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Identification and analysis of the perturbed $c(v = 1)-X$ and $k(v = 5)-X$ absorption bands of carbon monoxide

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Identification and analysis of the perturbed $c^3\Pi(v=1)-X^1\Sigma^+$ and $k^3\Pi(v=5)-X^1\Sigma^+$ absorption bands of carbon monoxide

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Two new red-degraded bands in the room-temperature vacuum-ultraviolet absorption spectrum of carbon monoxide have been identified in the 94 000–94 500 cm^{-1} energy region and analyzed. One of the bands at $\approx 94\,225\text{ cm}^{-1}$ (106.1 nm) has three observable bandheads and is partially overlapped with the strong $C^1\Sigma^+-X^1\Sigma^+$ (1–0) transition at lower energy. It is assigned to the $c^3\Pi-X^1\Sigma^+$ (1–0) transition. The other band at $\approx 94\,437\text{ cm}^{-1}$ (105.9 nm) with one clear bandhead is assigned to the $k^3\Pi-X^1\Sigma^+$ (5–0) transition. A strong homogeneous perturbation was found to exist between the two upper states that strongly influences the line positions and shapes of these bands. A rotational deperturbation analysis was performed and molecular rotational constants for both upper states were determined. These deperturbed molecular constants are entirely consistent with the expected values for the $k^3\Pi$ valence and $c^3\Pi$ Rydberg states. The Hamiltonian interaction term between these two states is found to be separable into vibrational and electronic factors and the electronic factor is determined to be $H_e=323\pm 40\text{ cm}^{-1}$. A discrepancy in the literature regarding the location of the $c^3\Pi(v=1)$ state is identified and discussed. © 2005 American Institute of Physics. [DOI: 10.1063/1.2136869]

INTRODUCTION

The $c^3\Pi$ Rydberg state of carbon monoxide is isoconfigurational with the better-known $E^1\Pi$ state with an electronic configuration consisting of a $2\Sigma^+ \text{CO}^+$ ionic core and a $3p\pi$ Rydberg electron. The triplet splitting in the $c^3\Pi$ state is weak and it is described approximately by Hund's coupling case b. Only the $v=0$ vibrational level is well known and its fluorescence to the $a^3\Pi$ valence state forms the well-known 3A band system.^{1–6} The $v=0$ level has also been observed in near-IR fluorescence to the $b^3\Sigma^+$ Rydberg state⁷ and in vacuum-ultraviolet (vuv) absorption from the ground state.^{8–10} It has also been observed in multiphoton absorption via the $a'^3\Sigma^+$ state.¹¹ It is moderately perturbed having an apparent anomalous sign of the centrifugal distortion constant. This perturbation is due to a homogeneous interaction with the $k^3\Pi(v=2)$ valence state.⁹ A recent reanalysis of the $c^3\Pi-b^3\Sigma^+$ (0–0) emission band has enabled a set of deperturbed molecular constants to be determined for the $c^3\Pi(v=0)$ state.¹²

There is less information available for the $v=1$ level of the $c^3\Pi$ state and what is available appears contradictory. Mazeau *et al.*¹³ in an electron-energy-loss study first reported the observation of this level. It was reported as being overlapped with the $C^1\Sigma^+(v=1)$ state with a similar electron-scattering cross section at threshold electron energies and

high scattering angles ($\vartheta=115^\circ$). Its position was located at $11.69\pm 0.01\text{ eV}$ above the $X^1\Sigma^+$ ground state, corresponding to a term value of $94\,285\pm 81\text{ cm}^{-1}$. [Note all term values in this article are referenced to the $X^1\Sigma^+(v=0)$ ground vibronic state unless specified otherwise]. More recently Hakalla^{14,15} has reported new but weak rotationally resolved bands in the 3A emission band system of $^{12}\text{C}^{16}\text{O}$ and its isotopomer $^{13}\text{C}^{16}\text{O}$. The upper state of these bands was assigned to the $c^3\Pi(v=1)$ state but only a partial rotational analysis was given, where it was reported that the state had an unidentified perturbation. An energy difference of $1775.7665\pm 0.0041\text{ cm}^{-1}$ between the $v=0$ and 1 levels for $^{12}\text{C}^{16}\text{O}$ was reported¹⁵ from which a $c^3\Pi(v=1)$ state term value of $93\,852\text{ cm}^{-1}$ can be derived. This value appears significantly different by about 430 cm^{-1} (0.05 eV) to that determined by Mazeau *et al.*¹³

