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Microwave optical double resonance of HNO: Rotational spectrum in $\tilde{A}\,^1A''$(100)

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Rotational transitions in the $\tilde{A}\,^1A''$(100) state of HNO were observed using the technique of microwave optical double resonance. The HNO molecule was produced in a fast flow system by the reaction of discharged oxygen with a mixture of propylene and NO. Eighteen rotational lines observed in the frequency regions of 8 to 157 GHz and rf were analyzed to give rotational constants and centrifugal distortion constants. Perturbations were found in the K-type doubling frequencies of $K_{-1} = 1$ and 2.

INTRODUCTION

The electronic absorption spectrum of HNO was first observed by Dalby[1] in the region from 650–770 nm using the flash photolysis technique. The spectrum was assigned to $\tilde{A}\,^1A'' \leftarrow \tilde{X}\,^1A'$($\nu_{00} = 13\,154.38$ cm^{-1}) and molecular constants were determined both for the ground state and for some excited vibronic states. Chemiluminescence from the reaction of the H atom with NO was observed by Cashion and Polanyi.[2] Clement and Ramsay[3] studied this emission spectrum in detail and found in some bands a sharp breaking off of K-rotational structures, which was attributed to the predissociation in the $\tilde{A}\,^1A''$ state for levels lying at about 17 000 cm^{-1} above the ground state. Bancroft, Hollas, and Ramsay[4] extended the observation of the absorption spectrum into the visible region. The dissociation limit was confirmed by observing the broadening of the lines of the (101) $\leftarrow$ (000) band.

The intensity of the chemiluminescence was measured to study the mechanism of the reaction by Clyne and Thrush[5,6] who discussed a predissociation route involving the $^3A''$ state. Ishiwata, Akimoto, and Tanaka[7,8] estimated the origin of the $^3A''$ state to be 6820 cm^{-1} above the ground state using the sensitization of the HNO chemiluminescence by $O_2(^1\Delta_g)$. Freedman[9] measured the rotational dependence of the line broadening of the (101) $\leftarrow$ (000) band and suggested an accidental predissociation route via the $\tilde{X}\,^1A'$ state.

The vibrational frequencies of HNO first observed in matrices[10–13] were recently determined in gas phase by Clough *et al.*[14] Johns and Mckellar[15] studied the ν_2 and ν_3 fundamental bands of HNO in the 6.5 μm region by the technique of laser Stark spectroscopy and determined accurate molecular constants for the ground state and vibrational states. The microwave spectrum of HNO was observed in its ground state.[16–18] The interstellar HNO molecule was detected in Sgr B2 and NGC 2024 by Ulich, Hollis, and Snyder.[19]

The present work was initiated to develop experimental techniques in the microwave optical double resonance (MODR) method suitable for HNO and other short-lived molecules, and to extend the microwave spectroscopic investigation to HNO in excited electronic states. In this paper we report the observation of the rotational transitions of HNO in the $\tilde{A}\,^1A''$(100) state using the MODR technique.

When our work was started the observation of laser excited fluorescence (LEF) for HNO had not been reported. After our first detection of the MODR signal, Yamada *et al.*[20] reported the observation of the LEF signal from the $\tilde{A}\,^1A''$ (011) and (010) states to determine the fluorescence lifetime of these states. Dixon and Noble[21] communicated to us that they observed the LEF signals of HNO from several vibronic states and found breaking off of rotational structures, intensity anomalies, and frequency perturbations.

EXPERIMENTAL

The HNO molecule was produced in a fast flow system by the reaction of discharged oxygen with a mixture of propylene and NO at a total pressure of 10–20 mTorr. The reaction products were introduced directly into an MODR cell made of copper. The chemiluminescence was observed just after the mixing zone but it was quenched in the metal cell. We also tried the reaction of discharged hydrogen with NO, which was successfully used in the study on the microwave spectrum of HNO.[16] However, this reaction gave a strong chemiluminescence in the glass cell which made it difficult to detect LEF signals. In the metal cell an LEF signal was observed but was too weak to be used in MODR experiments.

