

Hyperfine and Λ -Doubling Parameters for the $v = 1$ State of NO from Infrared–Radiofrequency Double Resonance

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Hyperfine Λ -doubling transitions have been measured for a number of rotational levels with $2.5 \leq J \leq 20.5$ in the ${}^2\Pi_{1/2}$ $v = 0$ and 1 states of ${}^{14}\text{N}{}^{16}\text{O}$. The measurements were made with infrared–radiofrequency double-resonance spectroscopy, utilizing close coincidences between CO laser lines and NO 1–0 band transitions in the $5.4\text{-}\mu\text{m}$ region. A combined fit of the present and previous data gives new information for NO in the $v = 1$ state: greatly improved Λ -doubling parameters and the first determination of hyperfine interaction parameters.

I. INTRODUCTION

The ${}^2\Pi$ ground electronic state of NO has been the subject of a remarkably large number of spectroscopic studies. Among the many papers in recent years, extensive high-resolution data on ${}^{14}\text{N}{}^{16}\text{O}$ are available from molecular beam electric resonance spectroscopy (1, 2) (hyperfine Λ -doubling transitions within $v = 0$), from conventional microwave spectroscopy (3) and laser sideband spectroscopy (4) (rotational transitions), and from Fourier transform infrared spectroscopy (5) (vibration–rotation transitions). These studies yield very precise spin–orbit, rotational, and centrifugal distortion parameters for both $v = 0$ and 1, and Λ -doubling and hyperfine parameters for $v = 0$ (2, 4). However, for $v \geq 1$, Λ -doubling parameters are rather less accurately known and hyperfine parameters are not available. This is because hyperfine splittings are not fully resolved in Doppler-limited infrared spectra of NO. Sub-Doppler spectra may be obtained by various laser techniques (6–9), but the results have not been sufficiently extensive and/or precise to determine hyperfine parameters or refine Λ -doubling parameters.

This paper reports measurements of hyperfine Λ -doubling transitions within the

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${}^2\Pi_{1/2}$ $v = 0$ and 1 states of ${}^{14}\text{N}{}^{16}\text{O}$ that were made using infrared-radiofrequency double-resonance spectroscopy. This technique utilizes close coincidences between CO laser lines and NO 1-0 band absorption lines, and was first applied to NO by Dale *et al.* (7), who used one such coincidence to measure transitions within the $v = 0$, $J = 5.5$ and $v = 1$, $J = 4.5$ levels. Five more coincidences are studied here to probe a number of rotational levels with J between 2.5 and 20.5. The laser lines lie in the range 1800 to 1920 cm^{-1} , and the measured transition frequencies lie in the range 0.9 to 6.5 GHz. By fitting these new data, hyperfine parameters for $v = 1$ are determined for the first time, and greatly improved Λ -doubling parameters are also obtained.

II. EXPERIMENTAL DETAILS

The measurements were made in Ottawa with an apparatus similar to those used previously for double-resonance studies with CO (7, 10) and CO_2 (11) lasers. The laser was sealed off, and could be used with various isotopic species of CO in order to increase the available number of laser oscillation frequencies. Inside its optical cavity was placed an absorption cell constructed as a 50-ohm coaxial rf transmission line with a length of about 30 cm. The main difference from previous experiments (7, 10) was in the detailed design of this cell, which featured a carefully tapered transition section between the rf cable and cell body to present a nearly constant 50-ohm impedance to the rf radiation over its length. This design minimized unwanted reflections at the ends of the cell, and gave nearly flat rf transmission from 0 to beyond 7 GHz. In contrast, the earlier cell (7, 10) could not be used at frequencies much above 2 GHz.

The rf radiation, with power levels in the range 0.2 to 8 W, was frequency modulated at ~ 50 kHz. Double-resonance signals were detected by phase-sensitive amplification of the laser output signal at the modulation frequency, resulting in a nominally first derivative lineshape. Observed linewidths were about 300 kHz, and most measurements were made with the rf sweeper frequency locked to the NO signal by a servo loop. This enabled the center frequency to be counted for many seconds, and measurements could be made to better than 10 kHz. However, the exact position and shape of each double-resonance line was a function of the laser power level. We attempted to measure each frequency at the lowest possible laser power, but the uncertainties introduced by these infrared saturation effects limited the accuracy to about 30 kHz. The behavior of the NO line shapes with laser power was similar to that observed previously with NO_2 (see Fig. 2 of 10), though the effects were less severe in the present case.

