# High Resolution Spectroscopy Using a Stabilized Diode Laser: the $2\nu_9$ Band of $HNO_3$ [1]

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The high resolution spectrum of the $2\nu_9$ band of $HNO_3$ has been recorded by a tunable diode laser spectrometer with a newly developed frequency stabilization technique. The spectral data were digitally stored and processed by a dedicated micro-computer in order to improve the sensitivity and the precision of the measurements. In addition to the anomalies due to the Fermi resonance with the $v_5 = 1$ state, we have observed the line doubling caused by the internal rotation of the OH group.

## Introduction

The frequency stabilization technique developed recently in our laboratory [1] specifically for diode laser spectroscopy has been applied successfully to molecular spectroscopy with a newly constructed digital data acquisition system. Stimulated by the increasing interest in the chemistry of the atmosphere, we have measured the diode laser spectra of nitric acid, $HNO_3$, which plays an important role in atmospheric photochemical processes. The atmospheric (including stratospheric and tropospheric) spectra of this molecule have often been observed in emission and absorption in the 11 μm region, where a Fermi diad of the $\nu_5$ and $2\nu_9$ bands appears.

In the laboratory, a low resolution spectrum of $HNO_3$ in the 11 μm range was measured by Chevillard and Giraudet [2]. Their measurements supplied us with sufficiently good starting parameters to identify lines from the complicated and confusing band structures of $\nu_5$ and $2\nu_9$ seen in the high resolution diode laser spectrum. Other diode laser spectra have been measured in several wavelength regions. Brockman et al. [3] measured diode laser spectra in the range from 891 $cm^{-1}$, where the R-branch transitions of the $\nu_5$ fundamental band and the Q branch of the $2\nu_9$ band are expected. Dana [4, 5] analyzed both bands. Recently Maki and Wells [6] have measured a fairly wide range covering P, Q, and R-branch transitions of the $\nu_5$ band (853 to 892 $cm^{-1}$) with a diode laser spectrometer. They determined accurate molecular parameters for this fundamental band and pointed out anomalies caused by the Fermi resonance between the $v_5 = 1$ and the $v_9 = 2$ states. However, for the $2\nu_9$ band, the constants were not well known due to the lack of accurate data.

In the present work, therefore, we have measured several transitions of the $2\nu_9$ band with our diode laser spectrometer, covering the range from 900 to 911 $cm^{-1}$, the region of the R-branch transitions. Because of the perturbation due to the Fermi resonance, assignment of lines has not yet been completed. Here we present results of a limited analysis of this band. We also discuss a novel frequency stabilization and averaging technique, developed for high sensitivity and fast data handling and processing.

## Experimental Procedure

Concentrated nitric acid vapor was dried by distillation and by $P_2O_5$, and then introduced into a 1.5 m glass cell with $BaF_2$ windows. The sample was found to be very aggressive to metal surfaces, so it was impossible to measure the sample pressure in the cell. The pressure was controlled by watching the line shape on the oscilloscope, and was reduced so that Doppler limited resolution could be obtained. The sample was photo-sensitive and was refilled after a few days when the color of the gas in the cell indicated the presence of $NO_2$.

The details of the stabilization technique for the diode laser have been reported by Reich et al. [1]. The method for calibration will be published elsewhere [7]. A block diagram of the spectrometer used in the pres-

