
The Absorption Spectrum of the Free NCO Radical

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Phil. Trans. R. Soc. Lond. A 1960 **252**, 165-192

doi: 10.1098/rsta.1960.0003

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THE ABSORPTION SPECTRUM OF THE FREE NCO RADICAL

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[Plates 1 and 2]

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Two systems of absorption bands have been observed in the visible and ultra-violet regions of the spectrum during the flash photolysis of several organic cyanates, and have been photographed under high resolution with long absorbing paths. Extensive vibrational and rotational analyses have been carried out for the bands of one system and show that the spectrum is due to an electronic transition $A(^2\Sigma^+) \leftarrow X(^2\Pi_i)$ of the free NCO radical, which is linear in both states.

All three vibrational frequencies and the first-order anharmonic constants have been obtained for the upper state, $A(^2\Sigma^+)$, and give a close fit to the term values of 21 observed vibrational levels. A Fermi resonance has been observed between ν_1' and $2\nu_2'$. In addition, the rotational constants B' and D' and their variations with all three fundamental vibrations have been obtained for this state.

Transitions have been observed from four excited levels of the bending vibration in the lower state, $X(^2\Pi_i)$, and the rotational constants have been determined for some of these levels. Interaction between the electronic and vibrational motions (Renner effect) complicates the vibrational structure of this state. The state belongs to Hund's coupling case (a), and the spin-orbit coupling gives a splitting $A'' = -95.6 \text{ cm}^{-1}$. In a $^2\Sigma^+$ vibronic level of this state (arising from $l = 1$ and $\Lambda = 1$) the spin splitting is proportional to $N + \frac{1}{2}$, but the spin-splitting constant γ is unusually large, and amounts to 30% of the B value.

The electronic states of NCO are correlated with those of its dissociation products. This shows that the bond dissociation energy of the CO bond is slightly greater than that of the CN bond in the three known states.

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1. INTRODUCTION

A system of violet degraded emission bands near 4000 \AA was observed at low dispersion by Holland and Style in the fluorescence from a number of aliphatic cyanates and isocyanates, and attributed by them to the NCO radical. These bands were also observed in absorption during the flash photolysis of similar compounds (Holland, Style, Dixon & Ramsay 1958) and showed rotational structure under high resolution. The vibrational and rotational analyses of these absorption bands have now been carried out and give confirmation of the assignment of the bands to the free NCO radical.

2. EXPERIMENTAL PROCEDURE

The flash photolysis apparatus was similar to that used by Callomon & Ramsay (1957), except for the use of a multiple reflexion mirror system and four photolysis lamps to give an increased radical absorption. The quartz reaction vessel was 60 cm long, and with a 50 cm multiple reflexion mirror system (White 1942) gave an absorbing path of up to 10 m. Four straight photolysis lamps were used, each 50 cm long, filled with xenon at 35 mm Hg pressure, with a common gas connexion at one end to ensure good synchronization. The same energy ($33 \mu\text{F}$, 7500 V) was discharged simultaneously through each of the lamps by means of a manual switch. The duration of the flash was about $50 \mu\text{s}$. The source of continuous background for the absorption spectrum was a length of quartz capillary tubing about 5 cm long and 3 mm internal diameter, with Duralumin electrodes. Through this passed a slow flow of argon at about 75 mm Hg pressure. A $2 \mu\text{F}$ condenser charged to 16000 V was discharged through this lamp by means of a triggered spark gap and a time delay circuit actuated by the photolysis flash. The light was observed from the side of the capillary, and gave a flash with a duration of 5 to $10 \mu\text{s}$.

The spectrum was photographed in the second and third orders of a 21 ft. concave grating spectrograph, with a resolving power of about 200 000, using Eastman Kodak 103a-O and I-O plates. The exposure required varied from 50 to 200 flashes, depending on the spectral region and the absorption path length. The strongest NCO absorption was obtained during the photolysis of HNCO at 25 mm Hg pressure about $10 \mu\text{s}$ after the maximum intensity of the photolysis flash. Well-known bands of NH, NH_2 , OH and CN were observed in addition to the NCO spectrum. The reaction vessel was pumped out immediately after each flash and refilled, otherwise the mirrors rapidly became filmed. From absorption plates taken at varying time delays it was estimated that the lifetime of the NCO radicals was of the order of $200 \mu\text{s}$ under these conditions.

A hollow cathode iron-arc lamp was used for wavelength calibration. The wavelengths of the reference lines were taken from the M.I.T. tables (Harrison 1939) and used with the vacuum corrections of Edlén (1953). Two plates of each band were each measured twice on a comparator equipped with a photo-electric scanning device similar to that described by Tomkins & Fred (1951). The relative accuracy of the frequencies of strong sharp lines is $\pm 0.03 \text{ cm}^{-1}$. Table 1, p. 185, gives the wavelengths and vacuum wave numbers of all the band heads observed between 3600 and 4500 \AA , with their assignments and visually estimated relative intensities. In addition to the measured bands a further series of red degraded bands occurs between 2620 and 3160 \AA . These belong to a second electronic

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transition which from the structure of the bands is probably $B(^2II_i) \leftarrow X(^2II_i)$, analogous to the similar system in the spectrum of the iso-electronic molecule CO_2^+ . These bands will form the subject of a separate paper (Dixon 1959*b*).

3. VIBRATIONAL ANALYSIS

The strongest band in the longer wavelength absorption system of NCO is that at 4400 Å. This band is also the strongest band in emission (Holland *et al.* 1958). To the red of this band there is only one very weak absorption band, whereas to the violet there are very many weaker bands (figure 1), and it would therefore appear that this is the 0-0 band of the electronic transition. This band has the four heads expected for a $^2II(a) \leftarrow ^2\Sigma$ or $^2\Sigma \leftarrow ^2II(a)$ transition (figure 2, plate 1). There are also many weaker heads on the violet side of the strong band which are too near to the strong band to represent vibrational intervals in the

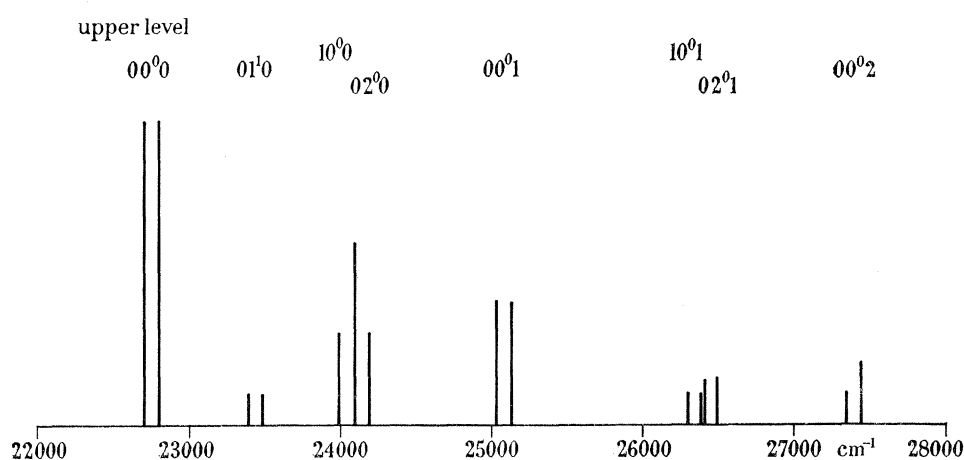


FIGURE 1. A schematic representation of the strongest bands in the absorption spectrum of the NCO radical.

upper state. These must therefore be 'hot' bands. Similar weak heads are observed to the violet side of other strong bands in the system. In figure 2 it is seen that the group of heads between 4220 and 4275 Å is very similar in appearance to the first group between 4345 and 4405 Å. The interval between the two heads at 4404 and 4275 Å, one in each group, is 681 cm^{-1} , which must be the upper-state bending frequency ν'_2 . Several arguments may be presented to prove that the transition is $^2\Sigma \leftarrow ^2II(a)$. For example: in II vibronic levels arising from the bending of a linear molecule in a Σ state appreciable l -type doubling can occur, but not in levels of other species. The P_1 head of the hot band at 4375 Å is double as a result of this (figure 2), indicating that the hot band is $\nu'_2 - \nu''_2$. A similar doubling is observed in the P_1 head of the band at 4275 Å, which is ν'_2 . The common upper level in these two bands must therefore be of species II , and the upper electronic state is therefore $^2\Sigma$. The complicated but similar patterns of 'hot' band heads in the two groups indicates that there is a vibrational-electronic interaction in the lower state (Renner 1934) and confirms that the electronic transition is $^2\Sigma \leftarrow ^2II(a)$; this is substantiated by the rotational analysis of the bands, which also shows that the $^2II(a)$ state is inverted. A consideration of the electron configuration in the two states (see §5) also leads to a 2II_i lower state and shows that the upper state is $^2\Sigma^+$. All but four very weak heads of the eighty-three observed band heads have been fitted into the vibrational array of such a transition.

(a) *The vibrational structure of the ground state $X(^2\Pi_i)$: the Renner effect*

It is usual in the spectra of linear triatomic molecules to indicate the identity of the vibrational levels by the four quantum numbers v_1, v_2, l and v_3 . v_1 and v_3 are the quantum numbers for the stretching vibrations ν_1 and ν_3 ($\nu_3 > \nu_1$), v_2 is that for the bending vibration ν_2 , and l is the quantum number indicating the angular momentum $lh/2\pi$ of this vibration. When the molecule is in a degenerate electronic state the electronic angular momentum $\Lambda h/2\pi$ may interact with the angular momentum of the bending vibration such that Λ and

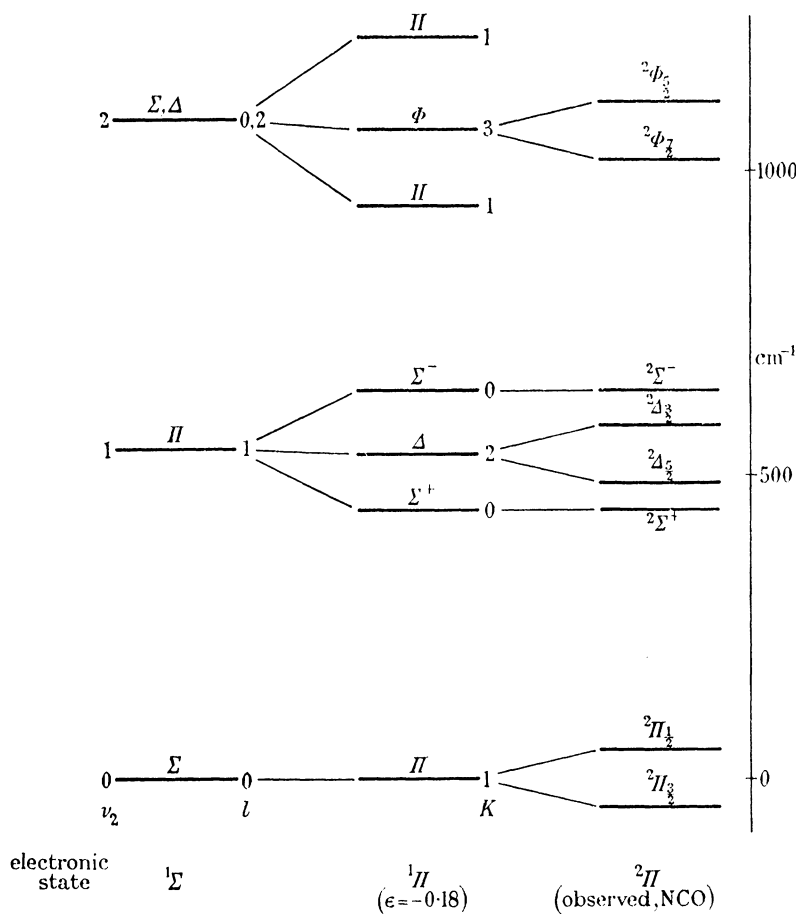


FIGURE 3. A correlation of the bending vibrational energy levels for $^1\Sigma$, $^1\Pi$ and $^2\Pi$.

l are no longer good quantum numbers, and the resultant angular momentum is characterized by $K = |\Lambda \pm l|$. The energy levels of such a system have been calculated by Renner (1934) in terms of a parameter ϵ which he defined as follows: When a linear molecule in a Π state is bent the electronic degeneracy is split, giving two electronic states. One of these will be symmetric with respect to the plane of the bent molecule, the other antisymmetric. In general there will therefore be two bending potential curves for the linear molecule, V^+ and V^- respectively, which Renner represented by $V_0(1 + \epsilon)$ and $V_0(1 - \epsilon)$. In figure 3 the levels arising from the bending of a molecule in a Π state are correlated with those of a Σ state, and also with the observed levels for the $X(^2\Pi_i)$ state of NCO, in which the energy level diagram is further complicated by spin splitting.

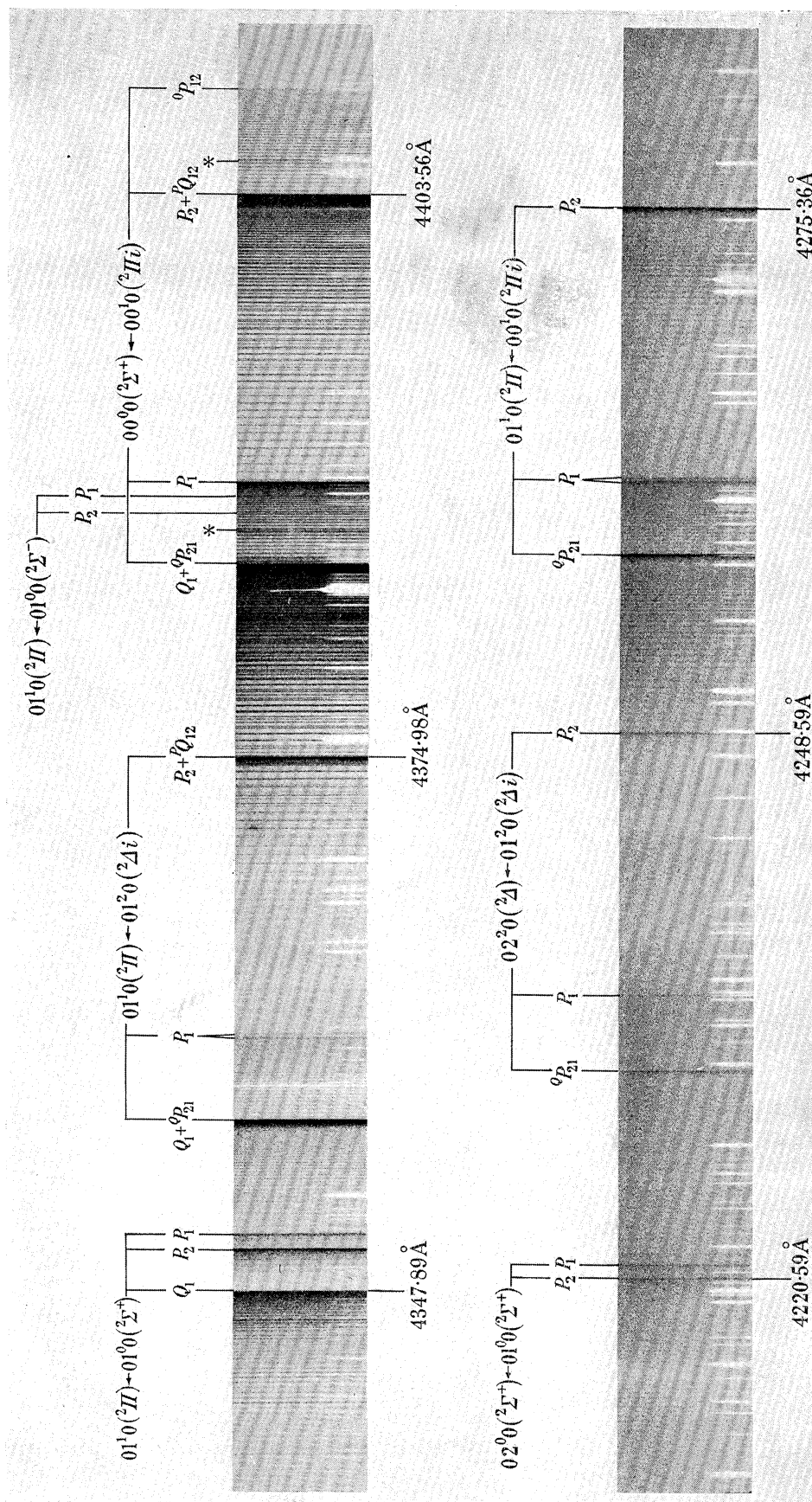


FIGURE 2. Two sections of the absorption spectrum of the NCO radical (* band heads of the isotopic molecule N^{13}O).

