# The Laser Magnetic Resonance Spectrum of the NCO Radical at 5.2 $\mu$ m

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### AND

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Lines in the  $\nu_3$  ("antisymmetric" stretch) fundamental of the NCO radical in the  $\tilde{X}^2\Pi$  state were studied by CO laser magnetic resonance. The observations were assigned to *P* and *R* lines in the vibration-rotation band and lead to a precise determination of the vibrational interval and the anharmonic correction to the rotational constant:  $\nu_3 = 1920.60645(19) \text{ cm}^{-1}$ ,  $\alpha_3 = 0.003338(21) \text{ cm}^{-1}$ . A single transition in the hot band (011)-(010),  ${}^{2}\Delta_{3/2}{}^{-2}\Delta_{3/2}$  was detected. This observation is used to determine the origin of the hot band as 1907.11892(20) cm<sup>-1</sup>, i.e., the anharmonicity parameter  $x_{23} = -13.48753(28) \text{ cm}^{-1}$ .

#### I. INTRODUCTION

Considerable interest has been shown recently in the theoretical description of the Renner-Teller effect (1, 2), much of it prompted by experimental studies of triatomic molecules in open shell states. The linear free radical NCO in its ground  $^{2}\Pi$  state has been particularly important in this respect. The first extensive study of the molecule in the gas phase was made by Dixon, who analyzed the electronic transitions  $\tilde{A}^2 \Sigma^+ - \tilde{X}^2 \Pi$  (3) and  $\tilde{B}^2 \Pi - \tilde{X}^2 \Pi$  (4), recorded in absorption by flash photolysis. A few years later, Carrington et al. (5) observed the EPR spectrum of NCO in three low-lying vibronic states. The observation of lines in the microwave spectrum followed soon after (6, 7), giving a precise determination of the rotational constant of NCO in the ground and (010) levels. The  $\tilde{A}^2 \Sigma^+ - \tilde{X}^2 \Pi$  electronic band system was reinvestigated at higher resolution by Bolman et al. (8) with the primary motive of determining the size of the Renner-Teller interaction more reliably. Taken together, these studies have provided much information on the ground and first two excited states of the NCO radical. Detailed studies have been made of the molecule in the levels (000) and (010) (6-8), leading to a determination of the bending frequency  $v_2$  as 535.4 cm<sup>-1</sup>, among other things. However, there has not vet been a gas phase determination of the two stretching frequencies,  $\nu_1$  and  $\nu_3$ .

The NCO radical has been studied in the solid state by Milligan and Jacox (9)

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using matrix isolation techniques. Both infrared and ultraviolet spectra were recorded, the former providing values for  $\nu_1$  and  $\nu_3$  for the ground <sup>2</sup> $\Pi$  state. A later study of the laser-induced fluorescence spectrum of NCO in a matrix by Bondybey and English (10) has confirmed these values. Milligan and Jacox were able to study the spectra of NCO suspended in a variety of matrix materials. The ultraviolet spectrum obtained with the photolysis of an Ar:HNCO system agreed best with the gas phase spectrum (3, 4) and was therefore used to determine the vibrational intervals. A single line at 1275 cm<sup>-1</sup> was assigned to  $\nu_1$  and a doublet at 1918 and 1925 cm<sup>-1</sup> was assigned to  $\nu_3$ , an intermediate value of 1922 cm<sup>-1</sup> being used by Milligan and Jacox in their force field calculations. Bondybey and English obtained a value of 1923 cm<sup>-1</sup> for  $\nu_3$  from their fluorescence study of NCO in an Ar matrix. An interesting result from the force field calculation (9) is that the vibrations  $v_1$ and  $\nu_3$  are better described as "symmetric" and "antisymmetric" stretching vibrations, respectively (rather than say CO and CN stretches), even though NCO does not have a center of symmetry. The practice of numbering the vibrations of a linear molecule ABC by analogy with those of a symmetric  $AB_2$  molecule is well justified in this case.

