Pi_{3/2} - {}^2\Pi_{3/2}$ state.					
P ₁₁ (16) ^c	52 893 939.3	P(28.5)	52 901 080.8(40)	10.0	0.3
			52 901 353.1(40)	23.3	3.3
P ₁₀ (17) ^d	53 418 100.5	P(24.5)	53 416 752.9(90)	3.4	0.6
			53 416 967.5(90)	10.3	0.3
P ₈ (19)	55 755 996.0	P(4.5)	55 764 932.9(80)	-16.2	1.2
P ₉ (10)	56 079 580.4	Q(16.5)	56 081 098.5(50)	-8.2	-4.5
			56 082 391.2(50)	-8.5	-8.7
P ₈ (16)	56 128 083.3	Q(13.5)	56 131 466.8(50)	-5.3	2.4
			56 132 213.7(50)	-8.2	3.3
P ₈ (13)	56 491 371.1	R(1.5)	56 490 591.7(50)	-2.4	-2.4
P ₆ (15)	57 778 876.1	R(15.5)	57 778 254.0(90)	-6.2	2.7

a) A normal isotope CO laser is used unless otherwise noted. The estimated uncertainty in the CO line center frequency is ± 3 MHz.

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

c) A ${}^{13}\text{C}^{16}\text{O}$ transition was used for the transfer oscillator.

d) A ${}^{12}\text{C}^{18}\text{O}$ transition was used for the transfer oscillator.

noise ratio of the derivative trace as observed on a recorder. The TDLs used in these measurements were sufficiently powerful (a few mW) that this contribution was comparatively small. The major uncertainty was due to the linewidth of the TDL. This uncertainty was taken as one-tenth of the averaged beatnote linewidth (the spectrum analyzer had storage capability with visual display). The diode lasers used in these experiments had larger linewidths than we have observed in some of our previous work and seemed to be more affected by the compressor vibrations. The beatnote, ν_{B2} , between the transfer laser and the TDL was averaged and a harmonic of an oscillator (whose frequency was counted) was used to mark the center of the averaged display. The frequency of the NO transition then was the algebraic combination of ν_{xfer} and ν_{B2} .

The absorption cell used for these measurements was 1.7 m long and fill pressures ranged from 30 to 600 Pa (0.2 to 4.5 Torr). The cell was slightly heated for some of the high- J measurements.

ANALYSIS OF THE MEASUREMENTS

Initially we had thought that the present measurements would be used only to improve the center frequencies for the ${}^2\Pi_{1/2}$ - ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ - ${}^2\Pi_{3/2}$ vibrational fundamentals. Instead, we were surprised to discover that the band centers are hardly shifted while the high- J P -branch transitions taken from the energy levels of Amiot *et al.* are too low by about 15 MHz and the R -branch transitions are too high by about 6 MHz. Table I gives the present measurements and the differences from the values calculated from the energy level tables of Amiot *et al.* In order to rectify this discrepancy it was necessary to modify more than the band center.

To fit the present measurements a nonlinear least-squares fitting program was written. This program was based on the Hamiltonian whose matrix elements are given explicitly in Eqs. (1a) to (1e) of Ref. (4). As a starting point all the constants (except the band center, ν_0 , and the A_1 term) were fixed at the value given by Pine *et al.* The unweighted rms deviation of that fit was 10 MHz. After converting the more accurate constants given by Van Den Heuvel *et al.* (5) to the appropriate values for our Hamiltonian, we also fit our measurements to their constants, again floating the ν_0 and A_1 term, and obtained an rms deviation of 9 MHz. These preliminary fits had systematic deviations that we believed were greater than the measurement error.

Four constants were needed to fit the data to within our estimate of the experimental accuracy. The fit could not be significantly improved by fitting several more constants, and the rms deviation only went to 3 MHz when all the constants were fit. Table II gives the constants used to fit the measurements in Table I. The unweighted rms

TABLE II
Constants^a (in cm^{-1}) for the $v = 0$ and $v = 1$ States of NO

constant ^a	$v = 0$	$v = 1$
ν_0	-----	1875.98918(3) ^b
A	123.1332612 ^c	122.888698(73)
$A_D \times 10^4$	3.4887958 ^d	3.39488(206)
B	1.696158343 ^d	1.678586433 ^d
$D \times 10^6$	5.4757882 ^d	5.492026(94)
$p \times 10^2$	1.1687266 ^e	1.1673809 ^e
$q \times 10^5$	9.4636136 ^e	9.3131095 ^e
$p_D \times 10^8$	0.287 ^e	0.287 ^e

a) The constants are based on the Hamiltonian given in Ref. (4)

b) The uncertainties in the last digits (one standard deviation) are given in parentheses after each fitted value. All parameters without an indicated uncertainty were fixed at the value given here.

c) See Ref. (4).

d) See Ref. (5).

e) See Ref. (6).