A typical setup of the MODR experiment is shown schematically in Fig. 1. Three MODR cells were used to cover the frequency region of rf to 157 GHz. The cell used in the millimeter-wave region is essentially a crossed RG-96/U waveguide (cross section of 7.1 mm × 3.55 mm). The laser beam is directed along an axis of one of the waveguides through which HNO is flowing. The other waveguide is used to introduce and monitor microwave power. A good microwave transmission was obtained at frequencies up to 157 GHz. LEF was observed through a slit at the center of the cross. Millimeter-wave power sources were OKI klystrons which were frequency modulated by several MHz by a 10 kHz square wave.

For the centimeter-wave region a similar cell made

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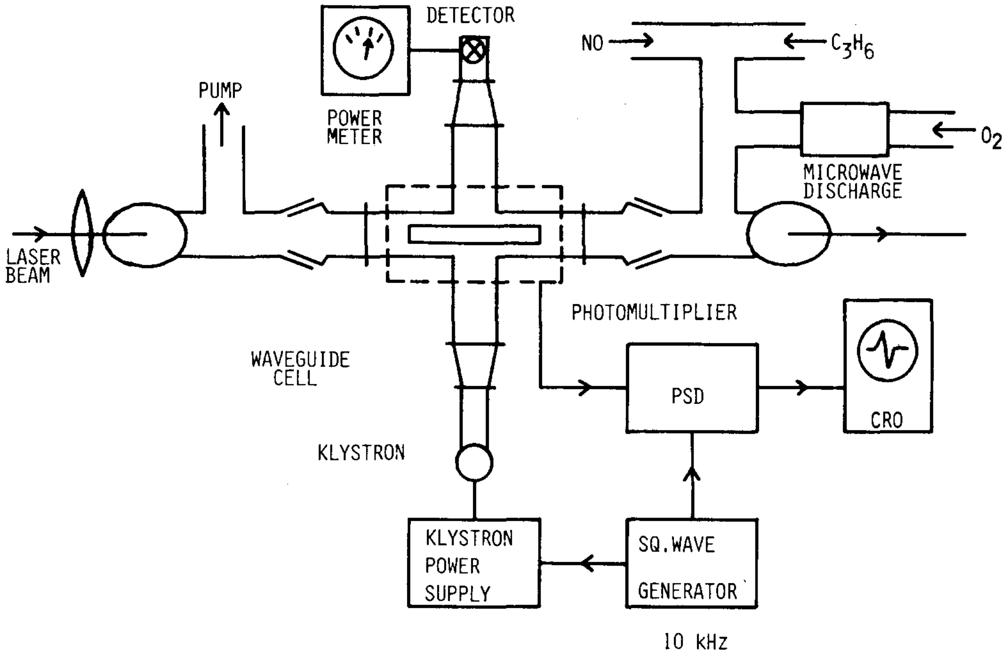

FIG. 1. Block diagram of a setup for the MODR experiment when the microwave power source is a klystron.

of the X-band waveguide was used. A TWT amplifier (Logimetrics A102X) driven by an X-13 was used as a power source in the X-band region, which was 100% amplitude modulated by a 10 kHz square wave.

In the rf region the cell is a coaxial transmission line with inner and outer diameters of 9 and 21 mm, respectively, its characteristic impedance being nearly 50 Ω. At the center of the outer conductor is a slit for the observation of LEF. The cell was terminated by a resistor of 50 Ω at one end and rf power up to 10 W was supplied from the other end by an amplifier (ENI 510L below 500 MHz or Hughes 1406H for 500–1000 MHz) driven by a VHF oscillator (HP 3200B). The VHF oscillator was 100% amplitude modulated by a 10 kHz square wave.