The $k^3\Pi$ valence state also occurs in this energy region and, as mentioned above, the $v=2$ level of this state is responsible for the perturbation in the $v=0$ level of the $c^3\Pi$ state. There have been several spectroscopic studies on the $k^3\Pi$ valence state.^{16–21} Berden *et al.*²⁰ showed that the vibrational labeling of the $k^3\Pi$ state in studies prior to 1997 needed to be incremented by one unit. In that study metastable $a^3\Pi(v=1)$ state CO molecules were prepared predominantly in the $J=1$ rotational level via pulsed narrow-band laser excitation of jet-cooled ground-state CO molecules. The metastable molecules were passed into a chamber where they were ionized via the $k^3\Pi$ state in a

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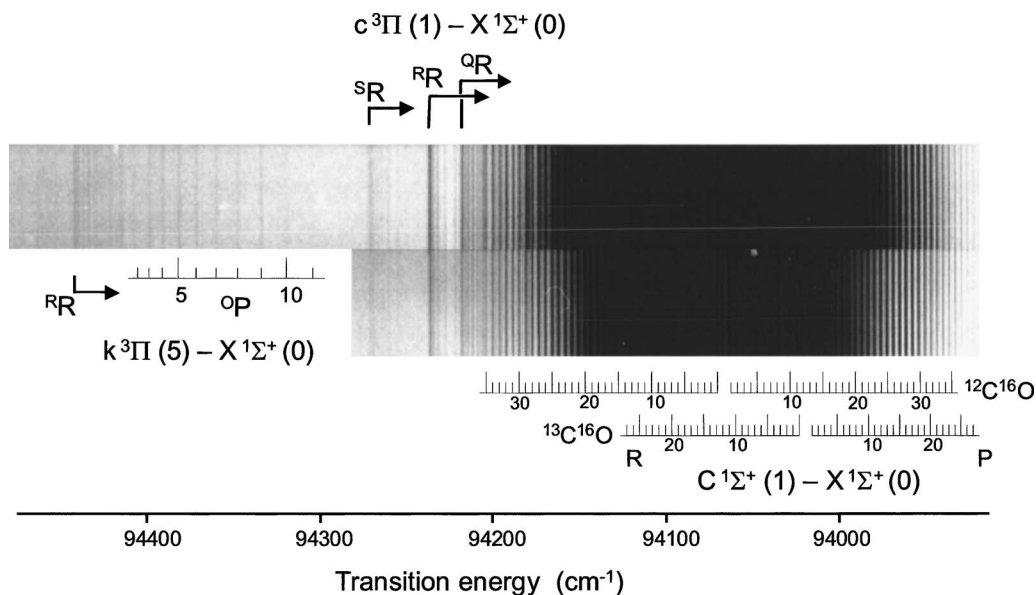


FIG. 1. Room-temperature absorption spectra of natural composition carbon monoxide over the 93 900–94 500 cm^{-1} transition energy range (105.82–106.49 nm) recorded at 0.5 (lower spectrum) and 1.5 Torr (upper spectrum). Indicated are the known $C^1\Sigma^+ - X^1\Sigma^+(1-0)$ transitions for $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ which form the most intense features in this spectral region. Also evident are two new weak bands, one labeled $k^3\Pi(v=5) - X^1\Sigma^+(v=0)$ at $\approx 94\,437\text{ cm}^{-1}$ and the other labeled $c^3\Pi(v=1) - X^1\Sigma^+(v=0)$ at $\approx 94\,225\text{ cm}^{-1}$. See text for further information.

1+1 resonance-enhanced multiphoton ionization (REMPI) process. For $^{12}\text{C}^{16}\text{O}$ three REMPI lines were attributed to $k^3\Pi(v=5)$ state resonances yielding a term value for this level of $94\,439\text{ cm}^{-1}$. Several unidentified REMPI lines were also observed and it was reported that the $k^3\Pi(v=5)$ state was perturbed and it was suggested that this could be due to an interaction with the $c^3\Pi$ state. Apart from that study there is no other published spectroscopic information on the $k^3\Pi(v=5)$ state.

In the present study we report on two new bands appearing in the room-temperature vuv absorption spectrum of carbon monoxide. These bands are weak, red degraded, and strongly perturbed. Their assignments are found to be consistent with ground-state transitions to the $c^3\Pi(v=1)$ and $k^3\Pi(v=5)$ states.