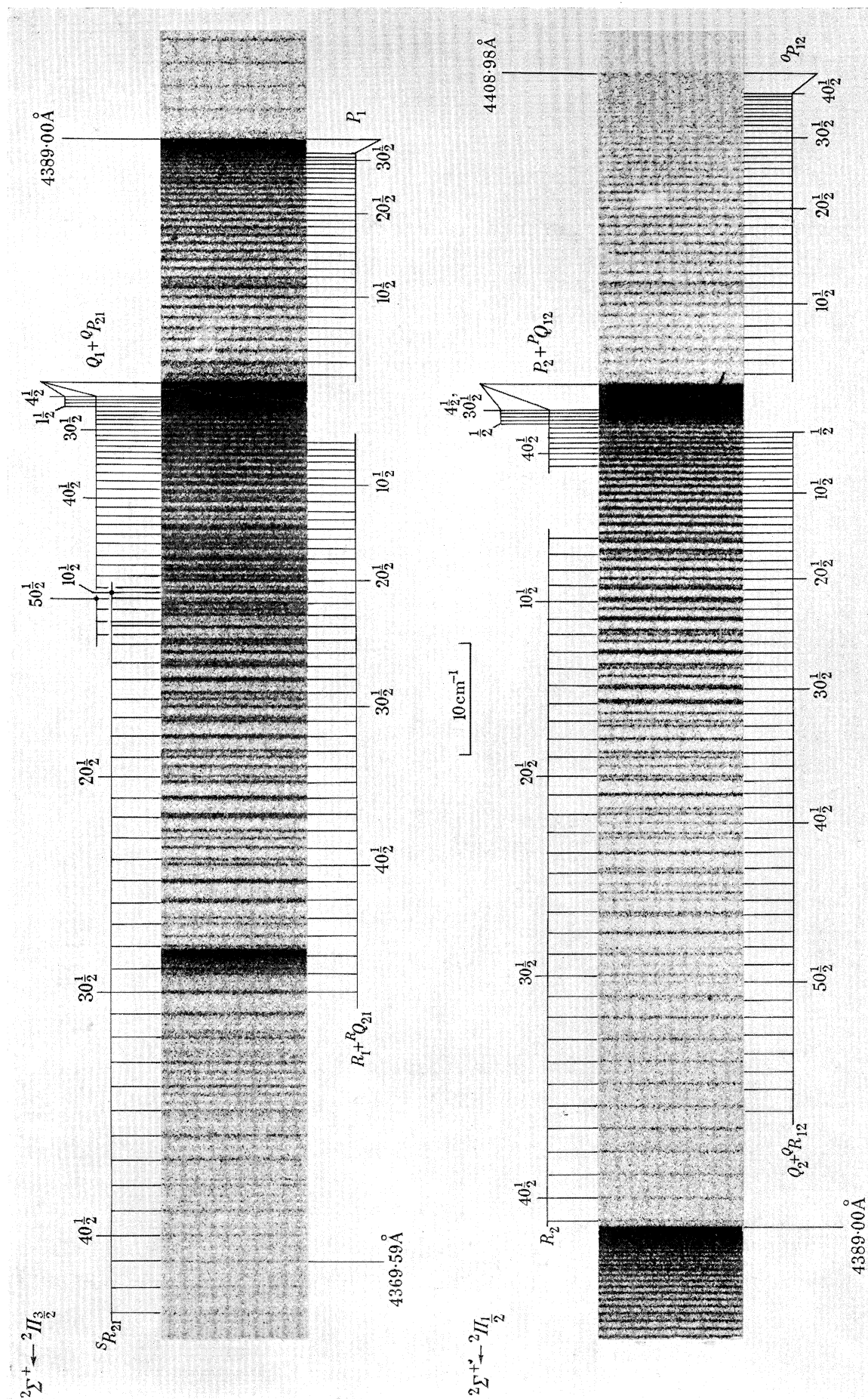


FIGURE 4. Line assignments for the $00^0 0 \leftarrow 00^1 0$ band of NCO.

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Renner's equations for the energies of the levels with $v_2 = 1$ and 2 in a Π state, referred to the zero level, are

$$v_2 = 1 \left\{ \begin{array}{ll} K = 0, \Sigma^- & E^0 = \omega_2(1 - \epsilon), \\ K = 2, \Delta & E^0 = \omega_2(1 - \frac{1}{2}\epsilon^2), \\ K = 0, \Sigma^+ & E^0 = \omega_2(1 + \epsilon); \end{array} \right. \quad (1)$$

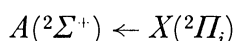
$$v_2 = 2 \left\{ \begin{array}{ll} K = 1, \Pi & E^0 = \omega_2(2 - \sqrt{2}\epsilon - \frac{1}{8}\epsilon^2), \\ K = 3, \Phi & E^0 = \omega_2(2 - \frac{5}{4}\epsilon^2), \\ K = 1, \Pi & E^0 = \omega_2(2 + \sqrt{2}\epsilon - \frac{1}{8}\epsilon^2). \end{array} \right.$$

These formulae ignore anharmonicity. By analogy with the usual energy level formula for a polyatomic molecule, additional small terms $x_{ij}v_i v_j$ and $x_{kk}K^2$ might be needed to represent observed levels. (In this paper the latter term is taken in the form $x_{kk}(K^2 - 1)$ to make it zero for the lowest vibrational level.)

In the designation of the vibrational levels in this state the value of K (rather than l) is given as a superscript to v_2 , i.e. $v_1 v_2^K v_3$. Where the species of a level is given this is the vibronic species (electronic \times vibrational).

(b) The vibrational structure of the upper state $A(2\Sigma^+)$

In the rotational analysis of the bands (see §4) no evidence of spin splitting in the upper state $A(2\Sigma^+)$ was observed. The vibrational and rotational levels in this state are therefore completely analogous to those of a molecule in a singlet state, such as CO_2 or N_2O in their ground states. As with these molecules, the stretching frequency ν_1 is approximately equal to twice the bending frequency ν_2 and Fermi resonance couples levels with quantum numbers v_1, v_2, l, v_3 and $v_1 - 1, v_2 + 2, l, v_3$ (Fermi 1931). The electronic transition



is between two states of NCO in which the equilibrium configuration is linear, and the difference in B value in the two states is about 3% (see §4). Herzberg & Teller (1933) have shown that for such a system the Franck-Condon principle indicates that there should be short progressions of bands involving the two upper state stretching vibrations ν'_1 and ν'_3 , and that any bands involving a change in the bending quantum number v_2 should be very weak (see also Sponer & Teller 1941). However, bands with $\Delta v_2 \neq 0$ do appear as a result of the Fermi resonance in the upper state. The effect of this resonance on the intensity of some of these bands has been discussed in detail in a separate publication (Dixon 1959*a*).

The vibrational energy levels of a linear triatomic molecule in a Σ state, referred to the zero level, can be written

$$G_0(v_1, v_2, l, v_3) = \sum_i \omega_i^0 v_i + \sum_{ij} x_{ij} v_i v_j + x_u l^2 \quad (i \leq j), \quad (2)$$

where the ω_i^0 can be expressed in terms of the zero-order vibration frequencies ω_i and the x_{ij} . In this paper the rotational energy term $-Bl^2$ and the vibrational energy term $x_u l^2$ have not been combined as $g_{22}l^2$, as is common in infra-red spectra, since this would not be consistent with the usage adopted in the ground state.

(c) Determination of band origins

A preliminary analysis of the spectrum was made with the frequencies of the band heads to give the vibrational intervals in the upper and lower states. In each band at least one branch comes to a head at low J value, and the use of these heads introduces no more than 1 or 2 cm^{-1} error into the vibrational intervals. Common combination differences were consistent to within this margin of error. From the rotational analysis of several of the bands values were obtained for B'_0 and all three vibration-rotation interaction constants α'_i in the upper state, and for the B'' values in three of the lower state levels. For all observed transitions the rotational constants of both the upper and the lower levels could therefore be calculated, and with these the band centre could be calculated from the various band-head frequencies. In averaging these determinations emphasis was placed on those branches forming heads at low J value. Where two or more upper-state levels are in Fermi resonance there is a mixing of the zero-approximation B values (Adel & Dennison 1933); hence to calculate the actual B values in these levels the mixing coefficients for the B values were calculated from the preliminary vibrational constants. With the revised vibrational constants thus obtained this iterative process was repeated and gave constant values for the band centres after one further cycle. For any band the various branches gave values for the band centre in agreement to $\pm 0.2 \text{ cm}^{-1}$, and the combination differences agreed to 0.15 cm^{-1} , with one exception where the extrapolation from band head to band centre was very long. Where a vibrational interval was available from the rotational analysis of two bands this value was used in the final analysis in preference to a value calculated from band heads.

(d) The vibrational constants in the lower state $X(^2II_i)$

In addition to bands arising from the zero level $00^1 0(^2II_i)$, bands were also observed arising from four excited levels of the bending vibration in the ground state: $01^0 0(^2\Sigma^+)$; $01^2 0(^2A_i)$; $01^0 0(^2\Sigma^-)$ and $02^3 0(^2\Phi_i)$. The existence of a weak band at 4483 \AA

$$[00^0 0(^2\Sigma^+) \leftarrow 01^0 0(^2\Sigma)],$$

681 cm^{-1} to the red of a hot band at 4348 \AA

$$[01^1 0(^2II) \leftarrow 01^0 0(^2\Sigma)]$$

proves that the lower level $01^0 0$ of these two bands has the vibronic species $^2\Sigma^+$, not $^2\Sigma^-$. Two weak heads of the corresponding band involving the Σ^- level $[01^1 0(^2II) \leftarrow 01^0 0(^2\Sigma^-)]$ are indicated in figure 2. Even though the lower-state levels $01^2 0(^2A_i)$ and $02^3 0(^2\Phi_i)$ exhibit a large spin splitting of the same order of magnitude as that in the zero level $00^1 0(^2II_i)$ [$A = -95.59 \text{ cm}^{-1}$], whereas the spin splitting in the levels $01^0 0(^2\Sigma^+)$ and $01^0 0(^2\Sigma^-)$ is small, the vibrational term values obtained from the band origins were found to fit the Renner equations (equation (1)) very satisfactorily. The Q head of the band

$$01^1 0(^2II) \leftarrow 01^0 0(^2\Sigma^-)$$

was obscured by another band. However, as there is probably little difference in B value between the two levels $01^0 0(^2\Sigma^+)$ and $01^0 0(^2\Sigma^-)$ the mean of the separations between the two P_1 heads or the two P_2 heads of the bands

$$01^1 0(^2II) \leftarrow 01^0 0(^2\Sigma^-) \quad \text{and} \quad 01^1 0(^2II) \leftarrow 01^0 0(^2\Sigma^+)$$

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was set equal to $2\omega_2''\epsilon$, and showed that ϵ is negative. Four vibrational intervals are thus obtained (table 2), and there are sufficient data to evaluate the constants ω_2 and ϵ , and two anharmonic constants. These are given in table 3.† As the band heads involving the level $02^3 0(2^2\Phi_i)$ are weak there is considerable probable error in its term value, and the values for the anharmonic constants x_{22}'' and x_{kk}'' are therefore only orders of magnitude.

TABLE 2. THE VIBRATIONAL LEVELS FOR NCO $X(^2\Pi_i)$

level		$G_0''(v_1, v_2, k, v_3)$ (cm ⁻¹)	
		observed	calculated
0, 1 ⁰ , 0	$^2\Sigma^+$	441.3 ₇ *	441.37
0, 1 ² , 0	$^2\Delta_i$	533.5 ₅ *	533.55
0, 1 ⁰ , 0	$^2\Sigma^-$	637.4	637.39
0, 2 ³ , 0	$^2\Phi_i$	1065.6	1065.58

* These values are calculated from rotational structure analyses.

TABLE 3. VIBRATIONAL CONSTANTS FOR NCO $X(^2\Pi_i)$

$$\begin{aligned} \omega_2^0 &= 539.4_6 \text{ cm}^{-1} & \epsilon &= -0.181_7 \\ x_{22} &= 0.6_9 \text{ cm}^{-1} & x_{kk} &= 0.7_7 \text{ cm}^{-1} \end{aligned}$$

(e) *The vibrational constants in the upper state $A(^2\Sigma^+)$*

The rotational structure was measured and analysed for bands involving the upper state levels $00^0 0$, $01^1 0$, $10^0 0$, $02^0 0$, $00^0 1$ and $00^0 2$, and the vibrational term values for these levels obtained to $\pm 0.04 \text{ cm}^{-1}$. In addition, the term values for sixteen other upper state levels were determined from band head measurements in the manner described in sub-section (c) with a probable error of $\pm 0.10 \text{ cm}^{-1}$. These values are collected in table 4.

Amat & Goldsmith (1955) have shown that the Fermi resonance interaction term W_{ij} between two levels W_i^0 and W_j^0 is dependent on all four quantum numbers, and can be represented by the formula

$$W_{v_1, v_2, l, v_3; v_1-1, v_2+2, l, v_3} = (W_0 - \lambda_1 v_1 - \lambda_2 v_2 - \lambda_l v_l - \lambda_3 v_3) \left(\frac{1}{2}\right) [(v_2 + 2)^2 - l^2]^{\frac{1}{2}} v_1^{\frac{1}{2}}. \quad (3)$$

When $v_1 > 1$ the energy matrix involves more than two vibration levels, and the perturbed energies W_i are solutions of the secular equation

$$\begin{vmatrix} W_1^0 - W, & W_{12}, & 0, & \dots \\ W_{21}, & W_2^0 - W, & W_{23}, & \dots \\ 0, & W_{32}, & W_3^0 - W, & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} = 0, \quad (4)$$

which cannot be solved analytically. However, the sum of the initial energies ΣW_i^0 is equal to the sum of the perturbed energies ΣW_i . The vibrational term values in table 4 can therefore be used to calculate some of the constants in equation (2) without a knowledge of the

† Footnote added in proof (28 October 1959). While this paper was in press Dr J. A. Pople completed calculations on the coupling of electronic spin angular momentum in a $^2\Pi$ state exhibiting the Renner effect, for the case where ϵ is small and $A < \omega_2$, (to appear in *Molecular Physics*). The significant difference between his expressions for the vibrational levels and those used in this analysis of the NCO ground state (equations (1)) is that the separation of the two levels $01^0 0$ ($^2\Sigma^+$ and $^2\Sigma^-$) is $(4\omega_2^2\epsilon^2 + A^2)^{\frac{1}{2}}$, not $2\omega_2\epsilon$. This leads to a revision of the constants in Table 3, which are then:

$$\begin{aligned} \omega_2^0 &= 538.9_4 \text{ cm}^{-1} & \epsilon &= -0.159_1 \\ x_{22} &= 0.6_9 \text{ cm}^{-1} & x_{kk} &= 0.2_5 \text{ cm}^{-1}. \end{aligned}$$

perturbation function W_{ij} by summing the energies in each resonating group. Unfortunately a study of the simultaneous equations which result from this treatment shows that the number of equations is always one less than the number of constants required to represent the term values, however many energy levels are used. In the infra-red spectrum of CO_2 this problem was overcome by Courtoy (1957) by using the B values of two levels in resonance. When two levels E_1^0 and E_2^0 of initial separation δ and with rotational constants B_1^0 and B_2^0 are in resonance, such that the separation of the levels becomes Δ , the effective B values in the two levels become

$$\left. \begin{aligned} B_1 &= \frac{\Delta + \delta}{2\Delta} B_1^0 + \frac{\Delta - \delta}{2\Delta} B_2^0, \\ B_2 &= \frac{\Delta - \delta}{2\Delta} B_1^0 + \frac{\Delta + \delta}{2\Delta} B_2^0. \end{aligned} \right\} \quad (5)$$