A Rh. B dye laser used (CR 599) produced 20–60 mW in a single mode in the 620 nm wavelength région. The laser beam was focused by lenses near the center of the MODR cell. LEF was focused on the photocathode of a photomultiplier (HTV R666S) through two filters blocking light of wavelength shorter than 720 nm. LEF signals of 0.5 μA or more were usually detected when the photomultiplier was operated at 1000 V. The 10 kHz component of the photomultiplier output was detected by a phase sensitive detector (PAR 124A).

OBSERVATIONS

An oscilloscope tracing of the MODR signal at 7883 MHz for the $2_{11}-2_{12}$ transition of the $\tilde{A}\,^1A''$ (100) state is shown in Fig. 2. The signal was obtained by scanning microwave frequency slowly while the dye laser was tuned to the ${}^rQ_0(2)$, $\tilde{A}\,^1A''$ (100)–$\tilde{X}\,^1A'$ (000) transition at 16 027.39 cm^{-1}. The time constant of PSD was 1 sec. A real line shape was displayed as the microwave was 100% amplitude modulated. Focusing the laser beam at the center of the cell was effective in increasing the intensity of the signals. A decrease of the input laser power by a factor of 2 caused a decrease of the signal intensity by a factor of more than 2. These observations show that saturation of the optical transition is necessary for the observation of the MODR signal. With the higher gain of the TWT amplifier, the microwave power applied to the molecules was so high that the MODR line was broadened. When the gain of the amplifier was decreased, the line width became smaller, but a residual width of 6.5 MHz could not be eliminated. This width is much wider than that expected from pressure broadening and may come from an unresolved quadrupole hyperfine structure. It is to be noted that the frequencies of the three strongest components of $2_{11}-2_{12}$, $F=3-3$, 2–2, and 1–1, calculated from the quadrupole coupling constant for the ground state, are $\nu_0-0.75$ MHz, $\nu_0+2.64$ MHz, and $\nu_0-2.64$ MHz, respectively, where ν_0 is the hypothetical unsplit frequency.

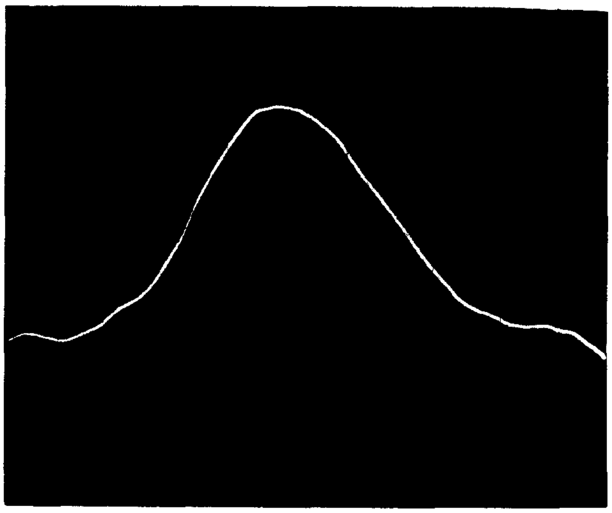

FIG. 2. Oscilloscope trace of $2_{11}-2_{12}$, $\tilde{A}\,^1A''$(100) at 7883 MHz. The optical pump was ${}^rQ_0(2)$, $\tilde{A}\,^1A''$(100)←$\tilde{X}\,^1A'$ (000) at 16 027.39 cm^{-1}. The time constant of PSD was 1 sec. The line width (FWHM) is 6.5 MHz.

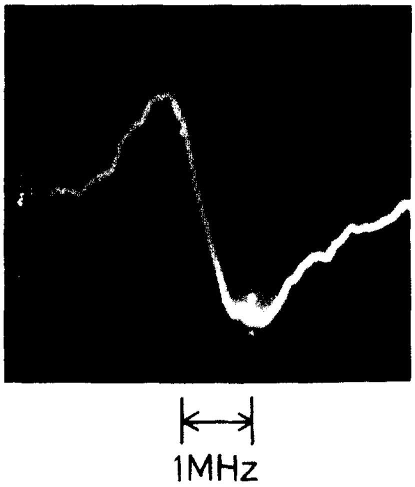

FIG. 3. Oscilloscope trace of $6_{16}-7_{07}$, $\tilde{A}^1A''(100)$ at 16 250 MHz. The optical pump was ${}^rQ_0(6)$, $\tilde{A}^1A''(100) \leftarrow \tilde{X}^1A'(000)$ at 16 023.82 cm^{-1}. The derivative of the line shape was displayed due to the frequency modulation of microwave. Two frequency markers are spaced by 1 MHz. The time constant of PSD was 0.3 sec.