The matrix isolation studies show that the  $\nu_3$  band of NCO falls within the frequency range covered by a carbon monoxide laser. Vibration-rotation transitions should therefore be detectable by the technique of Laser Magnetic Resonance (LMR), in which the molecular transition is tuned into coincidence with the laser frequency by application of a variable magnetic field (11). In this paper, we report the observation of such transitions. The spectrum is analyzed and used to determine the major parameters for NCO in the (001) vibrational level.

### **II. EXPERIMENTAL DETAILS**

The CO laser magnetic resonance spectrometer used in this work has been described in detail elsewhere (12). The beam from an Edinburgh Instruments CO laser (Model PL3) was passed through an absorption cell situated in the gap of a Varian 15-in. electromagnet and focused onto a gold-doped germanium detector. The laser output power was typically 1 W at 5.2  $\mu$ m. The magnetic field was modulated at a frequency of about 25 kHz with a pair of Helmholtz coils and the signal at this frequency was detected by a conventional lock-in amplifier system. The electric vector of the laser radiation was polarized perpendicular to the external magnetic field and the observed transitions obeyed the selection rules  $\Delta M_{L} = \pm 1$ .

Previous studies of the EPR spectrum of NCO (5) have shown that hydrogen abstraction from isocyanic acid (HNCO) is a reliable method of producing detectable quantities of NCO. In the present work, we mixed the products of a microwave discharge through flowing CF<sub>4</sub> with HNCO vapor in the cell at a total pressure of about 1/2 Torr. The isocyanic acid was prepared by a method similar to that described by Carrington *et al.* (5). A concentrated solution of potassium cyanate (KCNO) was added slowly to orthophosphoric acid in an evacuated flask. The resultant HNCO vapor was passed through two traps at about  $-40^{\circ}$ C (cooled in a diethyl ketone slush bath) to remove water and other condensible impurities and the product was collected in a third trap cooled by liquid nitrogen. Gaseous

| Laser Line<br>(cm <sup>-1</sup> ) | Transition | м <sub>ј</sub> ' + | • М <sub>Ј</sub> | Resonant Field<br>(Gauss) | Tuning Rate at<br>Resonant Field<br>(MHz/G) | "First Order"<br>Tuning Rate<br>(MHz/G) |
|-----------------------------------|------------|--------------------|------------------|---------------------------|---|---|
| 1018 5802                         | D/E (2)    | 2/0                | 1 /0             | 1550 6                    |   |   |
| 1910.3002<br>D(22) A              | P(5/2)     | -3/2               | -1/2             | 1558.6                    | -1,488                                      | -1.44                                   |
| r(23)5                            |            | -1/2               | 1/2              | 2645.7                    | -0.928                                      | -0.80                                   |
|                                   |            | -3/2               | -5/2             | 4/65.9                    | -0,49/                                      | -0.48                                   |
|                                   |            | 1/2                | 3/2              | 7098.0                    | -0.491                                      | -0.16                                   |
| 1918.6773                         | P(5/2)     | 3/2                | 1/2              | 411.0                     | 1,427                                       | 1.44                                    |
| P(13),b                           |            | 1/2                | -1/2             | 781.0                     | 0.769                                       | 0.80                                    |
|                                   |            | 3/2                | 5/2              | 1339.0                    | 0.452                                       | 0.48                                    |
| 1918.9788<br>P(17)6 <sup>a</sup>  | P(5/2)     | 3/2                | 1/2              | 7410.4                    | 1.148                                       | 1.44                                    |
| 1922.5564                         | R(3/2)     | -1/2               | -3/2             | 750.0                     | 1 464                                       | 1 44                                    |
| P(12)_b                           |            | 1/2                | -1/2             | 1330.0                    | 0.867                                       | 0.80                                    |
| /5                                |            | -5/2               | -3/2             | 2363.0                    | 0,007                                       | 0.00                                    |
|                                   |            | 3/2                | 1/2              | 4304.0                    | 0.353                                       | 0.16                                    |
| 1922.9829                         | R(3/2)     | -1/2               | -3/2             | 8908.3                    | 1.649                                       | 1.44                                    |
| P(22) <sub>5</sub> a              |            | 1/2                | -1/2             | 12794.2                   | 1.342                                       | 0.80                                    |
|                                   | R(5/2)     | 3/2                | 5/2              | 13682 2                   | -0 440                                      | -0.80                                   |
|                                   |            | 1/2                | 3/2              | 15451.7                   | -0,579                                      | -0.59                                   |
| 1923.1536<br>P(16).a              | R(3/2)     | -1/2               | -3/2             | 11970.0                   | 1.687                                       | 1.44                                    |
|                                   | R(5/2)     | 3/2                | 5/2              | 4753.7                    | -0.692                                      | -0.80                                   |
|                                   | -          | 1/2                | 3/2              | 6253.9                    | -0.552                                      | -0.59                                   |
|                                   |            | -1/2               | 1/2              | 9424.1                    | -0.379                                      | -0.37                                   |

