

## High-Resolution Tunable Spectroscopy of Rotational Transitions of NO Near $30\text{ cm}^{-1}$

F. C. VAN DEN HEUVEL, W. LEO MEERTS, AND A. DYMANUS

*Fysisch Laboratorium, Katholieke Universiteit, Toernooiveld, Nijmegen 6525 ED, The Netherlands*

The rotational spectrum of  $^{14}\text{N}^{16}\text{O}$  is studied in the far infrared. The monochromatic tunable far-infrared radiation is generated by mixing the radiation of an HCN laser with that of a tunable klystron. Five rotational transitions in both the  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  states are observed in the frequency region between 852 and 1053 GHz. The results are compared with the known RF, microwave, and IR data.

### 1. INTRODUCTION

Recently it was shown (1, 2) that it is possible to extend high-resolution spectroscopy towards the far infrared (FIR) by mixing the fixed frequency radiation of a submillimeter laser with that of a tunable klystron. The frequency of the generated radiation (laser sidebands) equals the sum or difference of the laser frequency and the klystron frequency. This radiation is tunable over the klystron range. We are now able to cover the spectral range from 780 to 1075 GHz ( $380\text{--}280\ \mu\text{m}$ ) using two lines (891 and 964 GHz) of an 8-m-long HCN laser and klystrons between 60 and 110 GHz. The absolute frequencies of five rotational transitions of NO in its ground vibrational electronic  $^2\Pi$  state are determined with an accuracy of  $3 \times 10^{-7}$ . The resolution was Doppler limited to 2 MHz.

The lowest rotational transitions in the ground vibrational state of NO were studied in the past by several investigators (3, 4, 5). Recently an accurate study of the microwave spectrum below 500 GHz has been carried out by Pickett *et al.* (6). The far-infrared spectra obtained in the present investigation are compared with this spectrum and with radiofrequency  $\Lambda$ -doubling (7) and IR vibrational spectra (8-11). In order to do so we carried out an overall fit of all these data. The present FIR results are consistent with the already existing data on NO.

### 2. EXPERIMENTAL DETAILS

The experimental setup, shown in Fig. 1, is essentially that of Bicanic *et al.* (1). Radiation from the laser and a klystron is propagated through two separate arms of a modified crossed waveguide harmonic mixer to a Schottky barrier GaAs crystal-whisker assembly. Sidebands generated in the diode are reradiated by the whisker and leave the mixer through the third arm. Either the sum- or the difference-frequency sideband is selected and separated from fundamental laser radiation in a monochromator containing a reflection grating. Finally the selected sideband passes through a 2-m light pipe absorption cell filled with NO gas. Video detection

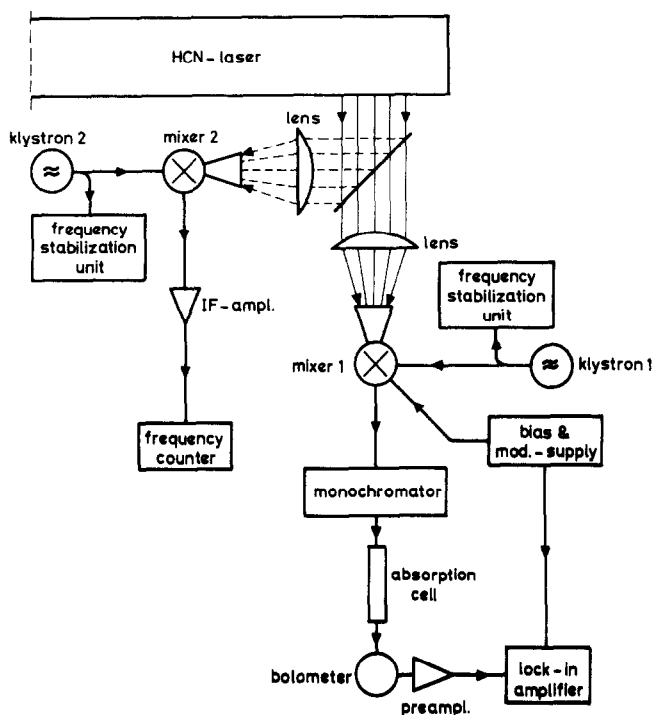


FIG. 1. Experimental setup with the sideband generator (mixer No. 1) and the laser frequency monitoring mixer (No. 2).

is applied with a helium-cooled bolometer. The sideband power at the input end of the monochromator is about  $0.1\text{--}1\ \mu\text{W}$  when a power of 50 and 150 mW enters the mixer from the laser and klystron, respectively. In an initial search for absorption lines the klystron was free-running and tuned mechanically and/or electrically. In precision measurements the klystron was phase-locked to a frequency standard.