TABLE I. Observed rotational transitions in $\tilde{A}^1A''(100)$ of HNO.

Transition	Frequency (MHz)	Optical transition
a-type		
$1_{01}-0_{00}$	76 919.03 ± 0.07	${}^pP_1(1)$, ${}^pQ_1(1)$
$2_{02}-1_{01}$	153 827.90 ± 0.3	${}^pQ_1(2)$
$2_{11}-1_{10}$	156 305.49 ± 0.3	${}^rR_0(1)$
$2_{12}-1_{11}$	151 050.96 ± 0.3	${}^rQ_0(1)$
$2_{11}-2_{12}$	7 883.37 ± 0.1	${}^rQ_0(2)$,
$3_{12}-3_{13}$	15 707.41 ± 0.15	${}^rQ_0(3)$
$4_{13}-4_{14}$	26 306.19 ± 0.1	${}^rQ_0(4)$
$5_{14}-5_{15}$	39 256.52 ± 0.1	${}^rQ_0(5)$
$6_{15}-6_{16}$	54 931.10 ± 0.15	${}^rQ_0(6)$
$7_{16}-7_{17}$	73 022.9 ± 1	${}^rQ_0(7)$
$3_{21}-3_{22}$	13.82 ± 0.02	${}^rQ_1(3)$
$5_{23}-5_{24}$	11.12 ± 0.08	${}^rQ_1(5)$
$6_{24}-6_{25}$	192.09 ± 0.08	${}^rQ_1(6)$
$7_{25}-7_{26}$	856.81 ± 0.05	${}^rQ_1(7)$
b-type		
$5_{15}-6_{06}$	101 043.48 ± 0.2	${}^pP_1(7)$, ${}^rQ_0(5)$
$6_{16}-7_{07}$	16 250.13 ± 0.08	${}^rQ_0(6)$
$8_{08}-7_{17}$	69 666.38 ± 0.03	${}^rQ_0(7)$
$9_{09}-8_{18}$	156 352.88 ± 0.2	${}^rQ_0(8)$

Figure 3 shows an oscilloscope tracing of the MODR signal at 16 250 MHz for $6_{16}-7_{07}$ when the dye laser was tuned to ${}^rQ_0(6)$ at 16 023.82 cm^{-1}. The derivative of the line shape appears due to the frequency modulation of the microwave. The line width is 1 MHz, which came from modulation broadening. The signal to noise ratio is 25 for the time constant of 0.3 sec. This was the strongest and the sharpest line observed in this work.

Figure 4 shows a recorder tracing of the rf optical double resonance signal for the $3_{21}-3_{22}$ transition at 13.8 MHz, when the dye laser was tuned to ${}^rQ_1(3)$ at 16 067.61 cm^{-1}.

The signal for the $1_{01}-0_{00}$ transition was obtained either by pumping ${}^pQ_1(1)$ or ${}^pP_1(1)$. The signal for ${}^pQ_1(1)$ was found to be much weaker than that for ${}^pP_1(1)$. This observation is explained as follows. In our experimental setup the laser beam and the microwave are polarized in the same direction, which is defined as the space fixed Z-axis. The pumping of ${}^pQ_1(1)$ populates directly only the $M = \pm 1$ levels of 1_{01} because the transition moments are proportional to M^2. On the other hand only the $M = 0$ level is involved in the microwave transition $1_{01}-0_{00}$. A weak signal is observed because the $M = 0$ level is populated by the collision induced transition from $M = \pm 1 - M = 0$ of 1_{01} (reorientation collision[22]). On the other hand, the pumping of ${}^pP_1(1)$ gives a stronger signal because it populates the $M = 0$ level directly.