| 0 | bserved | Resonances | in | the va | Fundamental of | ſ N | <b>JC</b> | Э |
|---|---------|------------|----|--------|----------------|-----|-----------|---|
|---|---------|------------|----|--------|----------------|-----|-----------|---|

 $^{\rm a}$  12  $_{\rm C}{}^{\rm 16}{}_{\rm 0}$  laser transitions. The subscript refers to the lower vibrational level of the laser transition.

<sup>b</sup> 12c<sup>18</sup>0 laser transitions.

impurities such as NH<sub>3</sub> or CO<sub>2</sub> were removed by pumping the contents of the third trap when warmed to about  $-70^{\circ}$ C; at this temperature, HNCO is a liquid but has a low vapor pressure. The product was used without further purification.

The magnetic flux densities at which resonances were observed were measured with a Bruker proton resonance magnetometer, model B-NM 20. The laser frequencies were calculated from the Dunham coefficients derived by Dale *et al.* (13). The major uncertainty in our measurements was caused by a lack of precise knowledge of these frequencies, since the laser was not locked to the center of the carbon monoxide gain profile. The longitudinal mode spacing of the laser is 80 MHz which sets a maximum to the frequency error of 40 MHz. By averaging several independent observations, we believe that the error has been reduced to less than 30 MHz.

The laser lines were loosely assigned by use of a small monochromator (Optical Engineering Model 16-C(CO)). A better assignment was made by reference to the behavior of the lines in the spectrum on variation of the laser operating conditions (discharge current, plasma coolant temperature, etc.), taking due account of pos-



FIG. 1. The LMR spectrum associated with the P(5/2) transition of the  $\nu_3$  fundamental of the NCO radical, observed with two separate laser lines. The  $M_J$  assignments are given below each transition.





sible interference by atmospheric water vapor lines. The  $P(16)_6$  line at 1923.15 cm<sup>-1</sup>, for example, was significantly reduced in intensity relative to the  $P(22)_5$  line at 1922.98 cm<sup>-1</sup> by water vapor absorption. The final, unambiguous assignment of the laser lines was made to satisfy the requirement of a consistent analysis of the lines in the NCO spectrum.

### **III. RESULTS**

Several magnetic resonance absorption lines have been observed in the region 1918–1923 cm<sup>-1</sup> of the CO laser and have been assigned to the  $\nu_3$  fundamental of the NCO radical. The measurements (and assignments) are given in Table I. The



FIG. 3. The energy levels involved in the R(5/2) LMR spectrum of NCO plotted as a function of magnetic flux density. The arrows indicate observed transitions. The three lower field lines are associated with one laser line and the two high field lines with another (see Fig. 2). The nonlinearity in the Zeeman effect can be clearly seen at higher magnetic fields.