TABLE 4. THE OBSERVED TRANSITIONS IN THE SYSTEM $A(^2\Sigma^+) \leftarrow X(^2\Pi_i)$ OF NCO , AND THE VIBRATIONAL LEVELS FOR THE $A(^2\Sigma^+)$ STATE

upper level	lower* levels	observed	calculated			obs.-calc.
			W^0	W_{ij}	W	
0, 1 ¹ , 0	0 [†] , 1 [†] , 2 [†] , 3	680.83 [‡]	680.83	—	—	0
1, 0 ⁰ , 0	0 [†]	1289.31 [‡]	1320.28	44.88	{1289.31 1385.33}	0
0, 2 ⁰ , 0	0 [†] , 1	1385.34 [‡]	1354.36			0.01
0, 2 ² , 0	2, 4	1361.7 ₃ [‡]	1361.72	—	—	0.01
1, 1 ¹ , 0	0, 1, 2	1952.3 ₅ [‡]	2003.77	62.34	{1952.36 2079.36}	-0.01
0, 3 ¹ , 0	0, 1, 2	2079.3 ₈ [‡]	2027.95			0.02
0, 3 ³ , 0	4	2042.4	2042.67	—	—	-0.2 ₇
0, 0 ⁰ , 1	0 [†]	2338.02 [‡]	2338.02	—	—	0
2, 0 ⁰ , 0	0	2564.0 ₁ [‡]	2632.58	63.64	{2564.03 2656.25}	-0.02
1, 2 ⁰ , 0	0	2656.2 ₇ [‡]	2679.96			0.02
0, 4 ⁰ , 0	0	2786.5 ₄ [‡]	2694.24	86.04	{2786.51 2619.16}	0.03
1, 2 ² , 0	—	—	2687.32			—
0, 4 ² , 0	4	2769.6 ₉	2701.60	74.96	{2769.76 —}	-0.07
0, 1 ¹ , 1	0, 1, 2	3005.9 ₆ [‡]	3005.96			—
1, 0 ⁰ , 1	0	3605.2 ₈ [‡]	3636.10	43.46	{3605.29 3697.41}	-0.01
0, 2 ⁰ , 1	0	3697.4 ₃ [‡]	3666.60			0.02
0, 2 ² , 1	4	3673.7 ₂	3673.96	—	—	-0.24
1, 1 ¹ , 1	—	—	4306.70	60.33	{4255.80 4378.20}	—
0, 3 ¹ , 1	2	4377.9 ₀	4327.30			-0.30
0, 0 ⁰ , 2	0 [†]	4653.11 [‡]	4653.12	—	—	-0.01
2, 0 ⁰ , 1	0	4857.2 ₈	4926.20	61.63	{4857.95 4947.01}	-0.67
1, 2 ⁰ , 1	0	4946.8 ₁	4970.00			-0.20
0, 4 ⁰ , 1	—	—	4980.70	83.20	{5071.94 —}	—
0, 1 ¹ , 2	1, 2	5308.3 ₁	5308.17			—
0, 0 ⁰ , 0	0 [†] , 1	origin of 0, 0 ⁰ , 0 ← 0, 0, 0 ¹ , 0 band; $\nu_{00} = 22753.98 \text{ cm}^{-1}$				

* The numbers refer to the levels; 0 ≡ 0, 0¹, 0(² Π_i); 1 ≡ 0, 1⁰, 0(² Σ^+); 2 ≡ 0, 1², 0(² Δ_i); 3 ≡ 0, 1⁰, 0(² Σ^-) and 4 ≡ 0, 2³, 0(² Φ_i).

† The rotational structure of these bands has been analyzed.

‡ Used in calculating the vibrational constants.

The value of $\alpha'_2 = -56.7 \times 10^{-5} \text{ cm}^{-1}$ was obtained from the B' values of the levels 00⁰0 and 01¹0, and used in calculating the zero approximation B' value of the level 02⁰0. With $E_1^0 = E(10^00)$ and $E_2^0 = E(02^00)$, equation (5) was then used to give a zero approximation separation for these levels of $\delta = 34.11 \text{ cm}^{-1}$. This provided the extra datum required for the

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solution of the simultaneous equations to give the upper-state vibration constants. Unperturbed term values were calculated for all the observed levels using these constants, and the secular equations of the second and third order (equation (4)) solved numerically to give various values of W_{ij} . The parameters in equation (3) for W_{ij} were thus determined, and are collected in table 5 with the other vibration constants. By means of these, the energies, including the effect of Fermi resonance, were calculated for all the observed levels, and are compared with the experimental values in table 4. The agreement between the observed and calculated energies (for those levels not used in the establishment of the constants) is almost as good as the accuracy of the measurements.

TABLE 5. THE VIBRATIONAL CONSTANTS FOR NCO $A(^2\Sigma^+)$, AND FOR COMPARISON, SOME OF THOSE FOR CO₂ $X(^1\Sigma_g^+)$ (CM⁻¹)

NCO $A(^2\Sigma^+)$		
$\omega_1^0 = 1324.2_7$	$\omega_2^0 = 680.8_0$	$\omega_3^0 = 2349.4_8$
$x_{11} = -3.9_9$	$x_{22} = -1.8_1$	$x_{33} = -11.4_6$
$x_{12} = 2.6_6$	$x_{1l} = 1.8_4$	$x_{23} = -12.8_9$
$x_{13} = -22.2_0$	—	—
$\omega_1 = 1336.7_0$	$\omega_2 = 689.5_3$	$\omega_3 = 2384.9_3$
Fermi resonance constants:		
$W_0 = 44.7_6$	$\lambda_1 = -0.1_2$	$\lambda_2 = 0.9_3$
$\lambda_l = -0.1_3$	$\lambda_3 = 1.4_2$	—
*CO ₂ $X(^1\Sigma_g^+)$		
$\omega_1 = 1354.91$	$\omega_2 = 673.00$	$\omega_3 = 2396.49$
$x_{11} = -3.75$	$x_{22} = -0.63$	$x_{33} = -12.63$
$x_{12} = 3.65$	$x_{1l} = 1.17$	$x_{23} = -12.53$
$x_{13} = -19.37$	$W_0 = 51.31$	—

* Courtoy (1957)

(f) Force constants

It would be interesting to compare the CN and CO bond stretching force constants in NCO. Unfortunately no determination of the force constants in either the upper or lower electronic states can be made without data from an isotopic molecule. However, one conclusion can be reached. If it is assumed that there is no interaction force constant k_{12} between the NC and CO bonds in the upper state $A(^2\Sigma^+)$, and the equations are set down for k_{11} and k_{22} in terms of ν'_1 and ν'_3 by Wilson's F and G matrix method (1939) it is found that these equations have complex roots. Real solutions are only possible for $k_{12} \geq 0.694 \times 10^5$ dynes/cm, and the sum of the two stretching force constants is then $k_{11} + k_{22} \simeq 30 \times 10^5$ dynes/cm. For the ground state of CO₂ $k_{12} = 1.268 \times 10^5$ dynes/cm.

4. ROTATIONAL ANALYSIS

(a) Rotational structure of levels in the lower state $X(^2\Pi_i)$

The energy levels of a $^2\Pi$ level in Hund's coupling case (a) have been calculated by Hill & Van Vleck (1928), but this treatment does not include the effect of centrifugal stretching. This is often added by analogy with Hund's case (b) (Herzberg 1950, p. 232). A more detailed calculation by Almy & Horsfall (1937) takes centrifugal stretching into account and the constant D appears in two places in their equations; in a term of power J^4 , and as a refinement to the spin uncoupling. For the purposes of this paper we shall adopt the Hill &

Van Vleck equations with the addition of the main centrifugal stretching term from Almy & Horsfall, and with the term $-B\Lambda^2$ replaced by $-BK^2$

$$F(J) = B_v[(J + \frac{1}{2})^2 - K^2] \pm [B_v^2(J + \frac{1}{2})^2 + \frac{1}{4}A_v(A_v - 4B_v)\Lambda^2]^{\frac{1}{2}} - D_v[(J - \frac{1}{2})(J + \frac{1}{2})^2(J + \frac{3}{2}) + 1]. \quad (6)$$

The + sign gives the level $F_2(J)$ [$J = N - \frac{1}{2}$] and the - sign $F_1(J)$ [$J = N + \frac{1}{2}$]. The important difference between this equation and the usual form of the Hill & Van Vleck equation (Herzberg 1950) is that the centrifugal stretching term is the same for the two levels with the same J , not with the same N .

The spin splitting ($A\Lambda$) arises from the interaction of the electron spin with the magnetic field along the internuclear axis caused by the orbital angular momentum $\Lambda h/2\pi$ of the electrons. In the excited bending vibrational levels Λ may no longer be a good quantum number; consequently, the observed splittings in these levels cannot yield the appropriate value of the spin splitting constant A . However, it is to be expected that within a group of levels with the same v_2 , the effective value of Λ will be close to 1 for that level with $k = v_2 + 1$, and the spin splitting ($A\Lambda$) _{v} will be approximately equal to A''_{0010} .

Every rotational level calculated from equation (6) is doubly degenerate, but for non-hydrides the splitting of this degeneracy is usually observed only in ${}^2\Pi_{\frac{1}{2}}$ sublevels. This Λ -doubling can be represented by a small term $\pm\phi(J)$ [$= \frac{1}{2}p(J + \frac{1}{2})$] added to equation (6) (Mulliken & Christy 1931). If evidence for such a doubling is found in one sublevel of a ${}^2\Pi(a)$ level it indicates that this is the ${}^2\Pi_{\frac{1}{2}}$ sublevel.

(b) *Rotational structure of levels in the upper state $A({}^2\Sigma^+)$*

If the spin splitting in a ${}^2\Sigma$ state is too small to be observed the rotational energy is characterized by N . The rotational term values for the vibrational levels of NCO in the $A({}^2\Sigma^+)$ state should thus be given by

$$F'(N) = B'_v[N(N+1) - l^2] - D'_v[N(N+1) - l^2]^2, (\Sigma, A, \Phi, \dots \text{ levels}), \quad (7)$$

$$F'(N) = B'_v[N(N+1) - l^2] - D'_v[N(N+1) - l^2]^2 \pm \frac{1}{2}q'_v N(N+1), (II \text{ levels}). \quad (8)$$

The small extra term in II levels is the l -type doubling familiar in infra-red and microwave spectra.

(c) *The constants for the upper level $00^00({}^2\Sigma^+)$*

In the 0-0 band of the system $A({}^2\Sigma^+) \leftarrow X({}^2\Pi_i)$ the complications of bending vibrations, such as l -type doubling and the Renner effect, are absent. This band therefore has the same structure as a similar transition in the spectrum of a diatomic molecule, and was analyzed by standard techniques (Jevons 1932). There are three main branches and three satellite branches in each subband ${}^2\Sigma^+ \leftarrow {}^2\Pi_{\frac{1}{2}}$ and ${}^2\Sigma^+ \leftarrow {}^2\Pi_{\frac{3}{2}}$. In the absence of spin splitting in the ${}^2\Sigma^+$ state, four of these satellite branches coincide with main branches, giving four branches to each subband. No splitting or broadening of these double branches was observed in this or any other band, even at the highest N values of about 60, thus setting an upper limit to the spin splitting of $|\gamma'| (N + \frac{1}{2}) = 0.10 \text{ cm}^{-1}$, or $|\gamma'| \leq 0.0015 \text{ cm}^{-1}$. The assignments of the lines of the 0-0 band are given in table 8, p. 187, and illustrated in figure 4, plate 2. The absence of 'missing' lines near the subband origins could not be proved, and the rotational assignments were therefore checked by comparing lower level combination differences with those from other bands having the same lower level.

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The upper level rotational constants B' and D' were obtained in the usual manner from the combination differences $\Delta_2 F'(N)$ using least squares (table 6).

Although the 0-0 band is the strongest in this absorption system, and lines were therefore measured to high J values, other bands at shorter wavelengths were photographed in a higher order of the grating, with a consequent increased precision. The determination of the rotational constants for the lower level $00^1 0(^2II_i)$ will therefore be postponed until subsection (e).

TABLE 6. THE ROTATIONAL CONSTANTS FOR NCO $A(^2\Sigma^+)$ (cm^{-1})

(a) Constants determined from rotational structure

$$B'_{0,0^0,0} = 0.40211 \quad D'_{0,0^0,0} = 0.177 \times 10^{-6}$$

$$q'_0 = 66.1 \times 10^{-5} \quad |\gamma'| \leq 0.0015$$

level	$B'_v - B'_{0,0^0,0}$
0, 1 ¹ , 0	56.7×10^{-5}
1, 0 ⁰ , 0	-65.1×10^{-5}
0, 2 ⁰ , 0	28.6×10^{-5}
0, 0 ⁰ , 1	-307.9×10^{-5}
0, 0 ⁰ , 2	-616.7×10^{-5}

(b) Derived constants

$$B'_e = 0.40384 \pm 0.00004 \quad \alpha_1 = 150.0 \pm 3 \times 10^{-5}$$

$$\alpha_2 = -56.7 \pm 2 \times 10^{-5} \quad \alpha_3 = 308.1 \pm 1 \times 10^{-5}$$

(d) The constants for other upper-state levels

The rotational structures of the bands $01^1 0$, $10^0 0$, $02^0 0$, $00^0 1$ and $00^0 2 \leftarrow 00^1 0$ were also measured, and the assignments are given in table 8. As some of these bands are weak, and the second two bands overlap one another, not all their branches were measured, and the determination of their rotational constants using upper level combination differences would be very inaccurate. However, the changes in B'_v and D'_v from those in the $00^0 0(^2\Sigma^+)$ level can be accurately determined from the separations of pairs of lines of the same branch and J value in the bands $v_1 v_2^l v_3 \leftarrow 00^1 0$ and $00^0 0 \leftarrow 00^1 0$, giving in addition the upper-level vibrational term value

$$\Delta\nu' = \nu(N'J'')_{v_1 v_2^l v_3 \leftarrow 00^1 0} - \nu(N'J'')_{00^0 0 \leftarrow 00^1 0}$$

$$= G'_0(v_1, v_2^l, v_3) - B'_{v_1 v_2^l v_3} l^2 + (B'_{v_1 v_2^l v_3} - B'_{00^0 0}) N'(N'+1)$$

$$- (D'_{v_1 v_2^l v_3} - D'_{00^0 0}) N'^2(N'+1)^2. \quad (9)$$

In order to use this method sufficient lines in at least two branches were measured so that the rotational assignments could be checked using lower level combination differences.

In levels unaffected by Fermi resonance the difference between D'_v and $D'_{00^0 0}$ should be negligible, and a plot of $\Delta\nu'$ (equation (9)) against $N'(N'+1)$ gave a straight line for the bands $01^1 0$ (see below), $00^0 1$ and $00^0 2 \leftarrow 00^1 0$. It is interesting to note from the last two of these bands that $(B'_{00^0 2} - B'_{00^0 0}) = 2(B'_{00^0 1} - B'_{00^0 0})$ to within $0.9 \times 10^{-5} \text{ cm}^{-1}$ (see table 6).

The band $01^1 0(^2II(b)) \leftarrow 00^1 0(^2II(a))$ is a parallel band, and the Q branches are therefore extremely weak. As all the Q branches are coincident with other branches this only affects the relative intensities of the branches, and each subband still has four branches. Every line in a $^2II-^2II$ band is double and the l -type doubling in the upper level of this band causes a line splitting of about 1 cm^{-1} at the highest J values. One line in each pair corresponds to the line observed in a $^2\Sigma^+ \leftarrow ^2II_i$ band, whereas the other line arises from the opposite Λ -type

component. The frequency of the second line in each pair must first be corrected for the Λ -type doubling in the lower level before equation (9) can be used. After this has been done we see from equation (8) that the mean of each pair of lines can be used in equation (9). A plot of the corrected separations for each pair of lines against $N'(N'+1)$ gave a straight line passing through the origin, with a slope of $66 \cdot 1 \times 10^{-5} \text{ cm}^{-1}$.