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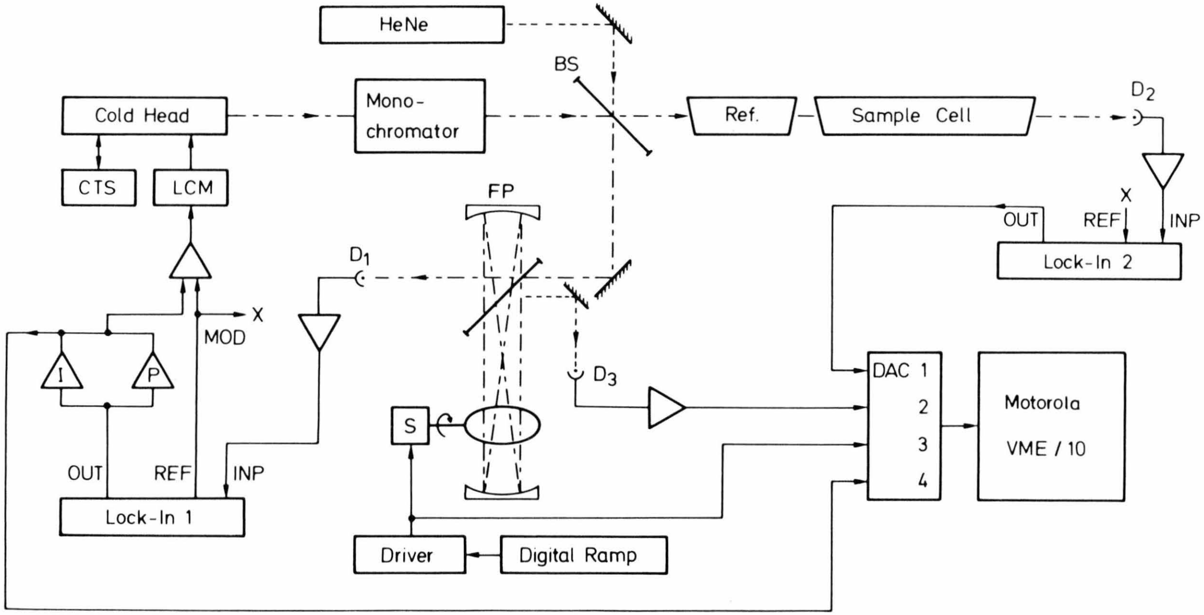
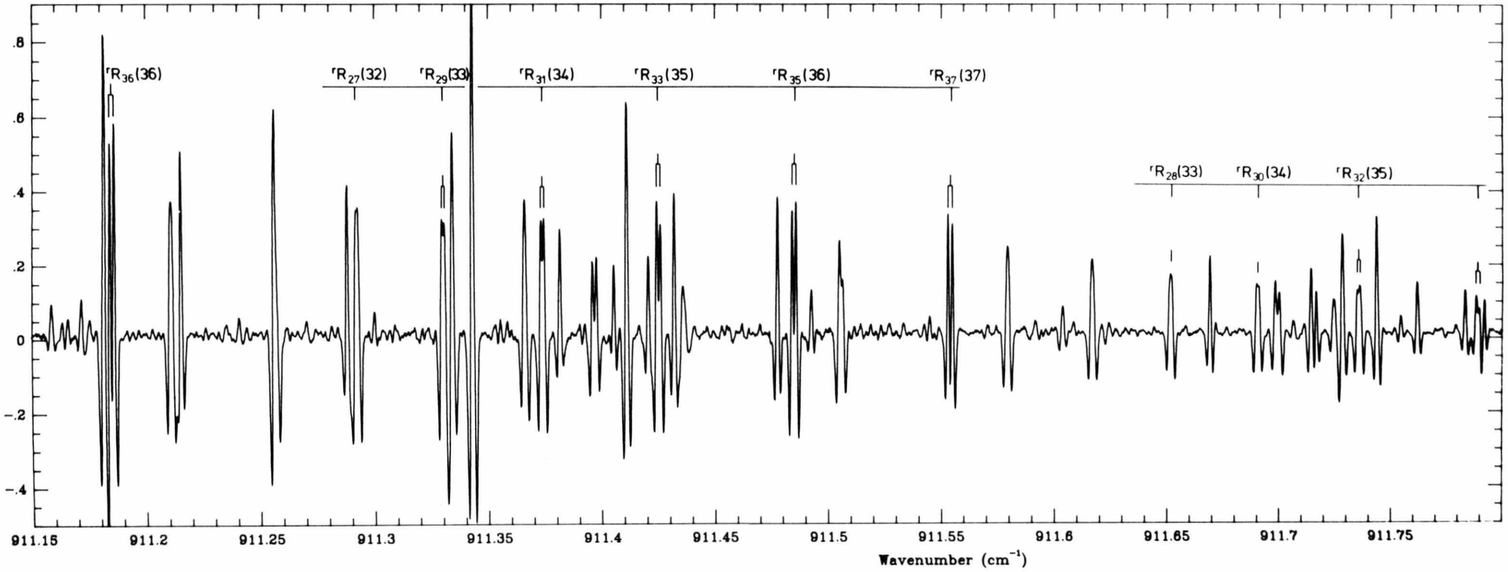


Fig. 1. Schematic diagram of the spectrometer is illustrated. Following symbols are used in the diagram; CTS: cryogenic temperature controller, LCM: laser controle module, BS: beam splitter, $D_1$ and $D_2$: HgCdTe detector at 77 K, $D_3$: pin photo-diode, S: galvanic scanner, I: integration amplifier, P: proportional amplifier.