TABLE III
Energy Levels (in cm^{-1}) for the $v = 0$ and $v = 1$ Levels of Nitric Oxide

J	$v = 0$				$v = 1$				J
	1/2		3/2		1/2		3/2		
	e	f	e	f	e	f	e	f	
0.5	0.00000	0.01188	----	----	1876.07635	1876.08821	----	----	0.5
1.5	5.00998	5.03370	124.91374	124.91377	1881.03499	1881.05868	2000.72656	2000.72659	1.5
2.5	13.36391	13.39942	133.51422	133.51434	1889.30335	1889.33882	2009.23690	2009.23702	2.5
3.5	25.06178	25.10899	145.55397	145.55427	1900.88141	1900.92856	2021.15047	2021.15077	3.5
4.5	40.10358	40.16237	161.03209	161.03269	1915.76912	1915.82784	2036.46639	2036.46698	4.5
5.5	58.48926	58.55948	179.94745	179.94849	1933.96644	1934.03658	2055.18354	2055.18456	5.5
6.5	80.21875	80.30023	202.29866	202.30032	1955.47325	1955.55465	2077.30055	2077.30217	6.5
7.5	105.29195	105.38450	228.08412	228.08659	1980.28945	1980.38192	2102.81583	2102.81825	7.5
8.5	133.70873	133.81212	257.30200	257.30550	2008.41485	2008.51817	2131.72759	2131.73102	8.5
9.5	165.46888	165.58289	289.95026	289.95502	2039.84924	2039.96318	2164.03381	2164.03848	9.5
10.5	200.57217	200.69652	326.02664	326.03293	2074.59232	2074.71662	2199.73226	2199.73842	10.5
11.5	239.01826	239.15269	365.52871	365.53680	2112.64375	2112.77815	2238.82054	2238.82846	11.5
12.5	280.80677	280.95099	408.45384	408.46402	2154.00308	2154.14730	2281.29604	2281.30601	12.5
13.5	325.93722	326.09092	454.79923	454.81180	2198.66981	2198.82354	2327.15599	2327.16831	13.5
14.5	374.40902	374.57190	504.56190	504.57718	2246.64331	2246.80624	2376.39745	2376.41243	14.5
15.5	426.22150	426.39322	557.73873	557.75705	2297.92285	2298.09468	2429.01732	2429.03527	15.5
16.5	481.37385	481.55409	614.32644	614.34812	2352.50761	2352.68800	2485.01235	2485.03360	16.5
17.5	539.86517	540.05358	674.32161	674.34699	2410.39663	2410.58525	2544.37915	2544.40403	17.5
18.5	601.69440	601.89065	737.72068	737.75010	2471.58882	2471.78533	2607.11418	2607.14303	18.5
19.5	666.86037	667.06412	804.51997	804.55377	2536.08297	2536.28704	2673.21378	2673.24694	19.5
20.5	735.36177	735.57267	874.71566	874.75420	2603.87773	2604.08901	2742.67417	2742.71197	20.5
21.5	807.19714	807.41484	948.30383	948.34745	2674.97159	2675.18975	2815.49144	2815.53423	21.5
22.5	882.36485	882.58901	1025.28045	1025.32949	2749.36292	2749.58761	2891.66157	2891.70969	22.5
23.5	960.86316	961.09343	1105.64135	1105.69616	2827.04991	2827.28080	2971.18042	2971.23421	23.5
24.5	1042.69015	1042.92618	1189.38228	1189.44321	2908.03062	2908.26735	3054.04375	3054.10356	24.5
25.5	1127.84373	1128.08518	1276.49887	1276.56626	2992.30293	2992.54518	3140.24721	3140.31337	25.5
26.5	1216.32167	1216.56821	1366.98667	1367.06086	3079.86457	3080.11200	3229.78635	3229.85920	26.5
27.5	1308.12157	1308.37286	1460.84110	1460.92242	3170.71311	3170.96540	3322.65661	3322.73648	27.5
28.5	1403.24087	1403.49658	1558.05751	1558.14628	3264.84597	3265.10278	3418.85334	3418.94055	28.5
29.5	1501.67684	1501.93664	1658.63112	1658.72768	3362.26038	3362.52139	3518.37178	3518.46666	29.5
30.5	1603.42658	1603.69016	1762.55707	1762.66175	3462.95343	3463.21832	3621.20707	3621.30993	30.5
31.5	1708.48705	1708.75409	1869.83041	1869.94352	3566.92203	3567.19049	3727.35426	3727.46542	31.5
32.5	1816.85502	1817.12519	1980.44607	1980.56793	3674.16294	3674.43465	3836.80829	3836.92806	32.5
33.5	1928.52710	1928.80011	2094.39891	2094.52982	3784.67273	3784.94739	3949.56400	3949.69269	33.5
34.5	2043.49975	2043.77528	2211.68366	2211.82394	3898.44784	3898.72515	4065.61614	4065.75405	34.5
35.5	2161.76924	2162.04700	2332.29498	2332.44491	4015.48452	4015.76419	4184.95935	4185.10679	35.5
36.5	2283.33170	2283.61139	2456.22741	2456.38730	4135.77888	4136.06061	4307.58818	4307.74543	36.5
37.5	2408.18309	2408.46443	2583.47540	2583.64553	4259.32685	4259.61035	4433.49707	4433.66442	37.5
38.5	2536.31922	2536.60190	2714.03329	2714.21396	4386.12421	4386.40920	4562.68036	4562.85809	38.5
39.5	2667.73570	2668.01946	2847.89532	2848.08681	4516.16657	4516.45277	4695.13228	4695.32067	39.5