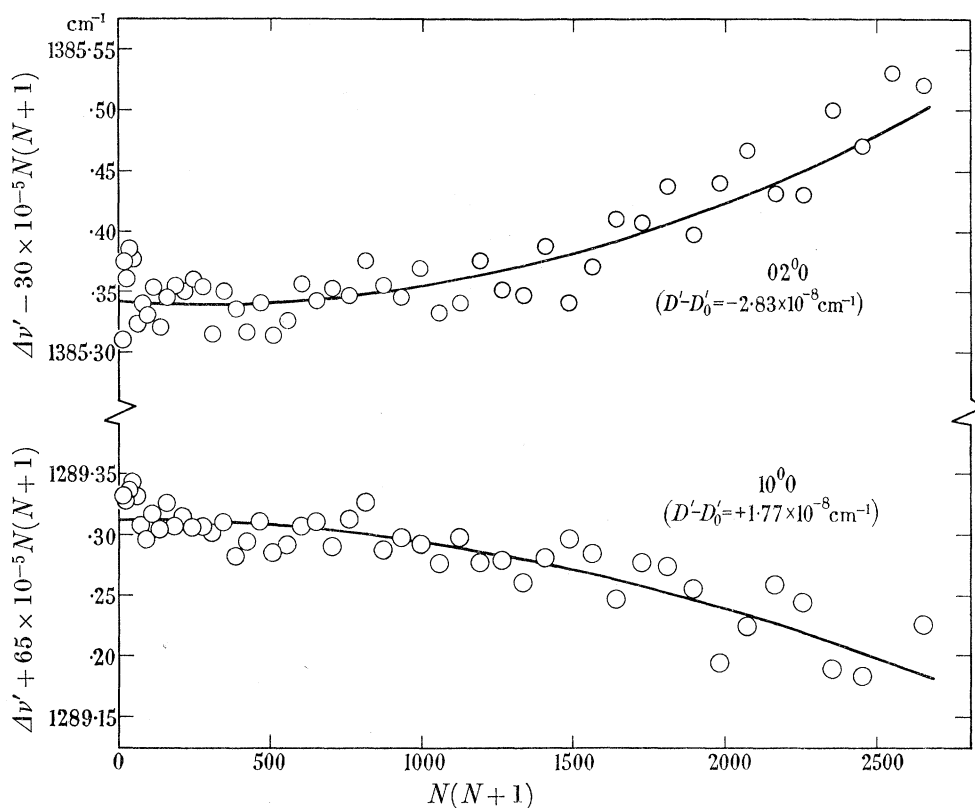


FIGURE 5. The effect of Fermi resonance on the centrifugal distortion constant D' for the levels 10^0_0 and 02^0_0 in the $A(2\Sigma^+)$ state of NCO. \circ , experimental values (means of all branches); —, least-squares lines, assuming calculated values of $\Delta D' N^2(N+1)^2$.

The l -type doubling constant q of II levels has been shown by de Heer & Nielsen (1952) to obey the equation

$$q_{v_1 v_2 v_3} = \frac{1}{2} q_0 (v_2 + 1). \quad (10)$$

The value of q_0 can be calculated from other vibrational and rotational constants of the molecule (Nielsen 1950)

$$q_0 = \frac{2B_e^2}{\omega_2} \left[1 + 4\omega_2^2 \left(\frac{\zeta_{21}^2}{\omega_1^2 - \omega_2^2} + \frac{\zeta_{23}^2}{\omega_3^2 - \omega_2^2} \right) \right]. \quad (11)$$

Unfortunately the coefficients ζ_{21} and ζ_{23} (which are connected by $\zeta_{21}^2 + \zeta_{23}^2 = 1$) cannot be calculated unless the complete geometry of the molecule is known. However, for a symmetrical molecule such as CO_2 $\zeta_{21}^2 = 0$ and $\zeta_{23}^2 = 1$, and as NCO is not too far from symmetrical we can write

$$q_0 \approx \frac{2B_e^2}{\omega_2} \left[1 + \frac{4\omega_2^2}{\omega_3^2 - \omega_2^2} \right] = 64 \cdot 6 \times 10^{-5} \text{ cm}^{-1}. \quad (12)$$

The experimental value of $q_{01^0_0} = 66 \cdot 1 \times 10^{-5} \text{ cm}^{-1}$ is slightly larger than this calculated value, which is to be expected from equation (11) as $\omega_3 > \omega_1 > \omega_2$.

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For the bands $10^0 0$ and $02^0 0 \leftarrow 00^1 0$ the upper level D' values are affected both by Fermi resonance and by l -type resonance. Similar effects have been found in the infra-red spectra of CO_2 (Courtoy & Herzberg 1955), DCN (Checkland & Thompson 1955) and C_2H_2 (Coburn, Rao & Nielsen 1956). The plots of $\Delta\nu'$ against $N'(N'+1)$ are definitely curved for these bands (figure 5) and $\Delta D' = D'_v - D'_0$ was estimated to be of the order of $1 \times 10^{-8} \text{ cm}^{-1}$ for $10^0 0$ and $-3 \times 10^{-8} \text{ cm}^{-1}$ for $02^0 0$. The theory of Nielsen, Amat & Goldsmith (1957) has been found to account satisfactorily for this effect in CO_2 , for which the measurements were more precise than those reported here. As the values chosen for $\Delta D'$ affect the values of $\Delta B'$ determined for these levels, this theory was used to calculate the changes in D' for NCO; $\Delta D' = 1.77 \times 10^{-8} \text{ cm}^{-1}$ for $10^0 0$ and $\Delta D' = -2.83 \times 10^{-8} \text{ cm}^{-1}$ for $02^0 0$. This curvature of the plots of $\Delta\nu'$ against $N'(N'+1)$ was then allowed for in the calculation by least squares of $G'_0(v)$ and $\Delta B'$ for these levels.

The observed B values in the $10^0 0$ and $02^0 0$ levels were combined with that for the $01^1 0$ level to give the zero approximation separation of the two levels in Fermi resonance, $10^0 0$ and $02^0 0$ (see equation (5)). $B_{10^0 0}^0$ was also calculated from these same three rotational constants. It was assumed that in the absence of Fermi resonance the B values obey

$$B'_{v_1 v_2 v_3} = B'_e - \alpha'_1(v_1 + \frac{1}{2}) - \alpha'_2(v_2 + 1) - \alpha'_3(v_3 + \frac{1}{2}), \quad (13)$$

and that B' does not depend on l .

Values have thus been determined for all three vibration-rotation interaction constants α_i for the $A(^2\Sigma^+)$ state. The rotational constants for this state are collected in table 6.

(e) *The constants for the lower level $00^1 0$ (2I_i)*

Although the rotational energy formula for a $^2II(a)$ level is complicated (equation (6)) the mean energy of $F_1(J)$ and $F_2(J)$ obeys the much simpler relation

$$\frac{1}{2}[F_1(J) + F_2(J)] = B''_v[(J + \frac{1}{2})^2 - K^2] - D''_v[(J - \frac{1}{2})(J + \frac{1}{2})^2(J + \frac{3}{2}) + 1]. \quad (14)$$

The values of B'' and D'' can therefore be obtained in the usual way from mean combination differences $\Delta_2 F''(J)$. Since there is Λ -type doubling, $\pm\phi(J)$, there are four second differences, $\Delta_2 F''_{1c}(J)$, $\Delta_2 F''_{1d}(J)$, $\Delta_2 F''_{2c}(J)$ and $\Delta_2 F''_{2d}(J)$ available from different branches, and the correct value of $\Delta_2 F''(J)$ to use is the mean of all four. Values of these combination differences were taken from the bands $00^0 0$, $10^0 0$, $02^0 0$ and $00^0 1 \leftarrow 00^1 0$. At low J it was not possible to obtain all four of these differences, so $\Delta_2 F''_{1d}(J)$ and $\Delta_2 F''_{2c}(J)$ were used to give the mean $\Delta_2 F''(J)$. This involves neglect of the Λ -type doubling, but subsequent determination of $\phi(J)$ showed that this omission introduced no appreciable error into $B''_{00^1 0}$ and $D''_{00^1 0}$ (table 7).

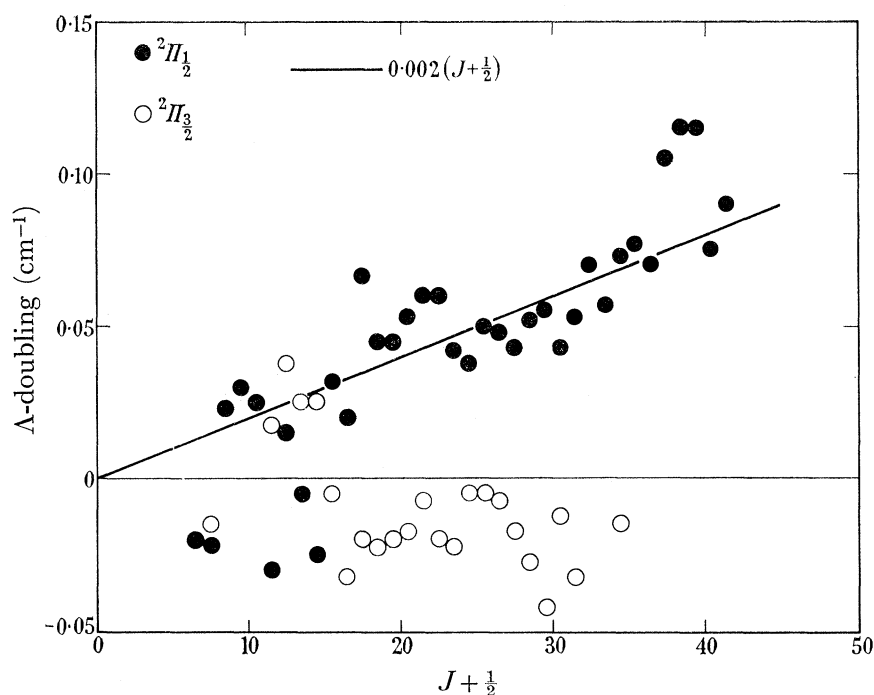
The Λ -type doubling of the $00^1 0$ level cannot be observed directly as a line splitting, but can be obtained from combination differences. As the P_2 and Q_1 branches come to a head the line measurements are possibly in error due to underlying lines of the returning branches, and a method was used that is independent of these branches

$$\left. \begin{aligned} \phi_2(J) + \phi_2(J+1) &= \frac{1}{2}\{ {}^Q R_{12}[Q_2](J) + Q_2(J+1) + Q_2(J+2) \\ &\quad - R_2(J) - R_2(J+1) - {}^0 P_{12}(J+2) \}, \\ \phi_1(J) + \phi_1(J+1) &= \frac{1}{2}\{ {}^S R_{21}(J) + {}^S R_{21}(J+1) + P_1(J+2) \\ &\quad - R_1(J) - {}^R Q_{21}[R_1](J+1) - {}^R Q_{21}[R_1](J+2) \}. \end{aligned} \right\} \quad (15)$$

TABLE 7. THE ROTATIONAL CONSTANTS FOR NCO $X(^2\Pi_i)$ (cm^{-1})

level 0, 0 ¹ , 0 ($^2\Pi_i$)	$B''_{0,0^1,0} = 0.38940 \pm 0.00004$	$(A'' - 2B'')_{0,0^1,0} = -96.37 \pm 0.02$
	$D''_{0,0^1,0} = 0.14_9 \times 10^{-6}$	$A''_{0,0^1,0} = -95.59 \pm 0.02$
	$^2\Pi_{\frac{3}{2}}; p \simeq 0.002$	
level 0, 1 ⁰ , 0 ($^2\Sigma^+$)	$B''_v = 0.39120 \pm 0.00005$	$\gamma''_v = \pm 0.118_3$
	$B''_v - B''_{0,0^1,0} = 180 \pm 7 \times 10^{-5}$	
level 0, 1 ² , 0 ($^2\Delta_i$)	$B''_v - B''_{0,0^1,0} = 106 \pm 2 \times 10^{-5}$	$[(A'' - 2B'') \Lambda]''_v = -95.70 \pm 0.02$
		$(A\Lambda)''_v = -94.92 \pm 0.02$
level 0, 2 ³ , 0 ($^2\Phi_i$)	$[(A'' - 2B'') \Lambda]''_v = -94.65 \pm 0.10$	$(A\Lambda)''_v = -93.87 \pm 0.10$

(The branches in square brackets, [], are main branches coincident with the satellite branches for which these equations are derived). Mean values of the right-hand side of these equations were taken from the bands 00^00 and $00^01 \leftarrow 00^10$, and are plotted against $(J+1)$

FIGURE 6. Λ -doubling in the ground state level $00^10(^2\Pi_i)$ of NCO.

in figure 6. It is seen that there is no significant Λ -type doubling in the lower energy sublevel, ($\phi_1(J) = 0$), but that a small doubling of the order of magnitude of

$$2\phi_2(J) = 0.002(J'' + \frac{1}{2}) \text{ cm}^{-1}$$

is present in the higher energy sublevel, which is therefore $^2\Pi_{\frac{3}{2}}$. Thus the $^2\Pi(a)$ state is inverted.

Values of $F''_2(J) - F''_1(J)$ can be obtained from the separations of lines in subbands involving $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{\frac{3}{2}}$, and can be used not only to determine the spin splitting constant A'' but also to test the validity of the Hill & Van Vleck spin decoupling expression (equation (6))

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for a polyatomic molecule. For the present case $A'' \gg B''(J + \frac{1}{2})$ and $\Lambda = 1$, and the square root of equation (6) can be expanded

$$F_2''(J) - F_1''(J) = |A'' - 2B''| + \frac{2B''^2}{|A'' - 2B''|} (J - \frac{1}{2})(J + \frac{3}{2}) - \frac{2B''^4}{|A'' - 2B''|^3} (J - \frac{1}{2})^2 (J + \frac{3}{2})^2. \quad (16)$$

Values of the left-hand side of this equation were obtained from six branches in each of the bands $00^0 0$, $10^0 0$, $02^0 0$ and $00^0 1 \leftarrow 00^1 0$, corrected for the Λ -type doubling determined above. To these were added values for the small term in $(J - \frac{1}{2})^2 (J + \frac{3}{2})^2$, calculated from a provisional value of A'' , and a plot of the resultant wave numbers against $(J - \frac{1}{2})(J + \frac{3}{2})$ was found to give a straight line. By least squares the intercept was found to be

$$|A'' - 2B''|_{00^1 0} = 96.37 \text{ cm}^{-1}$$

and the slope $316.0 \times 10^{-5} \text{ cm}^{-1}$. This slope is to be compared with

$$[2B''^2/|A'' - 2B''|]_{00^1 0} = 314.7 \times 10^{-5} \text{ cm}^{-1};$$

that is, equation (16) is a good representation of the spin uncoupling in the $00^1 0(^2I_i)$ level of this polyatomic molecule.

(f) The origin of the band system

The origin ν_{00} of the $00^0 0 - 00^1 0$ band was obtained from the frequencies of lines in the well-resolved branches by the equation

$$\begin{aligned} \text{or } \left. \begin{aligned} [{}^0P_{12}(J) + {}^S R_{21}(J) - \phi_2(J)] \\ [R_2(J) + P_1(J) + \phi_2(J)] \end{aligned} \right\} + 2(D' - D'')(J + \frac{1}{2})^4 \\ = [2\nu_{00} + B'' + 2B' + D'' - 4D'] + 2[B' - B'' - 13D' - D''](J + \frac{1}{2})^2. \quad (17) \end{aligned}$$

The intercept of a plot of the left-hand side of this equation against $(J + \frac{1}{2})^2$ yielded $\nu_{00} = 22753.98 \text{ cm}^{-1}$, and the slope of this line gave a check on the consistency of the determinations of B' and B'' . From this plot, $(B' - B'') = 1269.6 \times 10^{-5} \text{ cm}^{-1}$; from independent determinations, $(B' - B'') = 1271.1 \times 10^{-5} \text{ cm}^{-1}$.

(g) The band $01^1 0(^2I_i) \leftarrow 01^2 0(^2\Delta_i)$

The 'hot' band $01^1 0 \leftarrow 01^2 0$ is very similar in structure to the $00^0 0 \leftarrow 00^1 0$ band (see figure 2) with the exception of line splitting due to the l -type doubling in the upper level. A plot of the line splitting in this band against $N'(N' + 1)$ gave essentially the same value of $q_{01^1 0}$ as was derived above from the band $01^1 0 \leftarrow 00^1 0$. Thus there is no measurable Λ -type doubling in the $^2\Delta_i$ level. The lower-state term value $G_0''(01^2 0)$ was obtained from the two bands $01^1 0 \leftarrow 00^1 0$ and $01^1 0 \leftarrow 01^2 0$ in a manner similar to that described above for the upper state, using lines of common N' . The wave number differences $\Delta\nu''$ were plotted against $(J'' + \frac{1}{2})^2$ and the branches in the two pairs of subbands gave two different lines separated by about 0.68 cm^{-1} , indicating that the spin splitting $(A\Lambda)_v$ is slightly different in the two states $01^2 0$ and $00^1 0$. The mean intercept yields $G_0''(01^2 0) = 533.55 \text{ cm}^{-1}$ and the mean slope $(B_{01^2 0} - B_{00^1 0}) = 106 \times 10^{-5} \text{ cm}^{-1}$. The spin splitting $(A\Lambda)_{01^2 0}$ was determined more accurately from $F_2''(J) - F_1''(J)$ using the same method as for the $00^1 0$ level. The Hill & Van Vleck equation was again found adequate for the spin uncoupling; the slope of the

plot of $F_2''(J) - F_1''(J)$ against $(J - \frac{1}{2})(J + \frac{3}{2})$ (see equation (16)) being found by least squares to be $325 \times 10^{-5} \text{ cm}^{-1}$ compared with

$$[2B''^2/A'' - 2B'']_{01^20} = 319 \times 10^{-5} \text{ cm}^{-1}.$$

Although this is a poorer agreement than that for the 00^10 level the values of $F_2''(J) - F_1''(J)$ were not obtained to such high J values, and the difference is not significant. In both these levels 00^10 and 01^20 it was found that a considerably poorer fit of the data was obtained using the more usual form of the Hill & Van Vleck equations (see subsection (a) above).