FIG. 4. The LMR spectrum associated with the Q(5/2) transition of the (011)-(010),  ${}^{2}\Delta_{5/2}-{}^{2}\Delta_{5/2}$  hot band of the NCO radical, observed at a laser frequency of 1906.8558 cm<sup>-1</sup>. The three Lamb dips on each line arise from <sup>14</sup>N hyperfine structure.

spectra are shown in Figs. 1 and 2; a typical signal-to-noise ratio for the strongest lines was 100 to 1 with a 1-sec output time constant. The observed lines can be assigned to the P(5/2), R(3/2), and R(5/2) transitions of the molecule in the  ${}^{2}\Pi_{3/2}$  spin component. For a molecule in a  ${}^{2}\Pi$  state, low-J Q-branch transitions are the most favorable for detection with perpendicular polarization as used in this work. Unfortunately we have been unable to observe any Q-branch transitions since this is a relatively sparse region for CO laser lines. Our analysis shows that there are no suitable lines from a  ${}^{12}C^{16}O$  laser for the detection of Q-branch lines in NCO by LMR.

Following the observation and assignment of the lines in the  $\nu_3$  fundamental, we searched for transitions in the hot band (011)  $\leftarrow$  (010). The origin of this band is expected to lie about 16 cm<sup>-1</sup> below that of the fundamental (10) but despite extensive searches in this region, we were unable to detect any other signals. This failure was a little disappointing since Carrington *et al.* (5) observed EPR signals from NCO in the (010)  ${}^{2}\Delta_{5/2}$  vibronic state with an intensity close to one-thirteenth

of the ground-state signals, as expected for a Boltzmann equilibrium distribution at 300 K. On this basis, the signal-to-noise ratio of our observations should have been good enough to allow us to detect the stronger  ${}^{2}\Delta_{5/2} \leftarrow {}^{2}\Delta_{5/2}$  transitions. Since it seemed unlikely that the vibrational transition moment was markedly different for the hot band, we could only conclude that there were no satisfactory coincidences between the strongest lines in this band and the  ${}^{12}C{}^{16}O$  laser frequencies.

A search was therefore made by one of us (T.J.S.) using the LMR spectrometer at the National Research Council of Canada, Ottawa, with isotopically substituted CO. A spectrum was observed with the  $P(16)_5$  line of  ${}^{12}C{}^{18}O$  at 1906.8558 cm<sup>-1</sup>; it is reproduced in Fig. 4. The relative positions and intensities of the five main lines suggest immediately that it is the Q(5/2) line. The identity of the vibrational transition as  $(011) \leftarrow (010)$  is confirmed by the frequency of the observation. Despite using all the available isotopic modifications of CO, we were unable to detect any other lines in the  ${}^{2}\Delta_{5/2}{}^{-2}\Delta_{5/2}$  hot band. Weaker, rather indeterminate lines were observed with  ${}^{12}C{}^{18}O$  laser lines at 1905.6496 and 1898.0493 cm<sup>-1</sup>; these have not so far been assigned. Additional spectra for the P(5/2) and R(3/2) rotational transitions of the fundamental band were observed with the  ${}^{12}C{}^{18}O$  laser lines at 1918.6773 and 1922.5564 cm<sup>-1</sup>, respectively. The results for the fundamental band are listed in Table I and those for the hot band in Table IV.

There are several other transitions in addition to the  $(011) \leftarrow (010)$  hot band that fall within the region covered by the CO laser and may be detectable by the