Though the sidebands are highly monochromatic, there is an uncertainty in their absolute frequencies, because the free-running laser oscillates at an almost fixed but unknown frequency within its gain curve. This curve has a full width at half-height typically in the order of 2 and 3.5 MHz for the 964 and 891 GHz line, respectively. The uncertainty has been eliminated with the help of a second mixer that monitored the laser frequency during the measurements. A fraction of the laser beam traveling to the sideband generator is sent to this mixer, where the laser frequency beats with the 9th (891 GHz) or the 10th (964 GHz) harmonic of the frequency of a second phase-locked klystron operating at 99 or 96 GHz, respectively. A frequency counter monitors the amplified intermediate frequency (about 30 MHz) produced in the mixer. This technique has proven to be very effective for measuring the frequency of lasers in the entire far-infrared region (12, 13). The sideband frequency is known now with an accuracy of less than 50 kHz.

The transitions of NO were recorded with a signal-to-noise ratio of about 50 at a time constant of 1 sec and a cell pressure of 10 Pa. A typical recording is shown

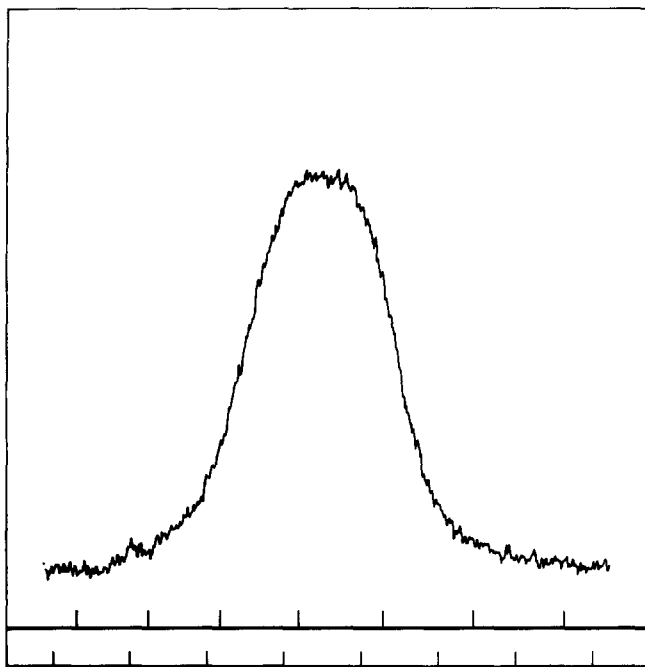


FIG. 2. Typical recording of a rotational transition  ${}^2\Pi_{1/2}$ ,  $J = 19/2 \leftarrow 17/2$  of NO at 952.464 GHz. Only one of the  $\Lambda$ -components is shown (+  $\leftarrow$  -). The frequency of the scanning klystron is represented by the upper set of markers (spacing 2 MHz), the frequency of the laser by the lower set (spacing 0.01 MHz).

in Fig. 2. The observed linewidths (FWHM) varied from 4 to 6 MHz, depending on the transition, and exceed the calculated Doppler widths (2–2.4 MHz). Broadening of the easily resolvable  $\Lambda$ -doubling components of the rotational transitions of NO is caused by the unresolved hyperfine structure. Since the hyperfine splittings are known from molecular beam electric resonance (MBER) work (7, 14) and the relative intensities can easily be calculated, this information was used to fit the observed lineshape to the calculated one assuming the same Doppler width for each hyperfine component. In Table I the frequencies of particular hyperfine line within each of the  $\Lambda$ -doubling components of a rotational transition are given.

### 3. THEORY

The basic Hamiltonian for the spin-orbit, rotational and  $\Lambda$ -doubling contributions has been described in the classical papers of Hill (15) and Van Vleck (16) and of Mulliken and Christy (17). It has been shown in many investigations that an effective Hamiltonian for a  ${}^2\Pi$  state can be constructed by applying a Van Vleck transformation to the  ${}^2\Pi$ ,  ${}^2\Sigma^s$  manifold of states in order to reduce the Hamilton matrix to two  $2 \times 2$   ${}^2\Pi$  blocks each with different parity.