(h) *The band $01^10(2II) \leftarrow 01^00(2\Sigma^+)$*

From figure 2 we see that this band has three heads separated by only 15 cm^{-1} . The lower level is vibronically $2\Sigma^+$, but it arises from $l = 1$ and $\Lambda = 1$, and it would not be surprising if it showed an anomalous spin splitting. On the violet side of the 4348 \AA head two series of lines were picked out and were assigned to the R_1 and R_2 branches. The upper-level combination differences $\Delta_2 F'(N)$ were known from the analysis of the band $01^10 \leftarrow 00^10$. By adding these differences to the wave numbers of the P heads and comparing these wave numbers with those of the R branch lines it was possible to determine the N numbering in the R branches, and then to assign those P branch lines that are resolved in the intervals between the heads. The l -type doubling in the upper level of this band does not cause a line splitting. Instead, the Q branch transitions involve the lower l -type components

$$(B'_{\text{effective}} = B'_{01^10} - \frac{1}{2}q_{01^10})$$

and the P and R branch transitions involve the upper components

$$(B'_{\text{effective}} = B'_{01^10} + \frac{1}{2}q_{01^10});$$

a situation analogous to that in the infra-red band ν_2 of CO_2 . This was noted in the calculation from the R branch lines of the expected Q branch frequencies using calculated upper level combination differences $\Delta_1 F'(N)$. Many Q lines of high N were assigned in this way (see table 8).

The spin splitting in the lower level 01^00 was determined from the separations of pairs of lines of the same N in the two P , Q or R branches, and is plotted against $(N'' + \frac{1}{2})$ in figure 7. The splitting is definitely linear in N , and yields $|\gamma''| = 0.118_3 \text{ cm}^{-1}$. This is anomalously large, amounting to 30 % of the B value in this level.

Presumably this large splitting arises in the following way: in the lowest vibrational level 00^10 the magnetic field produced by the orbital angular momentum $\Lambda h/2\pi$ of the electrons gives rise to a spin splitting $A = -96 \text{ cm}^{-1}$. In the $N = 0$ rotational level of the vibrational level $01^00(2\Sigma^+)$ the vibrational angular momentum $lh/2\pi$ and the electronic angular momentum $\Lambda h/2\pi$ compound to give a resultant angular momentum about the inter-nuclear axis of $Kh/2\pi = 0$. The magnetic field associated with Λ is therefore no longer coupled to the axis of the molecule, and its time average in any direction is zero. As a result the spin vector S does not interact with this magnetic field, and there is no spin splitting; this is usual in a 2Σ level. When $N > 0$ the molecular rotation tends to decouple l and Λ , causing a component of magnetic field in the direction of N which is proportional to the rotational velocity (which in turn is proportional to $[N(N+1)]^{\frac{1}{2}} \simeq (N + \frac{1}{2})$). This magnetic field causes a magnetic coupling between S and N , giving rise to a spin splitting $\gamma(N + \frac{1}{2})$.

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The anomalously large value of γ is understandable, as the magnetic field associated with Λ is large (since A is large) and the coupling energy of l and Λ is only of order ω_2'' , being vibrational rather than electronic in origin.

The B'' value for this band was determined by converting the frequencies of all observed lines in the band into Q branch frequencies using the calculated upper level combination differences $\Delta_1 F'(N)$ and plotting against $N''(N''+1)$. The effect of the spin splitting of the lower level was allowed for by adding $\frac{1}{2}|\gamma''|N''$ (calculated) to Q_1 frequencies and subtracting $\frac{1}{2}|\gamma''|(N''+1)$ from Q_2 frequencies. Allowance was also made for the difference in centrifugal

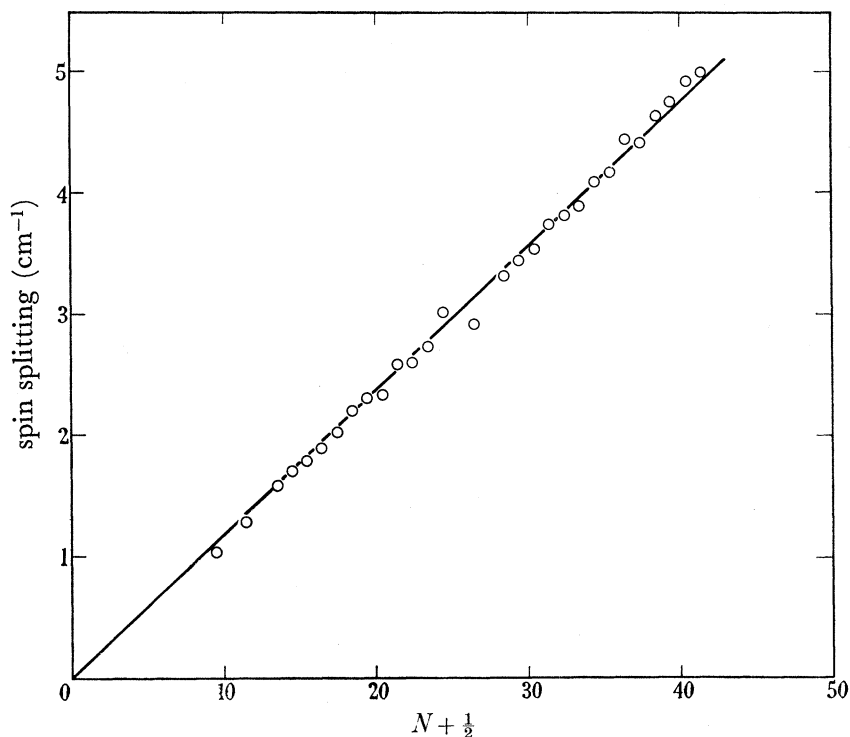


FIGURE 7. Spin splitting in the lower state level $01^0 0(2\Sigma^+)$ of NCO.

stretching in the two levels $(D' - D'') N^2(N+1)^2$. The slope of the line obtained in this way is $(B'_{01^1 0} - \frac{1}{2}q_{01^1 0} - B''_{01^0 0})$, and the intercept is the origin of the band. It is to be noticed from table 7 that there is an increase in the B'' value from $01^2 0(2\Delta_i)$ to $01^0 0(2\Sigma^+)$ of $74 \times 10^{-5} \text{ cm}^{-1}$, which is comparable with that from $00^1 0(2I_i)$ to $01^2 0(2\Delta_i)$ [$= 106 \times 10^{-5} \text{ cm}^{-1}$]. The vibrational-electronic interaction (Renner effect) therefore causes considerable perturbation of the rotational constants in levels of the same quantum number v_2 . Such a variation of B with K has also been observed in the spectrum of the NH_2 molecule (Dressler & Ramsay 1959).

(i) *The level $02^3 0(2\Phi_i)$*

Four bands were observed with lower level $02^3 0(2\Phi_i)$. Although these were too weak for the resolution of the rotational structure an estimate of the spin splitting

$$(A'' - 2B'')_{02^3 0} = -94.6_5 \text{ cm}^{-1}$$

was made from the separations of the Q_1 and P_2 heads in these bands. As these branches form heads at not too large J value ($14\frac{1}{2}$ – $27\frac{1}{2}$) the errors arising from an estimation of the B'' value in this level are not serious.

bending, and that very weakly. The three known states of CO_2^+ thus have the electron configurations

$$\left. \begin{aligned} &\dots(\sigma_u)^2 (\pi_u)^4 (\pi_g)^3 X(^2II_{gi}), \\ &\dots(\sigma_u)^2 (\pi_u)^3 (\pi_g)^4 A(^2II_{ui}), \\ &\dots(\sigma_u) (\pi_u)^4 (\pi_g)^4 B(^2\Sigma_u^+). \end{aligned} \right\} \quad (20)$$

The energies of the excited states of NCO are in the reverse order of that in CO_2^+ , and the relative binding energies of the molecular orbitals must therefore differ in NCO

$$\left. \begin{aligned} &\dots(\pi_1)^4 (\sigma)^2 (\pi_2)^3 X(^2II_i), \\ &\dots(\pi_1)^4 (\sigma) (\pi_2)^4 A(^2\Sigma^+), \\ &\dots(\pi_1)^3 (\sigma)^2 (\pi_2)^4 B(^2II_i). \end{aligned} \right\} \quad (21)$$

The suffixes 1 and 2 serve to distinguish the two π orbitals as the symmetry property g or u no longer has meaning.

The length of the CO bonds in the ground state of CO_2 is 1.162 \AA (Courtoy 1957), which is only 2% shorter than the mean bond length in NCO $A(^2\Sigma^+)$ ($\bar{r}_0 \leq 1.185 \text{ \AA}$), and therefore the absence of one σ electron does not affect the bond lengths very greatly. However, the mean bond length of NCO in the $X(^2II_i)$ state, ($\bar{r} \leq 1.204 \text{ \AA}$), is rather greater than that in the A state, and the red degradation of the 3160 \AA bands indicates that in the B state (2II_i) it is greater still. Thus one concludes that the effect on the bond lengths caused by an electron in each of the outer three NCO orbitals in equation (21) is

$$\left. \begin{aligned} &\sigma \text{ is weakly bonding,} \\ &\pi_2 \text{ is more bonding than } \sigma, \\ &\pi_1 \text{ is more bonding than } \pi_2. \end{aligned} \right\} \quad (22)$$

The similarity between the vibration constants of CO_2 $X(^1\Sigma_g^+)$ and NCO $A(^2\Sigma^+)$ is very striking, especially as regards the anharmonic constants (table 5), indicating how little an effect is caused by the absence of one σ electron. It is interesting to note that although the stretching frequencies ν'_1 and ν'_3 in NCO are slightly lower than in CO_2 (despite the slightly lighter mass), in agreement with the small drop in bonding, the bending frequency increases. The σ electron therefore has a weak tendency to bend the molecule. In contrast, the absence of a π_2 electron (NCO $X(^2II_i)$) causes a very considerable drop in the bending frequency.

The sign and order of magnitude of the coefficient ϵ of the Renner effect in the $X(^2II_i)$ state of NCO can be inferred from Walsh's diagrams, and agree with the observations. He shows that the $\pi_g (\equiv \pi_2)$ orbital splits into an $a_2 (\equiv a'')$ and a $b_2 (\equiv a')$ orbital on bending the molecule, and that the first of these orbitals has slightly more binding energy than the second. Thus the 2II state would split into a $^2A'$ state and a slightly higher energy $^2A''$ state on bending. As $^2A'$ is symmetrical with respect to the plane of the molecule and $^2A''$ is anti-symmetrical, Renner's coefficient ϵ should be negative and small (cf. table 3).

6. CONCLUSION

From the method of production of the spectrum described in this paper and the detailed vibrational and rotational analyses of the bands there can be no doubt about the assignment of the carrier to a linear NCO radical. The close similarity between the constants of the $A(^2\Sigma^+)$ state and those of the ground state of the CO_2 molecule is further evidence in favour

of the structure N—C—O, that is, the central atom in the molecule is a carbon atom. More conclusive evidence would be furnished by the study of an isotopically substituted radical.

In the NH_2 and HCO radicals the interaction between electronic and vibrational motion (Renner effect) is so strong as to split a Π state into one electronic state in which the molecule is linear, and another in which it is bent (Dressler & Ramsay 1959; Ramsay 1959). However, no spectrum has previously been analyzed in which the effects of a small splitting coefficient ϵ have been observed. An understanding of the results of such an interaction may lead to the assignment of many of the unexplained bands in the CO_2^+ spectrum (Mrozowski 1941-47).

The author wishes to thank Dr G. Herzberg, F.R.S., Dr A. E. Douglas and Dr D. A. Ramsay for many helpful discussions during this work. He is also indebted to the National Research Council for a postdoctorate fellowship, during the tenure of which this work was carried out.

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TABLE 1. BAND HEADS AND ASSIGNMENTS FOR THE SYSTEM $A(^2\Sigma^+) \leftarrow X(^2\Pi_i)$ OF NCO

λ (air) (Å)	ν (vac.) (cm ⁻¹)	int.	branch	assignment	
				upper level*	lower level
4483.63 ₆	22297.0 ₇	1	P_1	0, 0 ⁰ , 0 $^2\Sigma^+$	0, 1 ⁰ , 0 $^2\Sigma^+$
4482.83 ₄	22301.0 ₆	1	P_2	0, 0 ⁰ , 0 $^2\Sigma^+$	0, 1 ⁰ , 0 $^2\Sigma^+$
4408.98 ₅	22674.5 ₉	10	$^0P_{12}$	0, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4405.36 ₆	22693.2 ₂	1	P_2^\dagger	0, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4403.56 ₃	22702.5 ₁	100	P_2	0, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4389.00 ₂	22777.8 ₂	30	P_1	0, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4388.2 ₇	22781.6 ₆	1	P_1	0, 1 ¹ , 0 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^-$
4387.45 ₀	22785.8 ₈	1	P_2	0, 1 ¹ , 0 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^-$
4386.52 ₆	22790.6 ₈	1	Q_1^\dagger	0, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4384.79 ₁	22799.7 ₀	100	Q_1	0, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4374.98 ₃	22850.8 ₁	30	P_2	0, 1 ¹ , 0 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
4360.98 ₈	22924.1 ₄	5	P_1	0, 1 ¹ , 0 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
4360.77 ₂	22925.2 ₇	5			
4356.56 ₃	22947.4 ₂	30	Q_1	0, 1 ¹ , 0 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
4350.81 ₁	22977.7 ₆	10	P_1	0, 1 ¹ , 0 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^+$
4350.04 ₉	22981.7 ₉	20	P_2	0, 1 ¹ , 0 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^+$
4347.88 ₉	22993.2 ₀	30	Q_1	0, 1 ¹ , 0 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^+$
4346.48 ₀	23000.6 ₆	2	P_2	0, 2 ² , 0 $^2\Delta$	0, 2 ³ , 0 $^2\Phi_i$
4328.47 ₃	23096.3 ₄	5	Q_1	0, 2 ² , 0 $^2\Delta$	0, 2 ³ , 0 $^2\Phi_i$
4327.37 ₆	23102.2 ₂	1	?	?	?
4317.02 ₆	23157.5 ₈	1	?	?	?
4316.83 ₇	23158.6 ₀				
4314.15 ₃	23173.0 ₁	0	?	?	?
4309.45 ₀	23198.2 ₉	1	?	?	?
4275.35 ₈	23383.2 ₇	10	P_2	0, 1 ¹ , 0 $^2\Pi$	0, 0 ¹ , 0 $^2\Pi_i$
4261.68 ₉	23458.7 ₁	3	P_1	0, 1 ¹ , 0 $^2\Pi$	0, 0 ¹ , 0 $^2\Pi_i$
4261.50 ₃	23459.7 ₃	3			
4257.67 ₇	23480.3 ₇	10	$^0P_{21}$	0, 1 ¹ , 0 $^2\Pi$	0, 0 ¹ , 0 $^2\Pi_i$
4248.58 ₈	23530.6 ₁	2	P_2	0, 2 ² , 0 $^2\Delta$	0, 1 ² , 0 $^2\Delta_i$
4235.12 ₆	23605.4 ₀	1	P_1	0, 2 ² , 0 $^2\Delta$	0, 1 ² , 0 $^2\Delta_i$
4231.22 ₅	23627.1 ₆	2	$^0P_{21}$	0, 2 ² , 0 $^2\Delta$	0, 1 ² , 0 $^2\Delta_i$
4221.85 ₁	23679.6 ₂	0	P_2	0, 3 ³ , 0 $^2\Phi$	0, 2 ³ , 0 $^2\Phi_i$
4221.29 ₁	23682.7 ₆	2	P_1	0, 2 ⁰ , 0 $^2\Sigma^+$	0, 1 ⁰ , 0 $^2\Sigma^+$
4220.58 ₇	23686.7 ₁	2	P_2	0, 2 ⁰ , 0 $^2\Sigma^+$	0, 1 ⁰ , 0 $^2\Sigma^+$
4204.9 ₃	23774.9	0	Q_1	0, 3 ³ , 0 $^2\Phi$	0, 2 ³ , 0 $^2\Phi_i$
4166.93 ₆	23991.6 ₇	30	P_2	1, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4154.07 ₄	24065.9 ₇	10	P_1	1, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4150.25 ₂	24088.1 ₃	30	P_2	0, 2 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4150.09 ₅	24089.0 ₄	30	Q_1	1, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4144.40 ₃	24122.1 ₂	5	P_2	1, 1 ¹ , 0 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
4137.25 ₇	24163.7 ₉	10	P_1	0, 2 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4133.59 ₇	24185.1 ₈	30	Q_1	0, 2 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
4127.87 ₉	24218.6 ₅	5	Q_1	1, 1 ¹ , 0 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
4122.69 ₂	24249.1 ₆	10	$\{P_2$	0, 3 ¹ , 0 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
4122.63 ₁	24249.5 ₁				
4120.11 ₀	24264.3 ₅	3	Q_1	1, 1 ¹ , 0 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^+$
4106.32 ₀	24345.8 ₃	10	Q_1	0, 3 ¹ , 0 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
4101.23 ₁	24376.0 ₅	2	P_1	0, 3 ¹ , 0 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^+$
4100.57 ₃	24379.9 ₆	3	P_2	0, 3 ¹ , 0 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^+$
4098.64 ₁	24391.4 ₅	5	Q_1	0, 3 ¹ , 0 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^+$
4095.73 ₁	24408.7 ₈	1	P_2	0, 4 ² , 0 $^2\Delta$	0, 2 ³ , 0 $^2\Phi_i$
4079.80 ₉	24504.1 ₂	2	Q_1	0, 4 ² , 0 $^2\Delta$	0, 2 ³ , 0 $^2\Phi_i$
4055.00 ₈	24653.9 ₀	1	P_2	1, 1 ¹ , 0 $^2\Pi$	0, 0 ¹ , 0 $^2\Pi_i$
4039.01 ₃	24751.5 ₃	1	Q_1	1, 1 ¹ , 0 $^2\Pi$	0, 0 ¹ , 0 $^2\Pi_i$
4034.13 ₀	24781.4 ₉	2	P_2	0, 3 ¹ , 0 $^2\Pi$	0, 0 ¹ , 0 $^2\Pi_i$
4018.35 ₇	24878.7 ₆	2	Q_1	0, 3 ¹ , 0 $^2\Pi$	0, 0 ¹ , 0 $^2\Pi_i$
3992.59 ₆	25039.2 ₈	40	P_2	0, 0 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3981.45 ₇	25109.3 ₃	10	P_1	0, 0 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3977.05 ₇	25137.1 ₁	40	Q_1	0, 0 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$