|                |  | _  |  |  |  |
|----------------|--|--|--|--|--|
| J <sup>"</sup> | м <sub>ј</sub> '   | м_"  | Field (G)  | Frequency (cm <sup>-1</sup> )                        | obs-calc (cm <sup>-1</sup> )   |
| 5/2            | -3/2   | -1/2   | 1558.6   | 1918,5802  | $-0.49 \times 10^{-3}$   |
| 5/2            | -1/2   | 1/2  | 2645.7   |  | -0.14  |
| 5/2            | -3/2   | -5/2   | 4765.9   |  | +0.10  |
| 5/2            | 1/2  | 3/2  | 7098.0   |  | -0.06  |
| 5/2            | 3/2  | 1/2  | 411.0  | 1918.6773  | +0.79  |
| 5/2            | 1/2  | -1/2   | 781.0  |  | -0.06  |
| 5/2            | 3/2  | 5/2  | 1339.0   |  | -0.04  |
| 5/2            | 3/2  | 1/2  | 7410.4   | 1918,9788  | -0.15  |
| 3/2            | -1/2   | -3/2   | 750.0  | 1922,5564  | +0.43  |
| 3/2            | 1/2  | -1/2   | 1330.0   |  | -0.33  |
| 3/2            | -5/2   | -3/2   | 2343.0   |  | -0.32  |
| 3/2            | 3/2  | 1/2  | 4304.0   |  | -0.38  |
| 3/2            | -1/2   | -3/2   | 8908.3   | 1922.9829  | +0.54  |
| 3/2            | 1/2  | -1/2   | 12794.2  |  | -0.63  |
| 5/2            | 3/2  | 5/2  | 13682.2  |  | -0.59  |
| 5/2            | 1/2  | 3/2  | 15451.7  |  | +0.09  |
| 3/2            | -1/2   | -3/2   | 11970.0  | 1923.1536  | +0.78  |
| 5/2            | 3/2  | 5/2  | 4753.7   |  | +0.23  |
| 5/2            | 1/2  | 3/2  | 6253.9   |  | -0.00  |
| 5/2            | -1/2   | 1/2  | 9424.1   |  | +0.24  |
| 3/2            | 3/2  | 1/2  | 7921.61  | 0.30921  | 0.02   |
| 3/2            | 1/2  | -1/2   | 8374.35  |  | 0.00   |
| 3/2            | -1/2   | -3/2   | 8801.45  |  | -0.02  |
|                |  |  |  |  |  |
|                | J"<br>5/2<br>5/2<br>5/2<br>5/2<br>5/2<br>5/2<br>5/2<br>5/2<br>3/2<br>3/2<br>3/2<br>3/2<br>3/2<br>3/2<br>3/2<br>3/2<br>3/2<br>3 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | $J'' M_J' M_J'' Field (G) Frequency (cm-1)$ $5/2 -3/2 -1/2 1/2 2645.7$ $5/2 -1/2 1/2 2645.7$ $5/2 -3/2 -5/2 4765.9$ $5/2 1/2 3/2 7098.0$ $5/2 3/2 1/2 411.0 1918.6773$ $5/2 1/2 -1/2 781.0$ $5/2 3/2 5/2 1339.0$ $5/2 3/2 1/2 7410.4 1918.9788$ $3/2 -1/2 -3/2 750.0 1922.5564$ $3/2 1/2 -1/2 1330.0$ $3/2 -5/2 -3/2 2343.0$ $3/2 -1/2 -3/2 8908.3 1922.9829$ $3/2 -1/2 -3/2 13682.2$ $5/2 3/2 5/2 13682.2$ $5/2 3/2 5/2 4753.7$ $5/2 -1/2 -3/2 11970.0 1923.1536$ $5/2 3/2 5/2 4753.7$ $5/2 -1/2 -3/2 8904.3$ $3/2 -1/2 -3/2 11970.0 1923.1536$ $5/2 3/2 5/2 4753.7$ $5/2 -1/2 1/2 9424.1$ $3/2 3/2 1/2 -1/2 8374.35$ $3/2 -1/2 -3/2 8801.45$ |

TABLE II

Least-Squares Fit of NCO Magnetic Resonance Data<sup>a</sup>

<sup>a</sup> All infra-red data given an absolute weight of  $1 \times 10^6 \text{ cm}^2$ . EPR data given an absolute weight of  $9 \times 10^8 \text{ cm}^2$ . LMR technique. For example, the overtone band  $(040) \leftarrow (000)$  falls between 1900 and 1950 cm<sup>-1</sup> while the combination band (110)  $\leftarrow$  (000) is expected to occur at about 1820 cm<sup>-1</sup>. We have not yet searched for either of these transitions.