III. RESULTS

A list of near coincidences which were possible candidates for double-resonance signals was compiled by comparing the accurate NO fundamental band data of Amiot *et al.* (5) with known CO laser frequencies (12). This list included some coincidences involving the ${}^{14}\text{N}{}^{18}\text{O}$ and ${}^{15}\text{N}{}^{16}\text{O}$ isotopic species (5, 13) because it was hoped that double-resonance signals might be detected even in natural abundance NO samples. Similarly, some $v = 2 \leftarrow 1$ hot band transitions were

TABLE I

CO Laser Lines Used to Observe Infrared-Radiofrequency Double-Resonance Transitions in $^{14}\text{N}^{16}\text{O}$

CO Laser				NO Absorption		
Assignment			Wavenumber ^a	Assignment ^b	Wavenumber ^c	$\Delta\nu$ ^d
isotope	ν	J	(cm^{-1})		(cm^{-1})	(MHz)
$^{12}\text{C}^{18}\text{O}$	11-10	P(12)	1800.7234	P(20.5)	1800.7216	-54
$^{13}\text{C}^{18}\text{O}$	9-8	P(14)	1804.7322	P(19.5)	1804.7288	-102
$^{13}\text{C}^{16}\text{O}$	10-9	P(16)	1812.6418	P(17.5)	1812.6427	+27
$^{13}\text{C}^{16}\text{O}$	8-7	P(17)	1857.2742	P(5.5)	1857.2799	+171
$^{13}\text{C}^{16}\text{O}$	8-7	P(10)	1884.2908	R(1.5)	1884.2934	+78
$^{12}\text{C}^{16}\text{O}$	8-7	P(11)	1917.8610	R(12.5)	1917.8634	+72

^aDale *et al.* (12).^bAll NO transitions are within the $^2\Pi_{1/2}$ substate.^cCalculated frequency from Amiot *et al.* (5) for the Λ -doubling component closest to the laser frequency.^d $\Delta\nu \equiv \nu_{\text{NO}} - \nu_{\text{laser}}$.

also included. However, of the many coincidences searched, the five for which signals were observed (in addition to the one already studied (7)) all involved the 1-0 band of $^{14}\text{N}^{16}\text{O}$ in the $^2\Pi_{1/2}$ substate; Table I lists these laser lines and NO transitions. In all cases, the laser and NO transitions were sufficiently close (Table I) that the laser was effectively within the Doppler-broadened NO line profile. We were not successful in detecting double-resonance signals in cases with larger frequency differences (i.e., $\Delta\nu > 250$ MHz).

The measured double-resonance frequencies are listed in Table II, which includes the data previously reported by Dale *et al.* (7). It should be noted that two of these latter transitions, with $\nu = 0$ and $J = 5.5$, are actually better known from the molecular beam measurements of Meerts (2). Transitions within the $\nu = 0$, $J = 1.5$ level were observed during the present work while studying the $\text{NO} R(1.5)$ transition at 1884.3 cm^{-1} . However, they are also known very accurately from the molecular beam work (1) and are therefore not listed in Table II.

A given rotational level J of NO is split into two levels of opposite parity by Λ -doubling. This splitting lies in the range 0.3 to 7 GHz for $J = 0.5$ to 25.5 of $^2\Pi_{1/2}$. Each of these levels is further split for $^{14}\text{N}^{16}\text{O}$ by hyperfine interactions into three levels with total angular momentum $F = J - 1$, J , and $J + 1$. The observed double-resonance signals involve $\Delta J = 0$ transitions between the hyperfine Λ -doubling levels of opposite parity. The strongest transitions are the three possible hyperfine components with $\Delta F = 0$. The satellites with $\Delta F = \pm 1$ have some intensity for low J values, but become rapidly weaker as J increases. In the present case, both the $\Delta F = 0$ and the weak $\Delta F = \pm 1$ components were observed for $J = 2.5$, 4.5, and 5.5, but only the dominant $\Delta F = 0$ components were observed for $J = 12.5$ to 20.5 (see Table II).

TABLE II
Observed Λ -Doubling Transitions in the ${}^2\Pi_{1/2}$ State of ${}^{14}\text{N}^{16}\text{O}$ (in MHz)

J	F	$v=1$		$v=1$	
		Obs	Obs-Cal ^a	Obs	Obs-Cal ^a
20.5	21.5-21.5	6476.33	+0.321		
	20.5-22.5	6431.55	-3.092		
	19.5-19.5	6299.33	3		
19.5	21.5-20.5	6204.24	+0.201	111.1	+0.107
	19.5-21.5	6131.37	+3.111	1111.77	+3.226
	19.5-18.5	5993.12	+0.017	-132.74	+3.317
19.5	19.5-19.5			249.37	+3.317
	18.5-18.5			1594.12	+1.511
	17.5-17.5			1776.13	3
17.5	18.5-18.5	6747.45	+0.313		
	17.5-17.5	5661.70	+0.297		
	16.5-16.5	5433.42	-0.203		
16.5	17.5-17.5			5681.11	+3.301
	16.5-16.5			1621.77	+2.301
	15.5-15.5			5293.20	-0.018
13.5	14.5-14.5			4711.59	-0.025
	13.5-13.5			4631.12	-0.311
	12.5-12.5			4993.74	+3.026
12.5	13.5-13.5	3426.80	-0.210		
	12.5-12.5	3316.13	-0.017		
	11.5-11.5	3207.85	-0.013		
5.5 ^b	6.5-6.5	2207.865 ^b	-0.017		
	5.5-5.5	2087.257 ^b	-0.023		
	4.5-4.5	1980.393	-0.205		
	6.5-8.5	2160.487	-0.205		
	5.5-6.5	2134.597	-0.606		
	4.5-5.5	2034.677	-0.205		
4.5 ^b	5.5-5.5	2079.145	-0.038		
	4.5-4.5			1861.787	+0.010
	3.5-3.5			1738.575	+6.311
	2.5-2.5			1579.180	+0.010
	4.5-4.1			1814.190	+0.011
	4.5-3.5			1785.957	+0.208
2.5	3.5-3.5			1597.118	+0.011
	1.5-1.5			1676.435	+3.007
	3.5-1.5			1359.35	-0.001
2.5	1.5-1.5			1225.11	+6.011
	2.5-1.5			107.89	-0.001
	3.5-2.5			1113.19	+0.201
	2.5-3.5			1671.47	+3.007
	2.5-3.9			990.35	+6.006
	1.5-2.5			962.66	+0.014