* In the upper electronic state there is no observable spin splitting; that is the levels belong to Hund's case (b).

† Band of isotopic molecule N¹³CO.

TABLE I (cont.)

λ (air) (Å)	ν (vac.) (cm ⁻¹)	int.	branch	assignment	
				upper level*	lower level
3971.15 ₁	25174.5 ₀	15	P_2	0, 1 ¹ , 1 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
3956.72 ₇	25266.2 ₆	2	P_2	2, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3955.90 ₂	25271.5 ₄	20	Q_1	0, 1 ¹ , 1 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
3950.99 ₄	25302.9 ₃	2	P_2	0, 1 ¹ , 1 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^+$
3949.72 ₃	25311.0 ₇	1	P_2	0, 2 ² , 1 $^2\Delta$	0, 2 ³ , 0 $^2\Phi_i$
3948.64 ₀	25318.0 ₁	5	Q_1	0, 1 ¹ , 1 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^+$
3942.32 ₇	25358.5 ₅	4	P_2	1, 2 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3941.54 ₅	25363.5 ₈	2	Q_1	2, 0 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3934.74 ₆	25407.4 ₁	1	Q_1	0, 2 ² , 1 $^2\Delta$	0, 2 ³ , 0 $^2\Phi_i$
3927.25 ₇	25455.8 ₆	5	Q_1	1, 2 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3922.12 ₀	25489.2 ₀	1	P_2	0, 4 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3907.21 ₇	25586.4 ₂	2	Q_1	0, 4 ⁰ , 0 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3888.92 ₆	25706.7 ₆	2	P_2	0, 1 ¹ , 1 $^2\Pi$	0, 0 ¹ , 0 $^2\Pi_i$
3874.19 ₀	25804.5 ₇	2	Q_1	0, 1 ¹ , 1 $^2\Pi$	0, 0 ¹ , 0 $^2\Pi_i$
3800.31 ₉	26306.1 ₁	10	P_2	1, 0 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3786.96 ₆	26398.8 ₆	10	P_2	0, 2 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3786.21 ₅	26404.1 ₀	15	Q_1	1, 0 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3773.00 ₇	26496.5 ₃	15	Q_1	0, 2 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3752.20 ₁	26643.4 ₅	1	Q_1	0, 3 ¹ , 1 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
3655.06 ₇	27351.4 ₉	10	P_2	0, 0 ⁰ , 2 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3641.82 ₇	27450.9 ₂	20	Q_1	0, 0 ⁰ , 2 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3627.69 ₀	27557.9 ₀	0	P_2	2, 0 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3625.78 ₇	27572.3 ₆	1	Q_1	0, 1 ¹ , 2 $^2\Pi$	0, 1 ² , 0 $^2\Delta_i$
3619.52 ₅	27620.0 ₆	1	Q_1	0, 1 ¹ , 2 $^2\Pi$	0, 1 ⁰ , 0 $^2\Sigma^+$
3615.94 ₁	27647.4 ₄	0	P_2	1, 2 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3614.80 ₃	27656.1 ₄	0	Q_1	2, 0 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$
3603.14 ₃	27745.6 ₃	0	Q_1	1, 2 ⁰ , 1 $^2\Sigma^+$	0, 0 ¹ , 0 $^2\Pi_i$

* In the upper electronic state there is no observable spin splitting; that is the levels belong to Hund's case (b).

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TABLE 8. VACUUM WAVE NUMBERS AND LINE ASSIGNMENTS FOR THE BANDS OF NCO $A(^2\Sigma^+) \leftarrow X(^2II_i)$

J	Band 0, $0^0, 0 \leftarrow 0, 0^1, 0 (^2\Sigma^+ \leftarrow ^2II(a))$							
	$^0P_{12}$	$P_2(+^PQ_{12})$	$Q_2(+^RQ_{12})$	R_2	P_1	$Q_1(+^PQ_{21})$	$R_1(+^RQ_{21})$	$^S R_{21}$
$1\frac{1}{2}$	—	22 705.72*	22 706.55*	—	—	—	—	—
$2\frac{1}{2}$	—	705.35*	706.99*	—	—	22 801.73*	—	—
$3\frac{1}{2}$	—	705.01*	707.43*	—	—	801.40*	—	—
$4\frac{1}{2}$	—	704.66*	707.94*	—	22 798.79	801.07*	—	—
$5\frac{1}{2}$	22 701.22	704.39*	708.44*	—	797.71	800.84*	22 804.84*	—
$6\frac{1}{2}$	700.14	704.09*	708.98*	—	796.64	800.56*	805.45	—
$7\frac{1}{2}$	699.09	703.85*	709.52*	22 716.03	795.64	—	806.08	—
$8\frac{1}{2}$	698.06	703.61*	710.11	717.33	794.62	—	806.71	—
$9\frac{1}{2}$	697.04	—	710.70	718.70*	793.67	—	807.30	—
$10\frac{1}{2}$	696.05	—	711.31	720.19	792.72	—	807.99	—
$11\frac{1}{2}$	695.12	—	711.97	721.53	791.84	—	808.69	22 818.33*
$12\frac{1}{2}$	694.12	—	712.61	723.18*	790.94	—	809.42	819.91
$13\frac{1}{2}$	693.22	—	713.29	724.51	790.11	—	810.18	821.50*
$14\frac{1}{2}$	692.31	—	714.01	726.15*	789.28	head 22 799.70	810.99	823.02
$15\frac{1}{2}$	691.43	—	714.71	727.53	788.49	—	811.79	824.69
$16\frac{1}{2}$	690.57	—	715.49	729.15	787.73	—	812.61	826.20*
$17\frac{1}{2}$	689.72	—	716.25	730.65	786.98	—	813.51	827.99
$18\frac{1}{2}$	688.91	head 22 702.51	717.04	732.28	786.27	—	814.42	829.68
$19\frac{1}{2}$	688.10	—	717.86	733.90*	785.60	—	815.34	831.36*
$20\frac{1}{2}$	687.36	—	718.70*	735.53	784.94	—	816.32	833.18
$21\frac{1}{2}$	686.60	—	719.54	737.20	784.32	—	817.30	834.97
$22\frac{1}{2}$	685.87	—	720.42	738.84*	783.73	22 800.56*	818.33*	836.85*
$23\frac{1}{2}$	685.18	—	721.34	740.58	783.16	800.85*	819.35	838.58
$24\frac{1}{2}$	684.49	—	722.26	742.30	782.64	801.07*	820.40	840.49
$25\frac{1}{2}$	683.82	—	723.18*	744.05*	782.12	801.40*	821.50*	842.38
$26\frac{1}{2}$	683.18	—	724.17	745.80	781.63	801.73*	822.64	844.36
$27\frac{1}{2}$	682.54	—	725.16	747.62	781.19	802.07	823.79	846.28
$28\frac{1}{2}$	681.99	22 703.61*	726.15*	749.44	780.77	802.44	824.97	848.25
$29\frac{1}{2}$	681.42	703.85*	727.21	751.23*	780.37	802.84	826.20*	850.27
$30\frac{1}{2}$	680.86	704.09*	728.26	753.12	779.98	803.32	827.42	852.29
$31\frac{1}{2}$	680.34	704.39*	729.33	755.02	779.63	803.80	828.68	854.44*
$32\frac{1}{2}$	679.83	704.66*	730.48	756.91	779.34	804.28	829.97	856.43
$33\frac{1}{2}$	679.36	705.01*	731.57	758.84*	779.05	804.84*	831.36*	858.59
$34\frac{1}{2}$	678.88	705.35*	732.72	760.76	778.80	805.39	832.66	860.79
$35\frac{1}{2}$	678.46	705.72*	733.90*	762.75	778.56	805.91	834.04	862.95
$36\frac{1}{2}$	678.03	706.10	735.09	764.75	778.35	806.54	835.45	865.17
$37\frac{1}{2}$	677.66	706.55*	736.32	766.77	—	807.20	836.85*	867.45
$38\frac{1}{2}$	677.30	706.99*	737.55	768.78	—	807.83	838.35	869.62
$39\frac{1}{2}$	676.95	707.43*	738.84*	770.86	—	808.49	839.82	871.96
$40\frac{1}{2}$	676.62	707.94*	740.10	772.95	—	809.25	841.35	874.29
$41\frac{1}{2}$	676.30	708.44*	741.40	775.07	—	809.96	842.88	876.57
$42\frac{1}{2}$	676.05	708.98*	742.72	777.13	head 22 777.82	810.73	844.43	879.02
$43\frac{1}{2}$	675.79	709.52*	744.05*	—	—	811.50	846.10	881.35
$44\frac{1}{2}$	—	—	744.55	—	—	812.39	847.71	883.83
$45\frac{1}{2}$	—	—	746.84	—	—	813.22	849.37	886.26
$46\frac{1}{2}$	—	—	748.23	—	—	814.05	851.07	888.75
$47\frac{1}{2}$	—	—	749.68	—	—	815.05	852.77	891.27
$48\frac{1}{2}$	—	—	751.23*	—	—	815.96	854.44*	893.78
$49\frac{1}{2}$	—	—	752.66	—	—	816.90	—	896.35
$50\frac{1}{2}$	—	—	754.15	—	—	817.94	—	—
$51\frac{1}{2}$	—	—	755.69	—	—	818.96	—	—
$52\frac{1}{2}$	—	—	757.24	—	—	819.91*	—	—
$53\frac{1}{2}$	—	—	758.84*	—	—	820.84	—	—
$54\frac{1}{2}$	head 22 674.59	—	760.41	—	—	821.82	—	—
$55\frac{1}{2}$	—	—	762.02	—	—	—	—	—
$56\frac{1}{2}$	—	—	763.69	—	—	—	—	—
$57\frac{1}{2}$	—	—	765.33	—	—	—	—	—
$58\frac{1}{2}$	—	—	766.90	—	—	—	—	—
	—	—	768.40	—	—	—	—	—
	Band 1, $0^0, 0 \leftarrow 0, 0^1, 0 (^2\Sigma^+ \leftarrow ^2II(a))$							
$1\frac{1}{2}$	—	—	—	—	—	—	—	—
$2\frac{1}{2}$	—	—	23 996.79	—	—	—	—	—
$3\frac{1}{2}$	—	—	997.27	—	—	—	24 093.77*	—
$4\frac{1}{2}$	23 990.51	—	997.76	—	24 087.02	—	094.28*	—
$5\frac{1}{2}$	989.45	23 993.50	998.29	—	085.95	—	094.83	—
$6\frac{1}{2}$	988.36	993.19*	998.83	—	0.84.90	—	095.41	—
$7\frac{1}{2}$	987.34	992.89*	999.37	24 006.60	083.90	—	096.04*	—
$8\frac{1}{2}$	986.34	992.70*	999.96	007.93	082.92	—	096.65*	24 104.55
$9\frac{1}{2}$	985.31	—	24 000.56	009.39*	081.99	—	097.29*	—

* Denotes blended line.

TABLE 8 (cont.)

J	${}^0P_{12}$	$P_2(+{}^PQ_{12})$	$Q_2(+{}^RQ_{12})$	R_2	P_1	$Q_1(+{}^PQ_{21})$	$R_1(+{}^RQ_{21})$	${}^SR_{21}$
10 $\frac{1}{2}$	23 984.32	—	24 001.20	24 010.81	24 081.07	—	24 097.97*	24 107.53
11 $\frac{1}{2}$	983.36	—	001.84	—	080.19	—	098.66*	109.08
12 $\frac{1}{2}$	982.43	—	002.52	013.71	079.32	—	099.39*	110.68*
13 $\frac{1}{2}$	981.51	—	003.17	015.17	078.50*	—	100.14*	112.20
14 $\frac{1}{2}$	980.59	—	003.89	016.71	077.65*	head 24 089.04	100.91*	113.86*
15 $\frac{1}{2}$	979.73	—	004.61	018.20	076.85*	—	101.73*	115.39
16 $\frac{1}{2}$	978.85	—	005.34	019.78	076.10	—	102.58*	117.10*
17 $\frac{1}{2}$	978.04	—	006.12	021.27	075.37	—	103.46	118.70
18 $\frac{1}{2}$	977.22	head 23 991.67	006.91	022.93	074.68	—	104.37	120.45
19 $\frac{1}{2}$	976.44	—	007.72	024.57	074.02	—	105.32	—
20 $\frac{1}{2}$	975.63	—	008.55	026.17	073.40	—	106.28	123.88*
21 $\frac{1}{2}$	974.89	—	009.39	027.81	072.76*	—	107.26	125.73
22 $\frac{1}{2}$	974.18	—	010.28	029.50*	072.13*	—	108.30	127.52
23 $\frac{1}{2}$	973.46	—	011.17	031.17	071.58	—	109.32	129.38
24 $\frac{1}{2}$	972.76	—	012.09	032.89	071.04	—	110.38	131.22
25 $\frac{1}{2}$	972.08	—	013.02	034.65	070.56*	—	111.46*	133.17*
26 $\frac{1}{2}$	971.43	—	013.97	036.38	070.04*	—	112.60	135.05*
27 $\frac{1}{2}$	970.83	—	014.96	038.13	069.57	—	113.77	136.96*
28 $\frac{1}{2}$	970.25	23 992.70*	015.94	039.95	069.19	—	114.95*	138.89*
29 $\frac{1}{2}$	969.66	992.89*	016.96	041.76*	068.74*	—	116.11*	140.93
30 $\frac{1}{2}$	—	—	018.00	043.61	068.38	—	117.31	142.95
31 $\frac{1}{2}$	968.48	993.30	019.06	045.46	068.07*	24 092.86	118.56*	145.07
32 $\frac{1}{2}$	967.99	993.62	020.13	047.32	067.69	092.34*	119.85	147.11
33 $\frac{1}{2}$	967.51	993.91	021.27	049.23	067.44	093.83*	121.15	149.21
34 $\frac{1}{2}$	967.07	994.17	022.34	051.15	067.15	094.36*	122.49	—
35 $\frac{1}{2}$	966.52	994.57	023.52	053.15	066.92	094.91*	123.88*	—
36 $\frac{1}{2}$	966.14	994.89	024.64	055.06	066.67	095.47*	125.24	—
37 $\frac{1}{2}$	965.70	995.32	025.84	057.09	066.45	096.04*	126.65	—
38 $\frac{1}{2}$	965.32	995.71	027.06	059.04	—	096.65*	128.09	—
39 $\frac{1}{2}$	964.98	996.13	028.29	061.01	—	—	129.56*	—
40 $\frac{1}{2}$	—	996.62	029.50*	063.14	—	—	131.06	—
41 $\frac{1}{2}$	—	997.05	030.81	—	—	098.97	132.58	—
42 $\frac{1}{2}$	—	997.53	032.10	—	—	—	134.09	—
43 $\frac{1}{2}$	—	998.12	033.38	—	head 24 065.97	—	135.67	—
44 $\frac{1}{2}$	—	998.64	034.72	—	—	—	137.29*	—
45 $\frac{1}{2}$	—	999.18	036.08	—	—	—	138.89*	—
46 $\frac{1}{2}$	—	999.74	037.46	—	—	—	140.52*	—
47 $\frac{1}{2}$	—	24 000.30	038.89	—	—	—	—	—
48 $\frac{1}{2}$	—	000.86	040.25	—	—	—	—	—
49 $\frac{1}{2}$	—	001.58	041.76*	—	—	—	—	—
50 $\frac{1}{2}$	—	002.23	043.19	—	—	—	—	—