### IV. ANALYSIS AND DISCUSSION

The rotational transitions associated with the various sets of magnetic resonance lines can be assigned simply on the basis of the Zeeman patterns. On the assumption that the molecule is in a  ${}^{2}\Pi$  state, the relative positions and intensities of the Zeeman components of a particular rotational transition are quite characteristic of that transition, even if only part of the Zeeman pattern is within range of the spectrometer. Many examples of the various patterns that arise have been observed in the 5.3- $\mu$ m LMR spectrum of NO (14).

This method of assignment proved successful even though the Zeeman effect in NCO shows marked deviations from linear behavior. Since the rotational constant for NCO is quite small (about  $0.39 \text{ cm}^{-1}$ ), the rotational levels are close in energy and the "second-order" Zeeman effects caused by the mixing of adjacent rotational levels are quite pronounced. These effects can be appreciated by reference to the last two columns in Table I. The penultimate column lists the tuning rate for each transition frequency at the observed field as calculated by the computer program used to fit the data. The final column lists the first-order tuning rate (i.e., that

| Parameters for the $\nu_3$ Fundamental of NCO <sup>a</sup> |   |  |  |  |  |  |  |  |
|--|---|--|--|--|--|--|--|--|
| (A)  | <ul> <li>A) Parameter values constrained in the least-squares fit<sup>b</sup></li> </ul>      |  |  |  |  |  |  |  |
|  | $B_{000} = 0.3895161$ $g_S = 2.002009^{\circ}$  |  |  |  |  |  |  |  |
|  | $A_{000} = A_{001} = -95.585$   |  |  |  |  |  |  |  |
|  | $Y_{000} = Y_{001} = -0.0015$   |  |  |  |  |  |  |  |
|  | $D_{000} = D_{001} = 0.19 \times 10^{-6}$   |  |  |  |  |  |  |  |
| (B)  | Parameter values determined in the least-squares fit<br>$v_{a}$ = 1920.60645(19) <sup>d</sup> |  |  |  |  |  |  |  |
|  | $a_3 = 0.003338(21)$  |  |  |  |  |  |  |  |
|  | $g_L = 0.988773(55)$  |  |  |  |  |  |  |  |

### TABLE III

<sup>&</sup>lt;sup>a</sup> Values in  $cm^{-1}$ , where appropriate.

b Reference (8) unless indicated

<sup>&</sup>lt;sup>C</sup> Value used for EPR analysis, reference (5).

<sup>&</sup>lt;sup>d</sup> The numbers in parentheses represent one standard deviation of the fit in units of the last quoted decimal place.