EXPERIMENT

Absorption spectra were photographed in first order using the 10.68 m vuv spectrograph at the Meudon Observatory with an effective total path length of 21.4 m and a resolution limit of 0.0008 nm. The spectra were calibrated by recording atomic emission lines from a windowless hollow-cathode lamp and two ArI absorption lines appearing in the background continuum of the vuv light source used. Further details of the vuv spectrograph, continuum source, and calibration procedure are given in Ref. 22. Natural isotopic composition carbon monoxide (99.997% purity) was introduced into the spectrograph and the pressure was varied from 0.07 to 1.5 Torr. The photographic plates (Kodak SWR) were measured by means of the Meudon Observatory photoelectric comparator,²³ which has an accuracy of about $1\ \mu\text{m}$ (the plate factor is about $2.5 \times 10^{-5}\text{ nm}/\mu\text{m}$). The photographic plates have approximately a logarithmic response to the transmitted light between the threshold and saturation regions of the plate.

RESULTS AND ANALYSIS

Figure 1 shows the room-temperature absorption spectra of natural composition carbon monoxide over the 93 900–94 500 cm^{-1} range recorded at 0.5 and 1.5 Torr. The known $C^1\Sigma^+ - X^1\Sigma^+(1-0)$ transition of $^{12}\text{C}^{16}\text{O}$ forms the most intense feature in this energy region with a band origin at $94\,065.6\text{ cm}^{-1}$.²⁴ Also evident is the $C^1\Sigma^+ - X^1\Sigma^+(1-0)$ band of the isotopomer $^{13}\text{C}^{16}\text{O}$, which has a natural abundance of ca. 1.1%, with a band origin that is displaced to lower energy by 47 cm^{-1} .²⁴ To higher energy new absorption lines are observed. In the 94 300–94 500 cm^{-1} transition energy region there appears to be a very weak band consisting of a branch that forms a bandhead and another branch with successive lines showing increasing separation. This is a red-degraded band indicating that the upper state has a smaller rotational constant than the $X^1\Sigma^+$ ground state and its weakness indicates a forbidden transition. It occurs in the energy region where the $k^3\Pi - X^1\Sigma^+(5-0)$ band might be expected.

Figure 1 also shows another set of new absorption lines to lower transition energy in the 94 150–94 280 cm^{-1} region. These absorption lines, although weak, are stronger by about a factor of 10 than the lines of the higher-energy band and lie near to and are partially overlapped with the R branch of the $C - X(1-0)$ band. Three closely spaced bandheads are observed each associated with a red-degraded rotational branch. The weakness of these branches is consistent with an assignment to another forbidden transition while the three bandheads indicate the possibility that the upper state is a triplet state with the branches associated with the same band. Below we show that this band can be assigned to the $c^3\Pi - X^1\Sigma^+(1-0)$ transition. We now consider the assignment of these two new bands.

Figure 2 gives a densitometer recording of the photographic plate for the 94 270–94 500 cm^{-1} energy region, showing the higher-energy band, which has an origin at