Band 0, 2⁰, 0 ← 0, 0¹, 0 (2Σ⁺ ← 2Π(a))

1 $\frac{1}{2}$	—	—	—	—	—	—	—	—
2 $\frac{1}{2}$	—	—	—	—	—	—	—	—
3 $\frac{1}{2}$	—	—	24 092.86*	—	—	—	24 189.28	—
4 $\frac{1}{2}$	—	—	093.34*	—	24 184.10	—	189.80	—
5 $\frac{1}{2}$	24 086.65	—	093.83*	—	183.03	—	190.33	—
6 $\frac{1}{2}$	085.51	—	094.36*	—	182.01	—	190.86	—
7 $\frac{1}{2}$	084.42	—	094.91*	—	180.98	—	191.43	—
8 $\frac{1}{2}$	083.46	—	095.47*	—	179.97	—	192.06	—
9 $\frac{1}{2}$	082.39	—	096.04*	—	179.00	—	192.70	—
10 $\frac{1}{2}$	081.42	—	096.65*	24 105.49	178.08	—	193.39	—
11 $\frac{1}{2}$	080.46	—	097.29*	—	177.19	—	194.10	—
12 $\frac{1}{2}$	079.49	—	097.97*	—	176.32	—	194.83	—
13 $\frac{1}{2}$	078.50*	—	098.66*	109.90	175.48	—	195.60	—
14 $\frac{1}{2}$	077.65*	—	099.39*	111.46*	174.66	—	196.40	—
15 $\frac{1}{2}$	076.85*	—	100.14*	112.94	173.88	head 24 185.18	197.22	—
16 $\frac{1}{2}$	076.02	—	100.92*	114.53	173.12	—	198.06	—
17 $\frac{1}{2}$	075.16	—	101.73*	116.11*	172.40	—	198.95	—
18 $\frac{1}{2}$	074.35	head 24 088.13	102.58*	117.68	171.70	—	199.87	24 215.16
19 $\frac{1}{2}$	073.48	—	103.31	119.33	171.02	—	200.79	—
20 $\frac{1}{2}$	072.76*	—	104.15	120.97*	170.39	24 185.57	201.77	218.65
21 $\frac{1}{2}$	072.13*	—	105.02	122.61	169.77	185.81	202.77	220.38
22 $\frac{1}{2}$	071.30	—	105.93	124.38	169.20	186.05	203.79	222.29
23 $\frac{1}{2}$	070.56*	—	106.85	126.03*	168.65	186.29	204.85	224.16*
24 $\frac{1}{2}$	070.04*	—	107.77	127.83	168.11	186.58	205.94	226.03
25 $\frac{1}{2}$	069.29	—	108.73	129.56*	167.62	186.90	207.04	227.96
26 $\frac{1}{2}$	068.74*	—	109.73	131.43*	167.18	187.24	208.19	229.92
27 $\frac{1}{2}$	068.07*	—	110.68*	133.17*	166.74	187.64	209.37	231.87
28 $\frac{1}{2}$	—	—	111.77	135.05*	166.32	188.03	210.58	233.85*
29 $\frac{1}{2}$	—	—	112.83	136.96*	165.95	188.46	211.79	235.89
30 $\frac{1}{2}$	—	—	113.86*	138.78	165.61	188.91	213.07	238.00
31 $\frac{1}{2}$	—	—	114.95*	140.66	165.29	189.39	214.36	240.04
32 $\frac{1}{2}$	—	—	116.11*	142.60	164.98	189.90	215.68	242.18
33 $\frac{1}{2}$	—	—	117.10*	144.55	164.72	190.44	216.97	244.35
34 $\frac{1}{2}$	—	—	118.56*	146.48	164.51	191.01	218.43	246.51
—	—	—	119.65	148.53	164.29	191.61	219.81	—

* Denotes blended line.

ABSORPTION SPECTRUM OF THE FREE NCO RADICAL

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TABLE 8 (cont.)

J	${}^0P_{12}$	$P_2(+{}^PQ_{12})$	$Q_2(+{}^Q R_{12})$	R_2	P_1	$Q_1(+{}^QP_{21})$	$R_1(+{}^RQ_{21})$	$S R_{21}$
35 $\frac{1}{2}$	—	—	24 120.97*	—	—	24 192.24	24 221.23	—
36 $\frac{3}{2}$	—	—	122.12	—	—	192.88	222.71	—
37 $\frac{5}{2}$	—	24 092.80	123.31	—	—	193.59	224.16*	—
38 $\frac{7}{2}$	—	093.29	124.66	—	—	194.29	225.72	—
39 $\frac{9}{2}$	—	093.77*	126.03*	—	—	195.05	227.28	—
40 $\frac{11}{2}$	—	094.28*	127.33	—	—	195.83	228.84	—
41 $\frac{13}{2}$	—	—	128.65	—	—	196.62	230.46	—
42 $\frac{15}{2}$	—	—	130.08	—	—	197.47	232.04	—
43 $\frac{17}{2}$	—	—	131.43*	—	head 24 163.79	198.32	233.85*	—
44 $\frac{19}{2}$	—	—	132.90	—	—	199.25	235.44	—
45 $\frac{21}{2}$	—	—	134.35	—	—	200.15	237.17	—
46 $\frac{23}{2}$	—	—	135.79	—	—	201.07	238.88	—
47 $\frac{25}{2}$	—	—	137.29*	—	—	—	—	—
48 $\frac{27}{2}$	—	—	138.89*	—	—	203.11	—	—
49 $\frac{29}{2}$	—	—	140.52*	—	—	204.14	—	—
50 $\frac{31}{2}$	—	—	141.97	—	—	205.26	—	—
51 $\frac{33}{2}$	—	—	—	—	—	206.26	—	—
52 $\frac{35}{2}$	—	—	—	—	—	207.42	—	—

Band 0, 0⁰, 1 ← 0, 0¹, 0 (${}^2\Sigma^+ \leftarrow {}^2\Pi(a)$)

1 $\frac{1}{2}$	—	—	25 044.62	—	—	—	—	—
2 $\frac{3}{2}$	—	—	045.06	25 047.40*	—	25 139.87*	25 141.47*	—
3 $\frac{5}{2}$	—	25 043.07	045.48	048.60	—	139.52*	141.92*	—
4 $\frac{7}{2}$	—	042.73	045.93	—	—	139.19*	142.39*	—
5 $\frac{9}{2}$	25 038.12	042.44	046.39	—	25 135.68	138.91*	142.88*	—
6 $\frac{11}{2}$	037.01	042.11	046.90	052.49	134.60	138.61*	143.41*	—
7 $\frac{13}{2}$	035.95	041.81	047.40	053.82	133.56	138.36*	143.94*	25 150.35
8 $\frac{15}{2}$	034.89	041.53	047.92	055.09	132.52	138.11*	144.51*	151.65
9 $\frac{17}{2}$	033.85	041.27	048.46	056.40	131.51	137.86*	145.09*	153.03*
10 $\frac{19}{2}$	032.82	041.01	049.01	057.68*	130.53	—	145.69*	—
11 $\frac{21}{2}$	031.82	040.77	049.58	059.20*	129.57	—	146.33*	155.85
12 $\frac{23}{2}$	030.85	040.55	050.16	060.52	128.64	—	146.99*	157.41
13 $\frac{25}{2}$	029.84	040.35	050.77	061.85	127.72	—	147.65*	158.82
14 $\frac{27}{2}$	028.86	040.17	051.37	061.40*	126.82	—	148.36*	—
15 $\frac{29}{2}$	027.93	—	052.01	063.77	125.96	—	149.07*	161.84
16 $\frac{31}{2}$	026.98	—	052.66	066.16*	125.08	—	149.83*	163.42
17 $\frac{33}{2}$	026.09	—	053.33	067.66	124.25	—	150.59	164.87
18 $\frac{35}{2}$	025.18	—	054.00	069.07*	123.46	head 25 137.11	151.38	166.54
19 $\frac{37}{2}$	024.30	—	054.71	070.64	122.67	—	152.19	168.16*
20 $\frac{39}{2}$	023.45	—	055.42	072.08	121.91	—	153.03*	169.77
21 $\frac{41}{2}$	022.60	—	056.14	073.64	121.18	—	153.87	171.43
22 $\frac{43}{2}$	021.73	—	056.89	075.18*	120.45	—	154.75	173.07*
23 $\frac{45}{2}$	020.93	—	057.68	076.75	119.75	—	155.66	174.76
24 $\frac{47}{2}$	020.12	head 25 039.28	058.42	078.34*	119.08	—	156.57	176.51
25 $\frac{49}{2}$	019.34	—	059.20	079.90	118.44	—	157.51	178.27*
26 $\frac{51}{2}$	018.58	—	060.03	081.51	117.81	—	158.49	180.01
27 $\frac{53}{2}$	017.83	—	060.85	083.13	117.18	25 137.86*	159.48	181.77
28 $\frac{55}{2}$	017.10	—	061.70	084.77	116.62	138.11*	160.47	183.63
29 $\frac{57}{2}$	016.37	—	062.56	086.41	116.05	138.36*	161.51	185.39
30 $\frac{59}{2}$	015.68	—	063.40	088.08	115.51	138.61*	162.57	187.27
31 $\frac{61}{2}$	015.01	—	064.32	089.77	115.01	138.91*	163.65	189.14
32 $\frac{63}{2}$	014.33	—	065.22	091.48	114.51	139.19*	164.75	191.05
33 $\frac{65}{2}$	013.66	—	066.16*	093.19	114.04	139.52*	165.87	192.91
34 $\frac{67}{2}$	013.03	—	067.09	094.98	113.58	139.87*	167.01	194.87
35 $\frac{69}{2}$	012.40	—	068.05	096.71	113.15	140.25	168.16*	196.89
36 $\frac{71}{2}$	011.82	—	069.07*	098.43	112.77	140.64	169.36	198.85
37 $\frac{73}{2}$	011.22	—	070.00	100.23	112.37	141.05	170.56	200.86
38 $\frac{75}{2}$	010.65	—	071.01	102.03	112.01	141.47*	171.79	202.83
39 $\frac{77}{2}$	—	—	072.03*	103.87	111.67	141.92*	173.07*	204.93
40 $\frac{79}{2}$	—	—	073.06	105.66	111.33	142.39*	174.35	207.04
41 $\frac{81}{2}$	—	—	074.11	107.47	111.07	142.88*	175.62	209.09
42 $\frac{83}{2}$	—	—	075.18*	—	110.80	143.41*	176.92	211.18
43 $\frac{85}{2}$	—	—	076.28	—	110.54	143.94*	178.27*	213.27
44 $\frac{87}{2}$	—	—	077.37	—	—	144.51*	179.63	—
45 $\frac{89}{2}$	—	—	078.34*	—	—	145.09*	181.03	—
46 $\frac{91}{2}$	—	—	079.63	—	—	145.69*	182.40	—
47 $\frac{93}{2}$	—	—	080.79	—	—	146.33*	183.79	—
48 $\frac{95}{2}$	—	—	081.95	—	—	146.99*	—	—
49 $\frac{97}{2}$	—	—	083.13*	—	—	147.65*	—	—
50 $\frac{99}{2}$	—	—	084.36	—	—	148.36*	—	—
51 $\frac{101}{2}$	—	—	085.57	—	—	149.07*	—	—
52 $\frac{103}{2}$	—	—	086.78	—	—	149.83*	—	—
					head 25 109.33			

Band 0, 0⁰, 2 ← 0, 0¹, 0 (${}^2\Sigma^+ \leftarrow {}^2\Pi(a)$)

1 $\frac{1}{2}$	—	—	—	—	—	—	—	—
2 $\frac{3}{2}$	—	—	—	—	—	—	—	—
3 $\frac{5}{2}$	—	—	—	—	—	—	—	—
4 $\frac{7}{2}$	—	—	27 361.40	—	—	—	27 457.43	—
5 $\frac{9}{2}$	—	—	361.86	—	—	—	457.91	—
							458.32	—

* Denotes blended line.

TABLE 8 (cont.)

J	${}^0P_{12}$	$P_2(+PQ_{12})$	$Q_2(QR_{12})$	R_2	P_1	$Q_1(+QP_2)$	$R_1(+RQ_{21})$	${}^SR_{21}$
6½	—	—	27362·30	—	—	—	27458·86	—
7½	—	—	362·76	—	—	—	459·34	—
8½	—	—	363·25	—	27446·44	—	459·89	—
9½	—	—	363·76	—	445·35	—	460·43	—
10½	27347·74	—	364·25	—	444·36	—	461·00	—
11½	346·69	—	364·80	—	443·39	—	461·56	—
12½	345·52	—	365·30	—	442·42	—	462·18	—
13½	—	—	365·82	—	441·41	—	462·82	—
14½	—	—	366·37	—	440·44	—	463·43	—
15½	—	—	366·92	—	439·48	—	464·05	—
16½	—	—	367·47	—	438·61	—	464·73	—
17½	—	—	368·05	—	437·73	—	465·40	—
18½	—	—	368·60	—	436·80	—	466·10	—
19½	—	—	269·20	—	435·93	—	466·80	—
20½	—	—	369·82	—	435·00	—	467·54	—
21½	—	—	370·43	—	434·25	—	468·27	—
22½	—	—	371·03	—	433·43	—	469·06	—
23½	—	—	371·67	—	432·66	head 27450·92	469·83	—
24½	—	—	372·31	—	431·86	—	470·58	—
25½	—	—	372·95	—	—	—	471·41	—
26½	—	—	373·66	—	—	—	472·24	—
27½	—	—	374·29	—	—	—	473·15	—
28½	—	—	374·96	—	—	—	473·91	—
29½	—	—	375·63	—	—	—	474·75	—
30½	—	—	376·34	—	—	—	475·67	—
31½	—	—	377·08	—	—	—	476·57	—
32½	—	—	377·75	—	—	—	477·49	—
33½	—	—	—	—	—	—	478·45	—
34½	—	—	—	—	—	—	479·40	—
35½	—	—	—	—	—	—	480·39	—
39½	—	head 27351·49	—	—	—	—	—	—

Band 0, $I^1, 0 \leftarrow 0, 0^1, 0$ (${}^2II(b) \leftarrow {}^2II(a)$)

J	${}^0P_{12}$	QR_{12}	R_2	P_1	R_1	${}^SR_{21}$
1½	—	—	—	—	—	—
2½	—	—	—	—	23483·91	—
3½	—	—	—	—	484·33	23487·44
4½	23381·75	23388·82	—	23479·19	484·87	488·77
5½	380·63	389·26	—	478·16	485·42	490·16
6½	379·50	389·95	23396·44	477·07	485·99	—
7½	378·55	390·54	397·79	476·07	486·54	—
8½	377·47	391·16	399·22	475·09	487·18	494·29
9½	376·50	391·77	400·68	474·14	487·80	495·88*
10½	375·56	392·44	402·10	473·19	488·52	497·34
11½	374·60	393·10	403·67*	472·29	489·23	498·86*
12½	373·68	393·78	405·11*	471·42	489·98	500·35*
13½	372·79	394·56	06·60	469·78	490·74	502·06*
14½	371·87	395·15	06·77*	469·02	491·55	503·63*
15½	371·07	396·05	07·93*	468·28	492·37	505·23
16½	370·25	396·86	09·72	467·55	493·17	506·83*
17½	69·42	69·68	11·43*	466·90	494·11	508·64*
18½	68·73	—	12·83*	466·22	495·10	510·22
19½	67·92	—	13·03	465·62	95·88*	96·02
20½	67·11*	67·70	14·42*	465·62	96·85	97·16
21½	66·51*	67·11*	16·04	465·62	96·85	97·16
22½	65·80*	66·51*	16·42*	465·62	96·85	97·16
23½	—	65·80*	17·75	465·62	96·85	97·16
24½	—	—	18·07*	465·62	96·85	97·16
25½	—	—	19·41*	465·62	96·85	97·16
26½	63·04*	—	21·13	465·62	96·85	97·16
27½	62·46*	63·04*	21·60	465·62	96·85	97·16
28½	61·94*	62·46*	22·88	465·62	96·85	97·16
29½	61·39*	61·94*	23·33*	465·62	96·85	97·16
30½	61·01*	61·39*	24·69	465·62	96·85	97·16
31½	—	61·01*	25·12	465·62	96·85	97·16
32½	—	—	26·42	465·62	96·85	97·16
33½	—	—	28·22	465·62	96·85	97·16
34½	—	—	30·00	465·62	96·85	97·16
35½	—	—	31·98	465·62	96·85	97·16
36½	—	—	32·63	465·62	96·85	97·16
37½	—	—	33·74	465·62	96·85	97·16
38½	—	—	35·64	465·62	96·85	97·16
39½	—	—	37·59	465·62	96·85	97·16
40½	—	—	39·53	465·62	96·85	97·16
41½	—	—	41·56	465·62	96·85	97·16
42½	—	—	43·44	465·62	96·85	97·16
43½	—	—	45·50	465·62	96·85	97·16

P_2 (head) = 23383·27 at $J = 17½$.