^aData from Dale *et al.* (7).

^bThese transitions have been measured more accurately by Meerts (2) (207.677 and 2087.217 MHz).

IV. ANALYSIS AND CONCLUSIONS

The measurements were fitted in Nijmegen using an effective molecular Hamiltonian for interacting ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ states and a least-squares computer program described by van den Heuvel *et al.* (4). Further details are given in that paper, and the relevant matrix elements of the Hamiltonian are given in (4, 14) (rotation, spin-rotation, and Λ -doubling), (14) (hyperfine, except quadrupole), and (2) (quadrupole hyperfine). The results in Table II were added to the combined fit of infrared, microwave, and molecular beam data made in (4). All the relevant parameters were allowed to vary, but only those involving Λ -doubling and hyperfine splittings in $v = 1$ were significantly affected by the new data. Since in the present study all transitions were measured in the ${}^2\Pi_{1/2}$ state, only the hyperfine parameters ($a - (1/2)(b + c)$), d , eQq_1 , and eQq_2 were well determined. The final $v = 1$ parameters are listed in Table III, together with the corresponding $v = 0$ results. Only the $v = 0$ Λ -doubling parameters p and q were very slightly affected by the new data.

The hyperfine parameters for the $v = 1$ state are determined here for the first time. The $v = 1$ Λ -doubling constants p and q were obtained previously from Doppler-limited infrared spectra (4, 5), but the present work reduces the uncertainties in those parameters by almost two orders of magnitude.

Recently, Pine *et al.* (15) have made a careful determination of the Λ -doubling parameters p and q for the $v = 2$ state of NO from Doppler-limited spectra of the 2-0 overtone band. In comparing these $v = 2$ results with values of p and q for

TABLE III
A-Doubling and Hyperfine Parameters for $^{14}\text{N}^{16}\text{O}$ (in MHz)^a

parameter	v=0	v=1 ^d
p	350.37543(7) ^b	349.972(2)
q	2.83712(5) ^b	2.7920(2)
$a-\frac{1}{2}(b+c)$	92.660(6) ^c	92.46(8)
d	112.5974(1) ^c	112.568(9)
eQq ₁	-1.8565(3) ^c	-1.78(3)
eQq ₂	23.158(6) ^c	23.0(1)

^aUncertainties in parentheses are one standard deviation from the least-squares fit. All other parameters are as given in (4) and (2), except for: $D_p = 86(2)$ Hz and $D_q = 22.1(2)$ Hz.

^bThese values only very slightly changed from (4).

^cThese values are unchanged from (2). In terms of the notation of (2), $eQq_1 \equiv \zeta_1$ and $eQq_2 \equiv 2\zeta_2$.

^dParameters for v=1 not given here or in (4) were fixed at their v=0 values.

$v = 0$ and 1 from Amiot *et al.* (5), they noted that the expected linear relations ($p_v = p_e + \alpha_p(v + 1/2)$, and similarly for q) were not well satisfied. A similar comparison may now be made using the present values for p and q in $v = 0$ and 1 (Table III) and a linear extrapolation. This leads to predicted values of 349.569(4) and 2.7469(4) MHz for p_2 and q_2 , respectively, which may be compared with the values 349.542(20) and 2.754(2) MHz from Pine *et al.* (15). The agreement is thus now much more satisfactory. It should be noted that Pine *et al.* (15) fixed p_0 and q_0 at the values from (5), and their $v = 2$ results might change slightly if more accurate p_0 and q_0 values (2, 4) from molecular beam data were used.

Although hyperfine parameters for the $v = 1$ state of NO have not previously been determined, it has been noted in a number of papers (6, 8, 16) that the vibrational dependence of these parameters must be quite small. The present results fully confirm this observation. Sub-Doppler spectra, with 1.5-MHz resolution, of 2-0 band transitions of NO have recently been obtained (17) using an infrared laser-molecular beam-bolometer detector technique (8). When some problems with frequency calibration have been solved, these results should yield some of the $v = 2$ hyperfine parameters and thus give further insight into their vibrational dependence.

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