Fig. 2. A part of the observed spectra is reproduced after smoothing. The typical perpendicular band structure of a planar oblate top was identified as indicated. Each of these $2\nu_9$ vibration-rotation lines is a doublet caused by internal rotation tunneling.



ent study is illustrated in Figure 1. The frequency modulated laser beam (30 kHz sine wave) was coupled into a tunable Fabry-Perot cavity, and the laser frequency was locked at a peak of the fringe signal by a feedback loop. The resonance frequency of the Fabry-Perot cavity was tuned by rotating a KBr plate in the cavity with a galvanic scanner which was driven digitally. Thus the laser frequency was tuned smoothly following the rotation of the sanner plate. The optical pathlength of the tunable cavity was monitored by a frequency stabilized He-Ne laser whose beam was colinear with the IR diode laser beam in the cavity. The fringe signal arising from the He-Ne laser beam was used as a calibration scale for the wavenumber.

Since the diode laser was frequency modulated in order to stabilize the frequency, the spectral signal detected by a HgCdTe detector at 77 K was also modulated. The signal was demodulated by a lock-in amplifier operating in the 2f mode. Thus the second derivative spectra were recorded. The output signal of the lock-in amplifier was digitized by a 12 bit AD converter with a sampling interval of 500 µsec, and then processed by a micro-computer, Motorola VME/10.

The fringe signal of the He-Ne laser was detected by a pin photodiode. A trigger signal was generated at each maximum of the fringe, supplying the timing signal for storing the digitized spectral signal. Since the trigger interval was much larger, in slow scanning measurements, than the sampling interval of the AD converter, the digitized data were accumulated and averaged for the He-Ne-fringe trigger interval. With this procedures we measured the signal intensity with a spacing of approximately 5.5 MHz at 900 $cm^{-1}$. The scan could be precisely repeated as required, e.g., for signal averaging, since counting the He-Ne fringes guarantees that the IR-frequency is always the same at each fringe even if there are drifts of the electronics or temperature present.

A portion of the observed spectra is reproduced in Fig. 2, in which the obtained digital data were smoothed by a fit of a cubic polynomial [8] over 9 observed points. The wavenumber axis was calibrated by HNCO line positions [9]. By numerically differentiating the signal with a polynomial smoothing algorithm [8], we determined the line positions by the zero-crossing of the third derivative spectra. This algorithm prooves to be fast enough for on-line applications. The accuracy with which the HNCO lines are known is about 0.0007 $cm^{-1}$, which is considerably less accurate than the capabilities of the spectrometer [7]. Thus the HNCO data limit the accuracy of the present measurements. We emphacise that diode laser spectra can be measured by this technique to an unprecedented accuracy of $10^{-5}$ $cm^{-1}$, provided adequate calibration lines are available.

## Analysis and Results

As pointed out by Maki and Wells [6], the band type of $2\nu_9$ is expected to be the same as that of $\nu_5$, because the $2\nu_9$ band borrows its intensity from the fundamental band $\nu_5$ through state mixing due to Fermi resonance. Since the a-type transitions were found to be dominant in the $\nu_5$ band, we presume in the present analysis that the $2\nu_9$ band is also an a-type band.

Since wavenumbers predicted using the constants reported by Dana [5] could not be used for identification in the present spectra, we returned to the paper of Chevillard and Giraudet [2]. We used a bootstrap method for line assignments, predicting line positions by varying the parameters near the reported values. After a few trials, we found a set of parameters for which the calculated line positions agree fairly well with some of the observed spectral patterns. This led to a definite assignment of the first transitions and yielded improved parameters by a least-squares fit. With the improved parameters, we were able to repeat the procedure and assign more lines. By iterating this technique, we have definitely identified 25 R-branch lines listed in Table 1. The assigned transitions are of large $K_c$ (small $K_a$) and show the typical band structure of a perpendicular band of a planar near-oblate-top molecule as shown in Figure 2.

Most of the identified lines exhibit a doublet structure (see Figs. 2 and 3), which gave rise to confusion at the early stage of the assignment. The separation of the doublet is large for high $K_c$ transitions and decreases with decreasing $K_c$. Therefore the splitting behaves contrary to the well known behaviour of $K$-type doubling. The doubling in our lines must be caused by an internal rotation of the OH group. For the $v_9 = 1$ state, the first excited state of the OH torsional vibration, De Lucia and coworkers [10] have found a very small splitting (about 2 MHz) in the pure rotational spectra. A much larger splitting is expected for the $v_9 = 2$ state. Since no internal rotation dou-

Table 1. Transition Wavenumbers ($cm^{-1}$) of $HNO_3$ for the $2\nu_9$ Band.