${}^2P_{21}$ (head) = 23480·37 at $J = 13½$.

* Denotes blended line.

PHILMATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
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 TRANSACTIONS OF
 SOCIETY A

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TABLE 8 (cont.)

Band $0, 1^1, 0 \leftarrow 0, 1^2, 0$ (${}^2\Pi(b) \leftarrow {}^2A(a)$)

J	${}^0P_{12}$	$Q_2(+Q_{R_{12}})$	R_2	P_1	$R_1(+R_{Q_{21}})$	$S_{R_{21}}$
$1\frac{1}{2}$	—	—	—	—	—	—
$2\frac{1}{2}$	—	22 855.46	—	—	—	—
$3\frac{1}{2}$	—	855.85	22 859.19	—	22 951.65	—
$4\frac{1}{2}$	—	856.32	—	22 946.48	952.15	—
$5\frac{1}{2}$	22 849.77	856.79	—	945.38	952.65	—
$6\frac{1}{2}$	—	857.40	—	944.34	953.21	—
$7\frac{1}{2}$	—	857.96	—	943.30	953.78	22 960.24
$8\frac{1}{2}$	845.34	—	—	942.30	954.41	—
$9\frac{1}{2}$	—	859.03	—	941.33	955.03	—
$10\frac{1}{2}$	843.32	859.66	—	940.39	955.69	—
$11\frac{1}{2}$	—	860.25	869.89	939.46	956.37	965.97*
$12\frac{1}{2}$	—	—	871.44*	938.58	957.08	—
$13\frac{1}{2}$	—	862.25	—	937.68	957.84	—
$14\frac{1}{2}$	—	—	—	936.88	958.63	970.68
$15\frac{1}{2}$	—	863.65	877.30	935.28	960.24	73.82* 74.00
$16\frac{1}{2}$	—	64.38 64.55	—	934.52	61.06 61.16	75.49 75.65*
$17\frac{1}{2}$	—	— 65.22	80.37	33.73 33.86	61.91 62.08	77.12
$18\frac{1}{2}$	836.15	65.88 66.11	82.05* 82.32*	33.04 33.18	62.84 63.01	—
$19\frac{1}{2}$	—	66.71 67.02	83.62	32.33 32.54	63.72 63.97	—
$20\frac{1}{2}$	34.50	— 67.79	85.23	31.69 31.90	64.63 64.96	—
$21\frac{1}{2}$	—	68.40 68.66	86.89	31.02 31.30	65.67 65.97*	—
$22\frac{1}{2}$	—	69.27	— 88.89	30.40 30.76	66.67 67.01	—
$23\frac{1}{2}$	32.31	70.07 70.48	90.18 90.67	29.86 30.22	67.66 68.07	—
$24\frac{1}{2}$	—	71.02 71.44*	91.94* 92.39	29.27* 29.76	68.73 69.16	—
$25\frac{1}{2}$	31.98	— 72.39	93.57* 94.16	28.76* 29.27*	69.82 70.26	—
$26\frac{1}{2}$	—	72.86 73.41	95.44 96.01	28.30* 28.76*	70.94 71.43	—
$27\frac{1}{2}$	—	73.86	97.17 97.73	27.86* 28.30*	72.13 72.59	—
$28\frac{1}{2}$	—	74.83 75.48	98.96	27.49* 27.86*	7.24 73.82*	—
$29\frac{1}{2}$	—	75.88	900.84 900.51*	26.99* 27.49*	74.43 75.03	—
$30\frac{1}{2}$	—	76.87 77.54	02.57 03.31	26.57* 27.18	75.65* 76.28	—
$31\frac{1}{2}$	—	77.94 78.65	— 05.21	26.24* 26.99*	76.91	—
$32\frac{1}{2}$	—	— 79.73	06.25 07.04	25.88* 26.57*	—	—
$33\frac{1}{2}$	—	80.11 80.87	08.27 09.09	25.57* 26.24*	—	—
$34\frac{1}{2}$	—	— 82.05*	10.13	—	—	—
$35\frac{1}{2}$	—	82.19*	—	—	—	—
$36\frac{1}{2}$	—	83.26 84.43*	—	—	—	—
$37\frac{1}{2}$	—	84.43* 85.65	—	—	—	—
$42\frac{1}{2}$	—	—	—	—	head 25.27	—
$43\frac{1}{2}$	—	—	—	—	—	—
$44\frac{1}{2}$	—	—	—	—	head 24.14	—

 $P_2(+P_{Q_{12}})$ (head) = 22850.81 at $J = 19\frac{1}{2}$. $Q_1(+Q_{P_{21}})$ (head) = 22947.42 at $J = 14\frac{1}{2}$.

* Denotes blended line.

TABLE 8 (cont.)

N	P_1	P_2	Q_1	Q_2	R_1	R_2
0	—	—	—	—	—	—
1	—	—	—	—	—	—
2	—	—	—	—	—	—
3	—	—	head 22993-20	—	—	—
4	—	—	—	—	—	—
5	22989-06*	—	—	—	—	—
6	—	22989-06*	—	—	—	—
7	—	—	—	—	—	—
8	986-93*	—	—	—	—	—
9	986-37*	987-40	—	—	—	—
10	—	986-93*	—	—	—	—
11	985-08*	986-37*	—	—	—	—
12	—	—	—	—	—	—
13	984-00*	—	—	—	23005-66*	23005-97*
14	—	985-08*	—	—	006-73	007-27*
15	—	—	—	—	007-90	008-40*
16	—	—	—	—	009-01	009-68
17	—	984-00*	—	—	010-15*	010-89*
18	—	—	—	—	011-28	012-14
19	981-10	—	—	—	012-48*	013-48*
20	—	—	—	—	014-91*	014-91*
21	—	—	—	—	013-74*	016-17*
22	980-04	—	—	—	014-91*	017-49*
23	—	—	—	—	016-17*	018-83*
24	—	—	—	—	017-49*	020-22*
25	—	—	—	—	018-83*	021-84
26	—	—	—	—	020-22*	—
27	—	—	—	23002-11*	021-63	024-57
28	—	—	—	002-88	—	026-08
29	—	—	—	—	024-32	027-64
30	—	—	—	—	025-76	029-19
31	—	head 22981-79	23002-11*	—	027-22	030-75
32	—	—	—	005-97*	028-70	032-31
33	—	—	—	006-73*	030-17	033-96
34	—	—	003-59	007-48	031-72	035-50
35	—	—	004-25	008-40*	033-26	037-27
36	head 22977-76	—	004-99	009-17	034-81	038-97
37	—	—	005-66*	010-15*	036-40	040-76
38	—	—	006-44	010-89*	038-03	040-41
39	—	—	007-27*	011-85	039-61	044-28
40	—	—	008-08	012-87	041-25	045-98
41	—	—	—	013-74*	042-93	047-87
42	—	—	009-88	014-91*	044-70	049-64
43	—	—	—	—	046-50	—
44	—	—	—	—	048-25	—
45	—	—	012-48*	—	—	—
46	—	—	013-48*	—	—	—
47	—	—	—	021-01	—	—

* Denotes blended line.

† In this band the branches are numbered correctly for γ positive. Should γ be negative the suffixes 1 and 2 to the branches would be reversed.

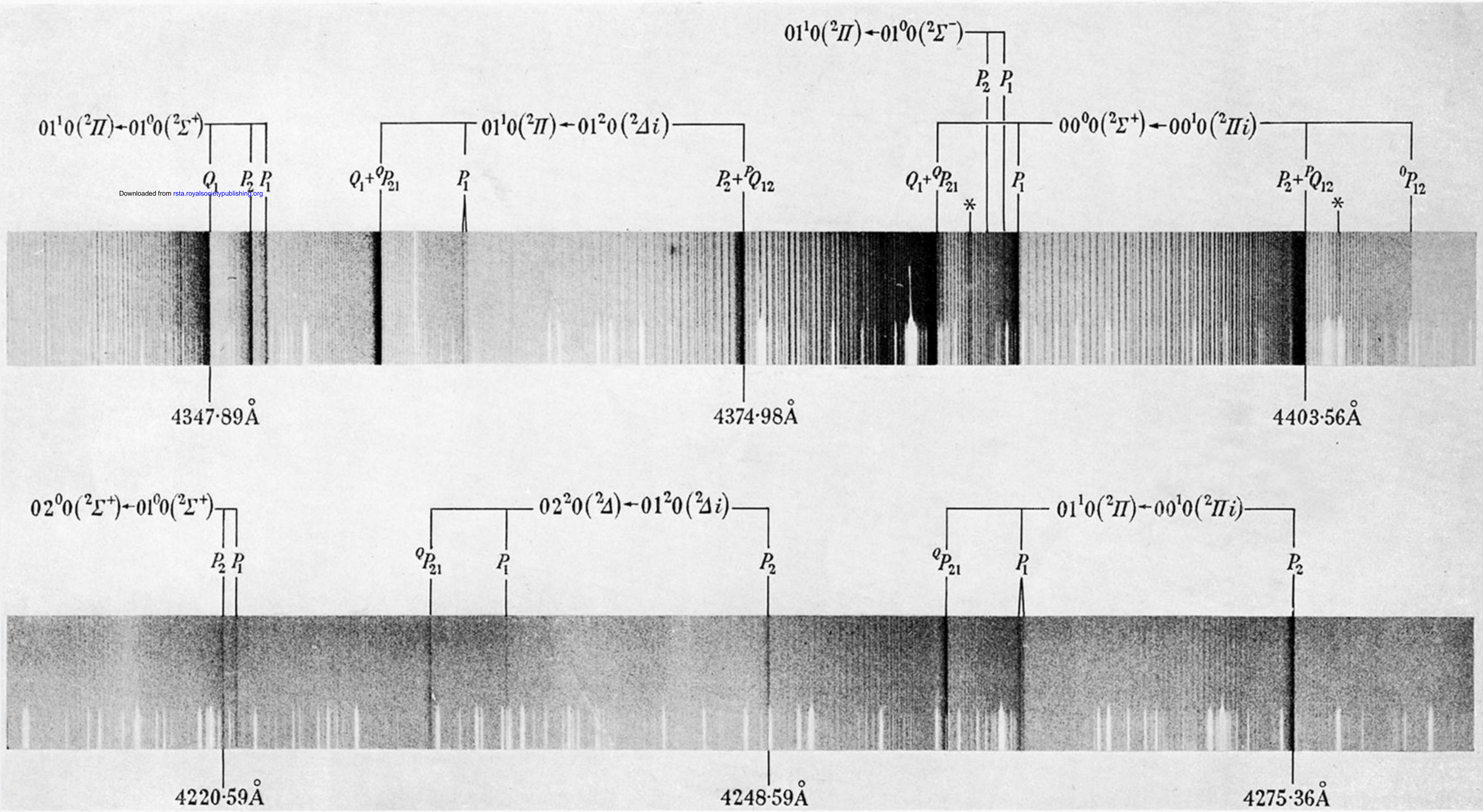


FIGURE 2. Two sections of the absorption spectrum of the NCO radical (* band heads of the isotopic molecule NC¹³O).

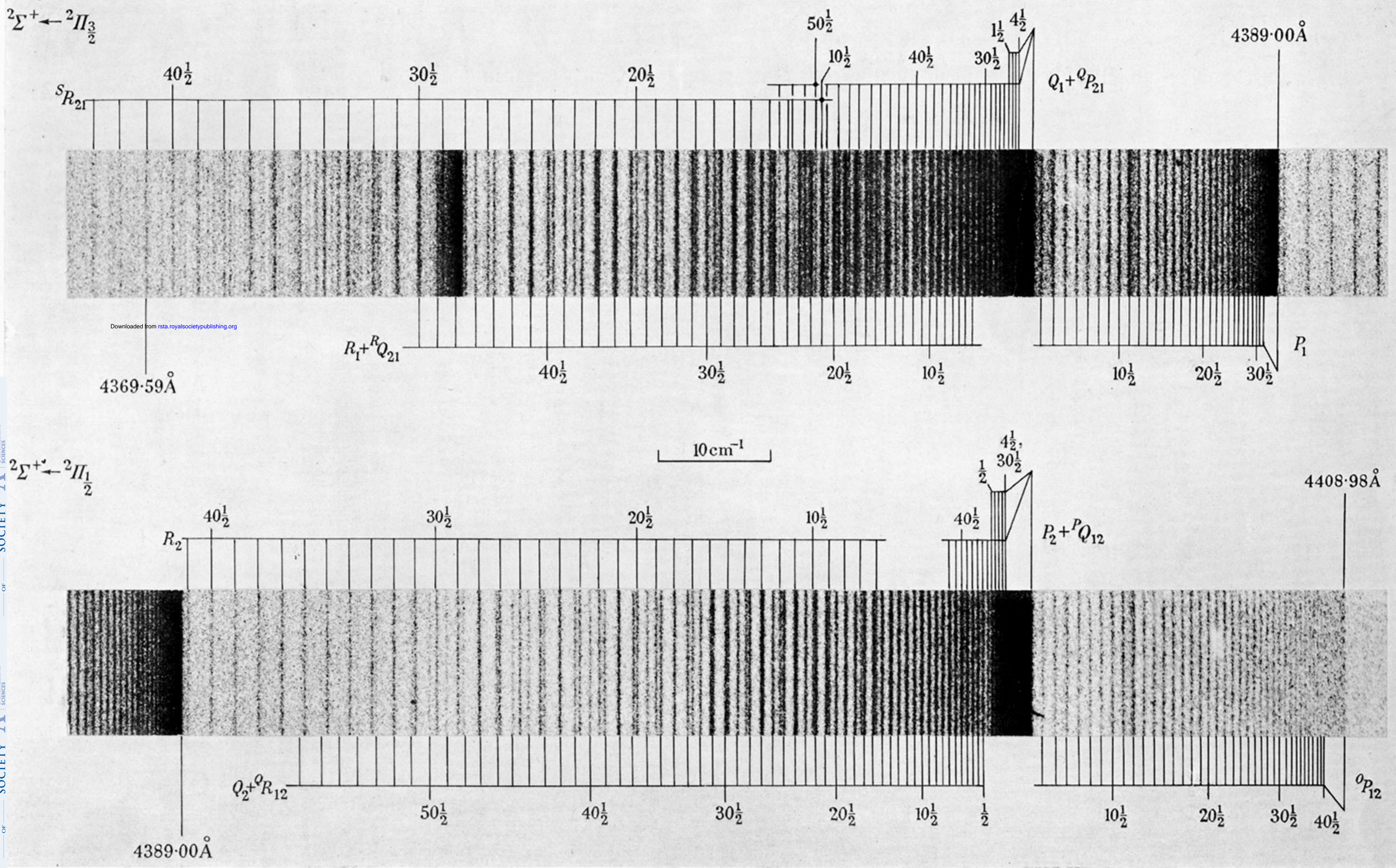


FIGURE 4. Line assignments for the $00^0 0 \leftarrow 00^1 0$ band of NCO.