As basis set we use the symmetrized Hund's case (a) wavefunctions (18)  $\{|{}^2\Pi_{1/2}^{\pm}J\rangle, |{}^2\Pi_{3/2}^{\pm}J\rangle\}$ . The effective Hamiltonian including the lowest-order cen-

TABLE I

Observed Rotational Transitions of <sup>14</sup>N<sup>16</sup>O in Its Ground Vibrational and Electronic States

$\Omega$	$J+1 \leftarrow J$	$F+1 \leftarrow F$	parity change	frequency <sup>a</sup>	obs.-calc. (MHz)	laser line (GHz)
1/2	17/2 $\leftarrow$ 15/2	15/2 $\leftarrow$ 13/2	+ $\leftarrow$ -	851 913.54	0.40	964
		15/2 $\leftarrow$ 13/2	- $\leftarrow$ +	852 239.91	0.47	964
1/2	19/2 $\leftarrow$ 17/2	17/2 $\leftarrow$ 15/2	- $\leftarrow$ +	952 145.08	-0.05	891
		17/2 $\leftarrow$ 15/2	+ $\leftarrow$ -	952 464.10	0.02	891
1/2	21/2 $\leftarrow$ 19/2	21/2 $\leftarrow$ 19/2	+ $\leftarrow$ -	1052 369.91	0.23	964
		19/2 $\leftarrow$ 17/2	- $\leftarrow$ +	1052 680.83	0.10	964
3/2	17/2 $\leftarrow$ 15/2	17/2 $\leftarrow$ 15/2	+ $\leftarrow$ -	875 930.36	0.00	964
		17/2 $\leftarrow$ 15/2	- $\leftarrow$ +	875 961.25	0.11	964
3/2	19/2 $\leftarrow$ 17/2	19/2 $\leftarrow$ 17/2	- $\leftarrow$ +	978 770.21	-0.07	891
		19/2 $\leftarrow$ 17/2	+ $\leftarrow$ -	978 808.04	-0.24	891

<sup>a</sup> The experimental accuracy is 0.3 MHz, except for both  ${}^2\Pi_{1/2}$ ,  $J = 17/2 \leftarrow 15/2$  transitions (1 MHz).

trifugal distortion and spin-rotation effects (19) can be written as

$$\begin{aligned}
 (\mathcal{H}) = & A \begin{bmatrix} -1/2 & 0 \\ 0 & 1/2 \end{bmatrix} + \frac{1}{2} A_D \begin{bmatrix} -(X+2) & 0 \\ 0 & (X-1) \end{bmatrix} \\
 & + \gamma \begin{bmatrix} 0 & -(1/2)X^{1/2} \\ -(1/2)X^{1/2} & 0 \end{bmatrix} + B \begin{bmatrix} (X+1) & X^{1/2} \\ X^{1/2} & (X-1) \end{bmatrix} \\
 & - D \begin{bmatrix} (X+1)^2 + X & 2XX^{1/2} \\ 2XX^{1/2} & (X-1)^2 + X \end{bmatrix} \pm (-1)^{J-1/2} \left( J + \frac{1}{2} \right) \begin{bmatrix} ((1/2)p+q) & qX^{1/2} \\ qX^{1/2} & 0 \end{bmatrix} \\
 & + \begin{bmatrix} (1/2)q^*(X+2) + (1/2)p^* + o & (1/2)(1/2p^* + q^*)X^{1/2} \\ (1/2)((1/2)p^* + q^*)X^{1/2} & (1/2)q^*X \end{bmatrix}, \quad (1)
 \end{aligned}$$

where  $X = (J + 1/2)^2 - 1$ . The various contributions in this order stand for the spin-orbit ( $A$ ), the centrifugal distortion in the spin-orbit coupling ( $A_D$ ), the spin-rotation effect ( $\gamma$ ), the rotational energy ( $B$ ), the first-order centrifugal distortion effect on the rotational energy ( $D$ ), the  $\Lambda$ -splittings contributions ( $p, q$ ), and the parity-independent contributions ( $p^*, q^*, o$ ) originating from the same interaction that produces the  $\Lambda$ -splitting. The constants  $A, A_D, \gamma, B$ , and  $D$  are defined as in the work of Zare *et al.* (19), while  $p, q, p^*, q^*$ , and  $o$  have been taken from the paper of Mulliken and Christy (17). As a consequence of the high correlations (20, 21) between the molecular constants from the Hamiltonian (1) an independent determination of all the molecular constants is not possible. Especially