| $J'$ | $K'_a$ | $K'_c$ | $J''$ | $K''_a$ | $K''_c$ | Observed | Caculated | Obs-Calc |
|---|---|---|---|---|---|---|---|---|
| 29 | 0 | 29 | 28 | 0 | 28 | | | |
| 29 | 1 | 29 | 28 | 1 | 28 | 908.1855 | 908.1849 | 0.0006 |
| 28 | 1 | 27 | 27 | 1 | 26 | | | |
| 28 | 2 | 27 | 27 | 2 | 26 | 908.1346 | 908.1345 | 0.0001 |
| 27 | 2 | 25 | 26 | 2 | 24 | | | |
| 27 | 3 | 25 | 26 | 3 | 24 | 908.0894 | 908.0901 | −0.0007 |
| 26 | 3 | 23 | 25 | 3 | 22 | | | |
| 26 | 4 | 23 | 25 | 4 | 22 | 908.0522 | 908.0517 | 0.0005 |
| 28 | 0 | 28 | 27 | 0 | 27 | | | |
| 28 | 1 | 28 | 27 | 1 | 27 | 907.8039 | 907.8042 | −0.0003 |
| 27 | 1 | 26 | 26 | 1 | 25 | | | |
| 27 | 2 | 26 | 26 | 2 | 25 | 907.7557 | 907.7556 | 0.0001 |
| 39 | 0 | 39 | 38 | 0 | 38 | | | |
| 39 | 1 | 39 | 38 | 1 | 38 | 911.9221 | 911.9220 | 0.0001 |
| 38 | 1 | 37 | 37 | 1 | 36 | | | |
| 38 | 2 | 37 | 37 | 2 | 36 | 911.8506 | 911.8497 | 0.0009 |
| 37 | 2 | 35 | 36 | 2 | 34 | | | |
| 37 | 3 | 35 | 36 | 3 | 34 | 911.7887 | 911.7886 | 0.0001 |
| 36 | 3 | 33 | 35 | 3 | 32 | | | |
| 36 | 4 | 33 | 35 | 4 | 32 | 911.7357 | 911.7363 | −0.0006 |
| 34 | 5 | 29 | 33 | 5 | 28 | | | |
| 34 | 6 | 29 | 33 | 6 | 28 | 911.6517 | 911.6515 | 0.0002 |
| 33 | 6 | 27 | 32 | 6 | 26 | | | |
| 33 | 7 | 27 | 32 | 7 | 26 | 911.6170 | 911.6171 | −0.0001 |
| 38 | 0 | 38 | 37 | 0 | 37 | | | |
| 38 | 1 | 38 | 37 | 1 | 37 | 911.5541 | 911.5545 | −0.0004 |
| 37 | 1 | 36 | 36 | 1 | 35 | | | |
| 37 | 2 | 36 | 36 | 2 | 35 | 911.4849 | 911.4849 | 0.0000 |
| 36 | 2 | 34 | 35 | 2 | 33 | | | |
| 36 | 3 | 34 | 35 | 3 | 33 | 911.4250 | 911.4256 | −0.0006 |
| 35 | 3 | 32 | 34 | 3 | 31 | | | |
| 35 | 4 | 32 | 34 | 4 | 31 | 911.3739 | 911.3744 | −0.0005 |
| 34 | 4 | 30 | 33 | 4 | 29 | | | |
| 34 | 5 | 30 | 33 | 5 | 29 | 911.3301 | 911.3299 | 0.0002 |
| 33 | 5 | 28 | 32 | 5 | 27 | | | |
| 33 | 6 | 28 | 32 | 6 | 27 | 911.2924 | 911.2910 | 0.0014 |
| 32 | 6 | 26 | 31 | 6 | 25 | | | |
| 32 | 7 | 26 | 31 | 7 | 25 | 911.2564 | 911.2573 | −0.0009 |
| 37 | 0 | 37 | 36 | 0 | 36 | | | |
| 37 | 1 | 37 | 36 | 1 | 36 | 911.1852 | 911.1854 | −0.0002 |
| 36 | 1 | 35 | 35 | 1 | 34 | | | |
| 36 | 2 | 35 | 35 | 2 | 34 | 911.1188 | 911.1184 | 0.0004 |
| 11 | 0 | 11 | 10 | 0 | 10 | | | |
| 11 | 1 | 11 | 10 | 1 | 10 | 901.1530 | 901.1526 | 0.0004 |
| 10 | 1 | 9 | 9 | 1 | 8 | | | |
| 10 | 2 | 9 | 9 | 2 | 8 | 901.1349 | 901.1365 | −0.0016 |
| 10 | 0 | 10 | 9 | 0 | 9 | | | |
| 10 | 1 | 10 | 9 | 1 | 9 | 900.7500 | 900.7506 | −0.0006 |
| 9 | 1 | 8 | 8 | 1 | 7 | | | |
| 9 | 2 | 8 | 8 | 2 | 7 | 900.7384 | 900.7366 | 0.0018 |

bling has been observed in the ground vibrational state, the spitting observed in the $2\nu_9$ band in the present study directly represents the splitting of the energy levels in the $v_9 = 2$ state. The transition wavenumbers given in Table 1 are the average of the doublets. The K-type doubling was not resolved at all for the assigned transitions.