Eighteen rotational transitions in the $\tilde{A}^1A''(100)$ state have been observed in the frequency range from 11 MHz–156 GHz, as shown in Table I. The first four lines are all the a-type, R-branch transitions for $J \leq 2$. The next six lines are the transitions between the K-type doublets of $K_{-1} = 1$ for $J = 2-7$. The last four lines are the transitions between the K-type doublets of $K_{-1} = 2$. The frequency of $4_{22}-4_{23}$ was estimated to be around 5.8 GHz from an analysis of the laser excitation spectrum. Since we did not have an appropriate power source in that region, its observation was not tried. Four b-type transitions occur below 180 GHz for $J \leq 17$, all of which were observed. They were found to be stronger than a-type transitions.

ANALYSIS

The observed spectrum does not fit with the usual asymmetric rotor pattern, as is evident from the irregular K-type doubling frequencies of $K_{-1} = 2$. This can also be seen in the plot of $B-C$ against J in Fig. 5, where $B-C$ values were determined from K-type doubling fre-

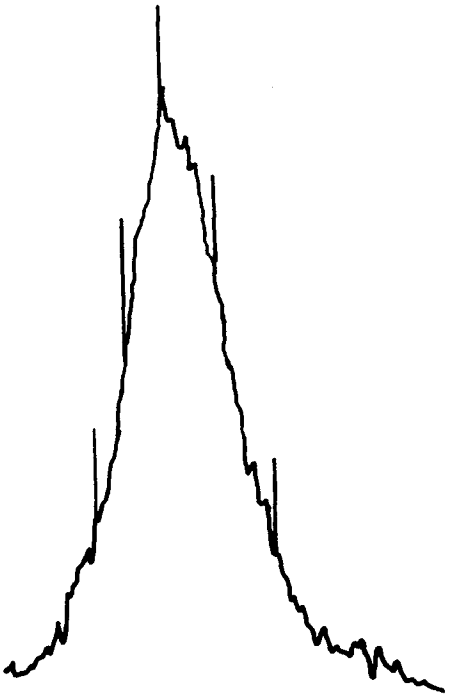

FIG. 4. Recorder trace of $3_{21}-3_{22}$, $\tilde{A}^1A''(100)$ at 13.82 MHz. The optical pump was ${}^rQ_1(3)$ at 16 067.61 cm^{-1}. The frequency markers are spaced by 1 MHz. The time constant of PSD was 0.3 sec.

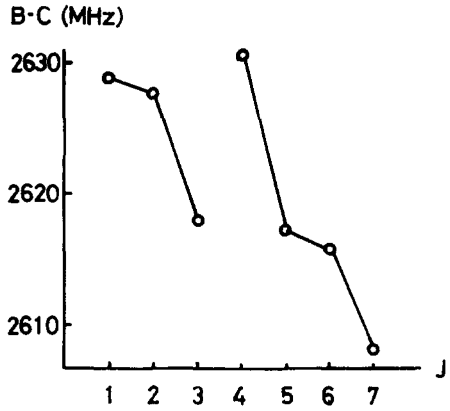

FIG. 5. Plot of $B-C$ values determined from K-type doubling frequencies of $K_{-1}=1$ for $J=1$ to 7.

quencies of $K_{-1}=1$ by neglecting the centrifugal distortion effect. A sudden decrease at $J=3$ and a sudden increase at $J=4$ shows the presence of a local perturbation. Aside from the perturbed levels the observed spectrum was fitted to the following equation for a rotational[17] level,

$$E=E_r-D_J J^2(J+1)^2-D_{JK}J(J+1)K^2$$
$$-D_K K^4 \mp \tfrac{1}{2} d_{EJ}\Delta E_r J(J+1)\ , \qquad (1)$$

where E_r is the rigid rotor energy, D_J, D_{JK}, and D_K terms give the centrifugal distortion energy in the symmetric top approximation, and the last term approximates the centrifugal distortion energy for an upper or lower K-type doublet whose separation is ΔE_r.