$A_D$  and  $\gamma$  are nearly totally correlated. The Hamiltonian (1) can be transformed into an effective Hamiltonian in which the correlations are removed

$$\begin{aligned}
 (\mathcal{H}) = & A_{\text{eff}} \begin{bmatrix} -1/2 & 0 \\ 0 & 1/2 \end{bmatrix} + \frac{1}{2} A_{D_{\text{eff}}} \begin{bmatrix} -(X+2) & 0 \\ 0 & (X-1) \end{bmatrix} \\
 & + B_{\text{eff}} \begin{bmatrix} (X+1) & X^{1/2} \\ X^{1/2} & (X-1) \end{bmatrix} - D \begin{bmatrix} (X+1)^2 + X & 2XX^{1/2} \\ 2XX^{1/2} & (X-1)^2 + X \end{bmatrix} \\
 & \pm (-1)^{J-1/2}(J+1/2) \begin{bmatrix} ((1/2)p+q) & qX^{1/2} \\ qX^{1/2} & 0 \end{bmatrix}, \quad (2)
 \end{aligned}$$

where

$$\begin{aligned}
 A_{\text{eff}} &= A - \frac{1}{2} p^* - o, \\
 A_{D_{\text{eff}}} &= A_D - \frac{2B}{A-2B} \left( \gamma - \frac{1}{2} p^* \right), \\
 B_{\text{eff}} &= B + \frac{1}{2} q^*. \quad (3)
 \end{aligned}$$

The relation for  $A_{D_{\text{eff}}}$  is an approximation valid for  $|A/B| \gg 1$ . Higher-order centrifugal distortion effects are not relevant for the present study while higher-order  $\Lambda$ -doubling contributions can be treated in a phenomenological way (18, 22).

The choice of the effective Hamiltonian (2) is only one of the various possibilities that all lead to an equivalent power series expansion in the rotational quantum number  $J$ , however, with different effective parameters. Several of these possibilities have been used recently (9-11, 23, 24) in the analysis of the rotation-vibration spectrum of NO. The effective constants used in the present work are identical to those of Dale *et al.* (23), Henry *et al.* (9) and Hallin *et al.* (11). Both Amiot *et al.* (10) and Pine *et al.* (24) use slightly different definitions. Comparison

TABLE II  
Effective Molecular Constants as Determined for NO in Various Investigations

	Present work <sup>a</sup>	Amiot <i>et al.</i> (10) <sup>b</sup>	Pine <i>et al.</i> (24) <sup>c</sup>
$A_{\text{eff}}$	$A - \frac{1}{2} p^* - o$	$A - \frac{1}{2} p^* - o - \frac{1}{2} p$	$A - \frac{1}{2} p^* - o - \frac{1}{2} p - [A_D - \frac{2B}{A-2B} (\gamma - \frac{1}{2} p^* - \frac{1}{2} p)]$
$A_{D_{\text{eff}}}$	$A_D - \frac{2B}{A-2B} (\gamma - \frac{1}{2} p^*)$	$\frac{1}{2} [A_D - \frac{2B}{A-2B} (\gamma - \frac{1}{2} p^* - \frac{1}{2} p)]$	$A_D - \frac{2B}{A-2B} (\gamma - \frac{1}{2} p^* - \frac{1}{2} p)$
$B_{\text{eff}}$	$B + \frac{1}{2} q^*$	$B + \frac{1}{2} q^* + \frac{1}{2} q$	$B + 2D + \frac{1}{2} q^* + \frac{1}{2} q$

<sup>a</sup> Same convention is used in ref. (9, 11, 23).

<sup>b</sup> Amiot *et al.* (10) use for  $A_{D_{\text{eff}}}$  the symbol  $A_{J(\text{eff})}$ .

<sup>c</sup> Pine *et al.* (24) have chosen to define the parameter  $o$  with an opposite sign.

of the results from the last two cited papers with those of the first group can be made with the help of Table II, where we express the effective constants in the basic molecular parameters from Eq. (1). Recently Young *et al.* (25) used a slightly different type of effective Hamiltonian. It is not possible to derive analytical relations similar to those of Table II between our effective constants and those of Young *et al.* since their energy expressions cannot be transformed to those of Eq. (2).