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### TABLE IV

Result of the Least-Squares Fit of the NCO Hot-Band Data

| J <sup>"</sup> | мј   | м <sub>ј</sub> ″   | Field (C)  | Frequency (cm <sup>-1</sup> )   | obs-calc (cm <sup>-1</sup> ) <sup>a</sup>            |
|----------------|--|--|--|---|--|
| 5/2            | 5/2  | 3/2  | 11049.1  | 0,30921   | +0.09 x 10 <sup>-4</sup>                             |
| 5/2            | 3/2  | 1/2  | 11403.7  |   | +0.19  |
| 5/2            | 1/2  | -1/2   | 11747.5  |   | -0.03  |
| 5/2            | -1/2   | -3/2   | 12079.6  |   | -0.12  |
| 5/2            | -3/2   | -5/2   | 12401.1  |   | -0.15  |
| 5/2            | 3/2  | 5/2  | 8636.0   | 1906.8558   | $-0.58 \times 10^{-3}$                               |
| 5/2            | 1/2  | 3/2  | 8851.0   |   | -0.42  |
| 5/2            | -1/2   | 1/2  | 9079.0   |   | +0.16  |
| 5/2            | -3/2   | -1/2   | 9287.0   |   | +0.28  |
| 5/2            | -5/2   | -3/2   | 9499.0   |   | +0.56  |
|                |  |  |  |   |  |
|                | _  |  |  |   |  |
|                | J"<br>5/2<br>5/2<br>5/2<br>5/2<br>5/2<br>5/2<br>5/2<br>5/2<br>5/2<br>5/2 | $\begin{array}{cccc} J^{''} & M_J^{'} \\ \hline 5/2 & 5/2 \\ 5/2 & 3/2 \\ 5/2 & 1/2 \\ 5/2 & -1/2 \\ 5/2 & -3/2 \\ 5/2 & 3/2 \\ 5/2 & 1/2 \\ 5/2 & -1/2 \\ 5/2 & -3/2 \\ 5/2 & -5/2 \end{array}$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | J" $M_{J}$ $M_{J}$ Field (C) $5/2$ $5/2$ $3/2$ $11049.1$ $5/2$ $3/2$ $1/2$ $11403.7$ $5/2$ $1/2$ $11403.7$ $5/2$ $1/2$ $11747.5$ $5/2$ $-1/2$ $12079.6$ $5/2$ $-3/2$ $-5/2$ $12079.6$ $5/2$ $-3/2$ $-5/2$ $12401.1$ $5/2$ $3/2$ $5/2$ $8636.0$ $5/2$ $1/2$ $3/2$ $8851.0$ $5/2$ $-1/2$ $1/2$ $9079.0$ $5/2$ $-3/2$ $-1/2$ $9287.0$ $5/2$ $-5/2$ $-3/2$ $9499.0$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ |

Parameter values constrained in the least-squares fit

 $B_{010} = 0.390547 \text{ cm}^{-1}$   $\alpha_3 = 0.003338 \text{ cm}^{-1} \qquad g_S = 2.002099$   $A_{010} = A_{011} = -94.191 \text{ cm}^{-1}$   $\gamma_{010} = \gamma_{011} = -0.0026 \text{ cm}^{-1}$   $D_{010} = D_{011} = 0.19 \times 10^{-6} \text{ cm}^{-1}$ 

Parameter values determined

= 1907.11892(20)  $g_L \approx 0.973200(44)$ 

Hence  $x_{23} = -13.48753(28) \text{ cm}^{-1}$ 

<sup>a</sup> EPR data given an absolute weight of 9 x 10<sup>8</sup> cm<sup>-1</sup>. LMR data given an absolute weight of 1 x 10<sup>6</sup> cm<sup>-1</sup>.

expected for an isolated rotational level). The differences between the figures in these two columns are significant. In the case of the R(5/2) transitions at about 13.7 and 15.5 kG on the  $P(22)_5$  laser line, they are very marked indeed, so much so that they lead to the apparent paradox that the higher field Zeeman component has a faster tuning rate than the lower field one. The energy levels involved in the R(5/2) transitions are shown in Fig. 3. The arrows in the diagram refer to the five observed transitions, attributed to two laser lines. The two high field transitions are the ones under consideration and it is clear from the diagram that the lower levels in each case deviate considerably from linear behavior. The second-order Zeeman effects destroy the symmetry of energy levels about the zero field value. This asymmetry was useful in practice because it removed the ambiguity caused by our lack of knowledge of the sign of the tuning rates.

A least-squares fit of all available magnetic resonance data for NCO was performed with a computer program specially written to fit to the parameters of two separate  ${}^{2}\Pi$  states. The effective Hamiltonian used is defined in the papers by Brown et al. (15, 16). More details of the computer program are to be published elsewhere (17). The data set consisted of the earlier EPR measurements (5) and the LMR measurements reported here, each weighted in accordance with the estimated experimental uncertainties  $(0.3 \times 10^{-4} \text{ cm}^{-1} \text{ and } 10^{-3} \text{ cm}^{-1}$ , respectively). The ground-state parameters are well known from an analysis of the microwave and optical spectra (8) and the appropriate parameters were constrained to these values in our fit. The only zero field parameters that could be determined reliably from our measurements were the upper-state B value and the vibrational interval. The spin-orbit (A), spin-rotation  $(\gamma)$ , and centrifugal distortion (D) parameters were therefore assumed to have the same value in both the (001) and (000) states. It was necessary to include all basis states up to  $\Delta J = \pm 3$  to avoid truncation errors in the calculation of eigenvalues. The results of the least-squares fit are given in Table II and the details of the parameters constrained or determined in the fit are given in Table III.