The frequency of $1_{10}-1_{11}$ is 2628.84 MHz, obtained from a combination of the observed frequencies. From the exact fit to this frequency and from the least squares fit to those of $5_{14}-5_{15}$, $6_{15}-6_{16}$, and $7_{16}-7_{17}$ the values of $B-C$ and d_{EJ} were determined. $B+C$, D_J and D_{JK} were determined by analyzing four a-type, R-branch transitions. The uncertainties in B and C were estimated from the experimental errors. The values of D_J and D_{JK} may change much when the higher J or K transitions are included in their evaluation. A was determined by using the $5_{15}-6_{06}$ transition while D_K was fixed to 370 MHz,[4] because only $A-D_K$ was determinable from the transitions observed. The constants obtained are given in Table II.

The calculated frequencies and their comparison with the observed ones are given in Table III. The discrepancies in the fitting of the K-type doubling frequencies of $K_{-1}=1$ reflect on the fitting of the b-type transition frequencies. In Table II our constants are compared with those of Bancroft, Hollas, and Ramsay.[4] The agreement is good for B and C, but not so good for A. The disagreement comes from the difference in the values of D_{JK}. It is to be noted, however, that only $K_{-1}=0$ and 1 levels are included in our analysis.

TABLE II. Rotational constants and centrifugal distortion constants in $\tilde{A}\,^1A''(100)$ of HNO (MHz).

	This work	Bancroft, Hollas, and Ramsay
A	621 600	620 906 ± 150
B	39 774.41 ± 0.3	39 818 ± 60
C	37 144.83 ± 0.3	37 120 ± 60
D_J	0.0527	···
D_{JK}	39.642	12.5 ± 0.6
D_K	370[a]	369 ± 6
d_{EJ}	$(1.4175 \pm 0.17)\times 10^{-4}$	···

[a] Assumed.

TABLE III. Calculated frequencies (MHz).

Transition	ν_{rigid}	$\Delta\nu_{\text{cent}}$	ν_{calc}	Obs−calc
a-type				
$1_{01}-0_{00}$	76 919.24	−0.21	76 919.03	0.00
$2_{02}-1_{01}$	153 829.59	−1.69	153 827.90	0.00
$2_{11}-1_{10}$	156 468.07	−163.24	156 304.83	0.66
$2_{12}-1_{11}$	151 208.89	−157.27	151 051.62	−0.66
$1_{10}-1_{11}$[a]	2 629.59	−0.75	2 628.84	0.00
$2_{11}-2_{12}$	7 888.76	−6.71	7 882.05	1.32
$3_{12}-3_{13}$	15 777.50	−26.84	15 750.66	−43.25
$4_{13}-4_{14}$	26 295.73	−74.55	26 221.18	85.01
$5_{14}-5_{15}$	39 443.26	−167.74	39 275.53	−19.01
$6_{15}-6_{16}$	55 219.73	−328.76	54 890.97	40.13
$7_{16}-7_{17}$	73 624.46	−584.44	73 040.02	−17.12
$3_{21}-3_{22}$	44.47	···	44.47	−30.65
$5_{23}-5_{24}$	311.23	···	311.23	−300.11
$6_{24}-6_{25}$	622.38	···	622.38	−430.29
$7_{25}-7_{26}$	1 120.06	···	1 120.06	−263.25
b-type				
$5_{15}-6_{06}$	102 463.43	−1429.86	101 033.57	9.91
$6_{16}-7_{07}$	18 082.50	−1798.28	16 284.22	−34.09
$8_{08}-7_{17}$	67 409.65	2189.80	69 599.45	66.93
$9_{09}-8_{18}$	153 957.50	2587.51	156 545.01	−192.13

[a] Observed frequency is obtained from a combination relation.