#### 4. RESULTS

Recently two independent high-resolution IR spectroscopic studies of the (0-1) band were made by Amiot *et al.* (10) and Valentin *et al.* (8). We started with a fit of the data of Amiot *et al.* The microwave and FIR transitions predicted from this fit agree within the accuracy of the prediction with the observed line frequencies of the present work, of those of Refs. (4, 5), and of Pickett *et al.* (6). The latter authors recently performed very accurate measurements (0.02-0.05 MHz) of the rotational transitions  $J = 5/2 \leftarrow 3/2$ ,  $7/2 \leftarrow 5/2$ , and  $9/2 \leftarrow 7/2$  for both the  ${}^2\Pi_{1/2}$  and  ${}^2\Pi_{3/2}$  substates and the  $3/2 \leftarrow 1/2$  transitions for the  ${}^2\Pi_{1/2}$  substate. If also these transitions are included in a combined fit with the data of Amiot *et al.* the constants obtained by Amiot *et al.* do not change but only the accuracy of many of them is improved.

We repeated the fit procedure starting with the data of Valentin *et al.* The microwave and far-infrared transitions predicted only from a fit of the IR data deviated from the experimental microwave and FIR frequencies outside the accuracy of the prediction. Furthermore, the best fit constants changed to values outside their error limits in a combined fit of Valentin's IR, all the available microwave data, and the results of the present investigation. In conclusion we feel that the data of Amiot *et al.* provide a slightly better overall consistency with the microwave and FIR spectra.

In a final least-squares fit we combined the 347 (0-1) IR transitions (Amiot *et al.*), the FIR transitions from the present work and the microwave transitions from Refs. (4-6) with the hyperfine  $\Lambda$ -doubling transitions from an MBER study (7, 14). The latter transitions determine mainly the  $\Lambda$ -doubling parameters  $p$  and  $q$ , as well as the hyperfine structure which we do not discuss here. The results of the calculations are presented in Table III. The overall fit is excellent. The combination of the MBER, microwave, FIR, and IR data improves considerably the accuracy of the rotational and the  $\Lambda$ -doubling constants. It should be noted here that the uncertainties in the constants  $B_{\text{eff}}$ ,  $D$ , and  $A_{D_{\text{eff}}}$  for the ground vibrational state are mainly determined by the microwave data of Pickett *et al.* (6). The differences between the predicted spectrum for the best fit constants and the present experimental frequencies are listed in Table I, demonstrating an excellent consistency between the present FIR and the microwave data of Ref. (6).

We have also tried to include the second-order centrifugal distortion effects described by the constant  $H$  (see, e.g., (19)). This gave no significant improvement of the fit, while only an upper limit ( $|H| < 2 \times 10^{-2}$  Hz) for  $H$  could be obtained.

TABLE III

Best-Fit Constants from a Fit of the IR Data (10) only, and of the IR, Microwave, FIR, and MBER Data

Quantity <sup>a</sup>	IR-data <sup>b</sup>	IR+MW+MBER-data <sup>c</sup>
$A_{eff\ 0}$	3 691.626(5)	3 691.619(3)
$A_{D\ eff\ 0}$	5.46(2)	5.496(2)
$B_{eff\ 0}$	50 847.7(1)	50 847.801(1)
$D_0$	0.1641(2)	0.16416(3)
$p_0$	350.8(3)	350.3750(2)
$q_0$	2.82(2)	2.8373(1)
$A_{eff\ 1}$	3 684.295(5)	3 684.290(4)
$A_{D\ eff\ 1}$	5.20(2)	5.230(8)
$B_{eff\ 1}$	50 321.0(1)	50 321.03(1)
$D_1$	0.1646(2)	0.16463(3)
$p_1$	348.9(3)	348.6(2)
$q_1$	2.81(2)	2.827(8)
No. lines	347	482
$\sigma$ <sup>d</sup>	0.63	0.75

<sup>a</sup> All constants are in units of MHz, except A, which is given in GHz.

<sup>b</sup> After the transformation given in Table II the set of constants becomes the same as obtained by Amiot *et al.* (10).

<sup>c</sup> IR ref. (10), FIR (present work), microwave ref. (4,5,6), MBER ref. (7,14). The centrifugal distortion corrections in  $p_0$  and  $q_0$  were also taken into account (18):  $D_{p_0} = 91(2)$  Hz and  $D_{q_0} = 21(2)$  Hz.