The primary quantity determined in the fit is the vibrational interval  $\nu_3$  of 1920.60645(19) cm<sup>-1</sup>. This value is consistent with the value of 1922-1923 cm<sup>-1</sup> obtained from the matrix isolation studies (9, 10); the discrepancy of about 2 cm<sup>-1</sup> between the gas phase and solid state measurements is quite typical (11). It should be remembered that the measured interval contains a small but significant contribution from the difference in the spin-orbit splittings for the two vibrational levels. It can be interpreted as  $\Delta G_{1/2} - (1/2)\alpha_3^A$ , where  $\alpha_3^A$  is the coefficient for the linear dependence of A on the vibrational quantum number  $v_3$ . Some feeling for the magnitude of this correction can be obtained from the value of the corresponding quantity for NO,  $\alpha_A = 0.1906$  cm<sup>-1</sup>. The anharmonic correction to the rotational constant,  $\alpha_3$ , is also well determined in our work. The value obtained, 0.003338(21) cm<sup>-1</sup>, is similar to that of  $\alpha_3$  for CO<sub>2</sub> in its ground state, 0.00309 cm<sup>-1</sup>.

Only one rotational transition has been detected in the (011)-(010),  ${}^{2}\Delta_{5/2}-{}^{2}\Delta_{5/2}$ hot band. Frequency pulling experiments were performed which showed that the resonances shifted to lower field with increase in laser frequency, i.e., the zero field frequency lies above the laser frequency and the spectrum arises from  $\Delta M_J$ = -1 transitions. In order to determine the hot-band origin, the data were fitted together with the EPR data for the  ${}^{2}\Delta_{5/2}$ , J = 5/2 level (5) using the same leastsquares program described above (except that it was modified to describe the rotational levels of a  ${}^{2}\Delta$  vibronic state). The rotational constant for the (010) level was taken from the fit of the microwave data (7). The results of the least-squares fit are given in Table IV. The hot-band origin is determined to be 1907.11892(20) cm<sup>-1</sup> so that, ignoring the small variation in the spin-orbit coupling parameter with vibrational level, the vibrational anharmonicity  $x_{23}$  is -13.48753(28) cm<sup>-1</sup>. The best previous estimate of this quantity was -16 cm<sup>-1</sup> by Bondybey and English (10).

Although magnetic resonance data for both the fundamental and hot bands depend primarily on the electron orbital and spin magnetic moments, they do not permit the separate determination of both quantities. We have chosen to fix the spin g factor at the free electron value corrected for relativistic effects (5) and to determine  $g_L$  from the fits. The values determined for the levels (000) and (010), 0.98877(5) and 0.97320(4), respectively, can be supplemented by the corresponding value for the (020), <sup>2</sup> $\Phi$  component of 0.954113(5), the latter being determined by a refit of the EPR data. Not only do these values deviate significantly from the expected value for  $g_L$  (very close to unity) but they also show a marked dependence on the bending vibrational quantum number,  $v_2$ . As has been discussed elsewhere (5, 8), this arises in part from Renner-Teller mixing of the bending vibrational levels of the <sup>2</sup> $\Pi$  state and in part from vibronic mixing of excited <sup>2</sup> $\Sigma$  and <sup>2</sup> $\Delta$  states. The parameter describing the latter effect,  $\Delta g_L^{(1)}$ , is revised slightly in value by the present work to -0.00689(1).

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