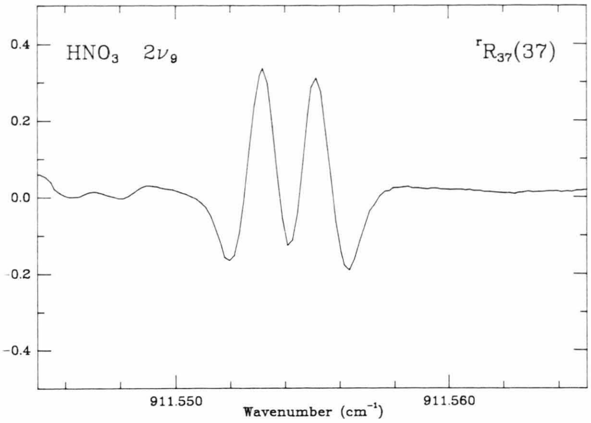


Fig. 3. High resolution trace of the doublet structure of ${}^{r}R_{37}(37)$ transitions of $HNO_3$ in the $2\nu_9$ band.

The transitions listed in Table 1 were analyzed by a least-squares fit to an $A$-reduced Watsonian [11] up to the sextic centrifugal corrections. We have used the $I^r$ axis choice, which was found to work well for this molecule by Maki and Wells [6], although this choice is physically not sensible. The ground state constants were fixed at the values given in Ref. [6]. Since we have not observed any $K$-type doubling, the off-diagonal parameters, $A$-$B$, $\delta_J$, $\delta_K$, $\varphi_J$, $\varphi_{JK}$, and $\varphi_K$ were undeterminable from the present data. These off-diagonal centrifugal constants were assumed to be equal to those of the ground state. $A$-$B$ was fixed at a value roughly estimated from the constants for the ground state, the $v_9 = 2$ state, and the $v_5 = 1$ state, which is the interacting partner. The diagonal parameter $\Phi_K$ could not be determined for the excited states, so it was fixed at the value of the ground state. The obtained constants are listed in Table 2.

We have also assigned lines other than those listed in Table 1. However, they can not be fitted with a simple effective Hamiltonian, because their positions are shifted by the Fermi resonance through the $\Delta K_c = \pm 2$ selection rule. At the moment, this anomaly prohibits the extension of the assignments to low $K_c$ lines, which are of interest for determining the inertial asymmetry. We have tried to identify the Q-branch transitions in the spectra reported by Brockman et al. [3], but without success. The reasons for that are complex: (1) their measurement accuracy lacks the precision necessary to arrive at a unique identification of lines in the very densely populated spectrum; (2) the calculated spectrum suggests that many of the

Table 2. Molecular Constants for the $v_9 = 2$ state[a].

| Constant | Value | Unit |
|---|---|---|
| $G$[b] | 896.4519 (8) | $cm^{-1}$ |
| $C$ | 6241.39 (18) | MHz |
| $(A+B)/2$ | 12489.88 (67) | MHz |
| $A-B$ | 1039.55[c] | MHz |
| $\Delta_J$ | 7.86 (29) | kHz |
| $\Delta_{JK}$ | −28.7 (43) | kHz |
| $\Delta_K$ | 81.2 (82) | kHz |
| $\delta_J$ | 3.7853[c] | kHz |
| $\delta_K$ | 7.4766[c] | kHz |
| $\Phi_J$ | −0.28 (12) | Hz |
| $\Phi_{JK}$ | −14.4 (20) | Hz |
| $\Phi_{KJ}$ | 63.1 (72) | Hz |
| $\Phi_K$ | 0.11416[c] | Hz |
| $\varphi_J$ | 0.0[c] | Hz |
| $\varphi_{JK}$ | 0.0[c] | Hz |
| $\varphi_K$ | 0.052488[c] | Hz |
| $\sigma$[d] | 23.5 | MHz |

[a] Numbers in parentheses are one standard deviation.
[b] Vibrational energy. [c] Assummed value.
[d] Standard deviation of the fit.

Q-branch transitions cannot be resolved even by Doppler limited spectroscopy; (3) our predictions miss the low $K_c$ transitions, which seem to be intense in the Q branch. It is certainly necessary to measure a much wider wavenumber range to obtain an ultimate set of assignments and constants.

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