<sup>d</sup>  $\sigma = \sqrt{\chi^2/(n-m)}$ , n number of lines, m number of parameters determined in the fit.

We conclude that the technique of sideband generation in combination with a continuous monitoring of the laser frequency is well suited for Doppler-limited high-resolution spectroscopy around  $30\text{ cm}^{-1}$ .

#### ACKNOWLEDGMENTS

The authors like to thank Dr. H. M. Pickett for communicating to us the results of his experiment prior to publication and Messrs. F. A. van Rijn and E. G. H. van Leeuwen for technical assistance.

RECEIVED: December 7, 1979

## REFERENCES

1. D. D. BICANIC, B. F. J. ZUIDBERG, AND A. DYMANUS, *Appl. Phys. Lett.* **32**, 367–369 (1978).
2. D. D. BICANIC, Ph.D. thesis, Katholieke Universiteit, Nijmegen, The Netherlands, 1978.
3. J. J. GALLAGHER AND C. M. JOHNSON, *Phys. Rev.* **103**, 1727–1737 (1956).
4. C. A. BURRUS AND J. D. GRAYBEAL, *Phys. Rev.* **109**, 1553–1556 (1958).
5. P. G. FAVERO, A. M. MIRRI, AND W. GORDY, *Phys. Rev.* **114**, 1534–1537 (1959).
6. H. M. PICKETT, E. A. COHEN, J. W. WATERS, AND T. G. PHILLIPS, 34th Symposium on Molecular Spectroscopy, Columbus, Ohio (1979); private communication.
7. W. L. MEERTS AND A. DYMANUS, *J. Mol. Spectrosc.* **44**, 320–346 (1972).
8. A. VALENTIN, A. HENRY, PH. CARDINET, M. F. LEMOAL, DA-WUN CHEN, AND K. NARAHARI RAO, *J. Mol. Spectrosc.* **70**, 9–17 (1978).
9. A. HENRY, M. F. LEMOAL, PH. CARDINET, A. VALENTIN, *J. Mol. Spectrosc.* **70**, 18–26 (1978).
10. C. AMIOT, R. BACIS, AND G. GUELACHVILI, *Canad. J. Phys.* **56**, 251–265 (1978).
11. K-E. HALLIN, J. W. C. JOHNS, D. W. LEPARD, A. W. MANTZ, D. L. WALL, AND K. NARAHARI RAO, *J. Mol. Spectrosc.* **74**, 26–42 (1979).
12. B. F. J. ZUIDBERG AND A. DYMANUS, *Appl. Phys. Lett.* **29**, 643–645 (1976).
13. V. J. CORCORAN, J. J. GALLAGHER, AND R. E. CUPP, *Opt. Spectra* **4**, 46–51 (1970).
14. W. L. MEERTS, *Chem. Phys.* **14**, 421–425 (1976).
15. E. HILL, J. H. VAN VLECK, *Phys. Rev.* **32**, 250–272 (1928).
16. J. H. VAN VLECK, *Phys. Rev.* **33**, 467–506 (1929).
17. R. S. MULLIKEN AND A. CHRISTY, *Phys. Rev.* **38**, 87–119 (1931).
18. W. L. MEERTS, J. P. BEKOORY, AND A. DYMANUS, *Mol. Phys.* **37**, 425–439 (1979).
19. R. N. ZARE, A. L. SCHMELTEKOPF, W. J. HARROP, AND D. L. ALBRITTON, *J. Mol. Spectrosc.* **46**, 37–66 (1973).
20. J. A. COXON, *J. Mol. Spectrosc.* **58**, 1–28 (1975).
21. D. L. ALBRITTON, W. J. HARROP, A. L. SCHMELTEKOPF, R. N. ZARE, AND E. L. CROW, *J. Mol. Spectrosc.* **46**, 67–88 (1973).
22. W. L. MEERTS, *Chem. Phys. Lett.* **46**, 24–28 (1977).
23. R. M. DALE, J. W. C. JOHNS, A. R. W. MCKELLAR, M. RIGGIN, *J. Mol. Spectrosc.* **67**, 440–458 (1977).
24. A. S. PINE, J. W. C. JOHNS, AND A. G. ROBIETTE, *J. Mol. Spectrosc.* **74**, 52–69 (1979).
25. L. D. G. YOUNG, A. T. YOUNG, S. A. CLOUGH, AND F. X. KNEIZYS, *J. Quant. Radiat. Transfer* **20**, 317–325 (1978).