DISCUSSION

Both the a-type and b-type rotational transitions of HNO in the electronically excited state, $\tilde{A}\,^1A''$ (100), were observed in the present work by the method of MODR. Only a few short-lived molecules have been subjected to the study of MODR spectroscopy.[23-27] This is because strong fluorescence is required for observations of MODR signals, whereas effective concentration of short-lived molecules is not high enough. In the initial stage of this work, where the reaction $H+NO \rightarrow HNO$ was used, it was difficult to observe the fluorescence of HNO. This difficulty was overcome by using a new reaction, $NO+CH_3-CH{=}CH_2+$discharged O_2, which produces HNO at higher concentration and gives weaker chemiluminescence. Furthermore, HNO turned out to be produced more effectively in the metal waveguide without deterioration of its lifetime. These two findings made it possible for us to use waveguide MODR cells and to observe many MODR signals of HNO over a wide frequency range of up to 157 GHz.

Several vibronic transitions $\tilde{A}\,^1A''(v_1v_2v_3)-\tilde{X}\,^1A'$ (000) of HNO fall in the tuning range of Rh.6G and Rh.B dye lasers. The similar MODR method applied here to $\tilde{A}\,^1A''$ (100) is applicable to $\tilde{A}\,^1A''$ (020) and (011), which lie lower than (100). In other vibronic states such as $\tilde{A}\,^1A''$ (101), (030), and (110) lying above the predissociation limit, most of the rotational levels are considered to be broad. Much weaker MODR signals are expected for those states than those for (100), because LEF signals from them are much weaker and microwave pumping is less effective for broader lines.

Bancroft, Hollas, and Ramsay[4] reported no significant perturbations in the low J and low K transitions for the $\tilde{A}\,^1A''$ (100)$\leftarrow$$\tilde{X}\,^1A'$ (000) band of HNO. However, in the present work remarkable perturbations were found in the rotational spectrum of the $^1A''$ (100) state. This is because MODR spectroscopy has essentially the same resolution as microwave spectroscopy does. A local perturbation noted in Fig. 5 suggests that the rotational levels of the $\tilde{A}\,^1A''$ (100) state cross at $J=3$ and 4 with those of a perturbing state. Also, the observed values for the K-type doubling frequencies of $K_{-1}=2$ for $J=3$, 5, 6, and 7 are much less than the values calculated with $B-C$ obtained from those of $K_{-1}=1$, while the frequency $4_{22}-4_{23}$ is estimated to be much larger, as was pointed out above. It is clear that there is an anomaly for $J=4$ and 5 in the K-type doubling frequencies of $K_{-1}=2$ similar to those of $K_{-1}=1$ for $J=3$ and 4.

These heterogeneous perturbations can be explained by Coriolis interactions. Since all the vibrational modes of HNO belong to the A' species of C_s symmetry, only two cases remain to be discussed; c-type Coriolis interaction with A'' vibronic states and b-type Coriolis interaction with A' vibronic states. In the former case, perturbing levels are within the same electronic state. The vibrational frequencies of ν_2 and ν_3 modes for the $\tilde{A}\,^1A''$ state are $\nu_2 = 1420.77$ cm^{-1} and $\nu_3 = 981.18$ cm^{-1}. These two modes are far from perturbing the (100) state ($\nu_1 = 2854.17$ cm^{-1}). The nearest vibronic level to (100) is (020), which is below (100) by 53 cm^{-1}.[4] The levels of $K_{-1}=2$ in (020) lie above those of $K_{-1}=1$ in (100) by 8 cm^{-1} for $J=2$, and the separation decreases gradually for higher J (e.g., 7 cm^{-1} for $J=7$). Since the separations are small, (020) $K_{-1}=2$ can perturb (100) $K_{-1}=1$ appreciably. However, this perturbation cannot explain the anomaly in K-type doubling frequencies for $J=3$ and 4. The perturbing levels should belong to the other electronic states; the highly excited vibrational states of the ground electronic state, $\tilde{X}\,^1A'$, or the triplet state, $a\,^3A''$. More information is needed to discriminate these two possibilities.

ACKNOWLEDGMENTS

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