deviation of the fit was 3.6 MHz. The largest contribution to the experimental error was the small asymmetry of the low- J transitions, due to unresolved hyperfine structure, and the incomplete resolution of the Λ -doublet structure for many of the transitions. No attempt was made to improve the line center measurements by fitting the line profile to Gaussian doublets as was done by Pine *et al.*

The constants given in Table II were used to prepare Table III which gives revised values for the energy levels of the $v = 0$ and $v = 1$ states of $^{14}\text{N}^{16}\text{O}$. We have also prepared a table of transition frequencies for NO in the spectral region from 1750 to 1960 cm^{-1} which is available from any of the authors.

ACKNOWLEDGMENTS

This work was supported in part through grants from the NASA Office of Upper Atmospheric Research. We thank our colleague, D. A. Jennings, for the computer program for the frequency synthesis. One of us (A.H.) thanks the NBS Time and Frequency Division for the warm hospitality experienced while here.

RECEIVED: March 13, 1986

REFERENCES

1. C. AMIOT, R. BACIS, AND G. GUELACHVILI, *Canad. J. Phys.* **56**, 251-265 (1978).
2. A. VALENTIN, A. HENRY, PH. CARDINET, M. F. LE MOAL, D. W. CHEN, AND K. NARAHARI RAO, *J. Mol. Spectrosc.* **70**, 9-17 (1978).
3. A. S. PINE AND K. W. NILL, *J. Mol. Spectrosc.* **74**, 43-51 (1979).
4. A. S. PINE, J. W. C. JOHNS, AND A. G. ROBIETTE, *J. Mol. Spectrosc.* **74**, 43-51 (1979).
5. F. C. VAN DEN HEUVEL, W. LEO MEERTS, AND A. DYMANUS, *J. Mol. Spectrosc.* **84**, 162-169 (1980).
6. R. S. LOWE, A. R. W. MCKELLAR, P. VEILLETTE, AND W. LEO MEERTS, *J. Mol. Spectrosc.* **88**, 372-377 (1981).
7. J. S. WELLS, A. HINZ, AND A. G. MAKI, *J. Mol. Spectrosc.* **114**, 84-96 (1985).
8. C. FREED AND A. JAVAN, *Appl. Phys. Lett.* **17**, 53-56 (1970).
9. F. R. PETERSEN, E. C. BEATY, AND C. R. POLLOCK, *J. Mol. Spectrosc.* **102**, 112-122 (1983).
10. C. FREED, L. C. BRADLEY, AND R. G. O'DONNELL, *IEEE J. Quantum. Electron.* *QE-16*, 1195-1206 (1980).
11. G. GUELACHVILI, D. DE VILLENUEVE, R. FARRENQ, W. URBAN, AND J. VERGES, *J. Mol. Spectrosc.* **98**, 64-79 (1983).