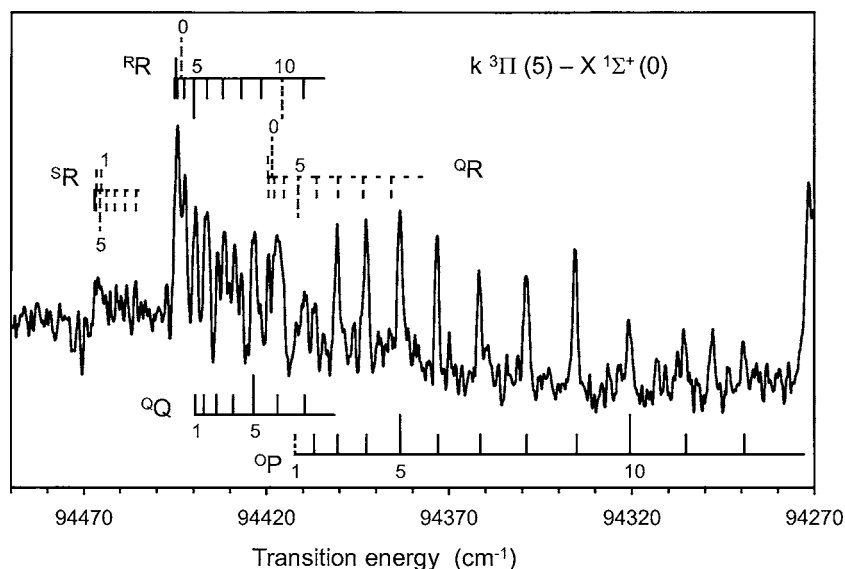


FIG. 2. Densitometer recording for the 94 270–94 500 cm^{-1} energy region recorded at 1.5 Torr showing the upper-energy band with the final branch assignments. Line positions that were not measured but are predicted (see later text) are indicated by dotted lines. Although no lines from the 3R branch were measured, the bandhead formed by this branch was identified and is evident in this figure. The region where the expected 2R bandhead is predicted is characterized by a partially resolved broad absorption feature.

$\approx 94\,437\text{ cm}^{-1}$. The densitometer recording has a lower resolution than the photographic plate and the noise is mainly associated with the granularity of the plate and the weakness of the absorption. As previously mentioned the band shown in Fig. 2 occurs in the energy region where the $k\ ^3\Pi-X\ ^1\Sigma^+(5-0)$ band is expected. A term value for the $k\ ^3\Pi(v=5)$ state of $T_{50}=94\,439\text{ cm}^{-1}$ can be derived from the work of Berden *et al.*²⁰ As described in the Introduction, Berden *et al.*²⁰ performed a 1+1 REMPI study on metastable $a\ ^3\Pi$ CO molecules. Three lines corresponding to 1+1 REMPI via the $k\ ^3\Pi(v=5)$ state of CO molecules, initially prepared in the $a\ ^3\Pi(v=1, J=1, \Omega=1, f\text{ parity})$ state, were identified and assigned. Six 1+1 REMPI lines were expected but only ionization via the $\Omega=1$ ($^3\Pi_1$) and 2 ($^3\Pi_2$) spin substates was assignable. However, these three lines were accompanied by six extra ionization lines, which were not assigned. Table I gives the term values of the three assigned upper-state levels of the $k\ ^3\Pi(v=5)$ state derived from Berden *et al.*²⁰

It seems clear that the new absorption band observed at $\approx 94\,437\text{ cm}^{-1}$ is assignable to the $k-X(5-0)$ transition. Its structure somewhat resembles the $k-X(3-0)$ and $k-X(4-0)$ absorption bands¹⁷ and it occurs in the correct transition energy region. The term values for the two rotational levels of the $^3\Pi_1$ spin substate derived from Berden *et al.* (see Table I) were used to determine a position of $94\,443.4\text{ cm}^{-1}$ for the

expected $^R R(0)$ branch line and to estimate a position of $94\,444.8\text{ cm}^{-1}$ for the $^R R(1)$ branch line, corresponding to ground-state transitions to the $J=1$ and 2 levels of the $k\ ^3\Pi_{1e}(5)$ substate, respectively. These positions lie within the location of the observed bandhead at $\approx 94\,445\text{ cm}^{-1}$, indicating the bandhead corresponds to the $^R R$ branch of the $k-X(5-0)$ transition. However, the rotational assignment of the band was a nontrivial matter because few branches were evident and only a few rotational lines could be followed within the branches before the intensity fell below the detection threshold. A $^3\Pi$ state consists of six substates; three spin states each split into two parity states. To confirm upper quantum state assignments one would ideally need to observe the same upper-state level in different branches, however, in this case it was not possible. Table II gives the measured line positions and final assignments for this band.

Figure 3 gives a densitometer recording of the photographic plate for the $94\,150\text{--}94\,280\text{ cm}^{-1}$ energy region, showing the lower-energy band with its distinctive three bandheads. There is some evidence to suggest that this band is assignable to the $c-X(1-0)$ band. The location of this new band relative to the $C-X(1-0)$ band is very similar to the location of the known $c-X(0-0)$ band relative to the $C-X(0-0)$ band, where the $c-X(0-0)$ band occurs on the high-energy side of the $C-X(0-0)$ band and is partially overlapped with the R branch. Since both the $c\ ^3\Pi$ and $C\ ^1\Sigma^+$ states are Rydberg in character with the same $X\ ^2\Sigma^+$ CO^+ ionic core, they would be expected to have similar $\Delta G_{1-0} = G(v=1) - G(v=0)$, vibrational energy-level separations and hence their relative band positions should be similar. For the $X\ ^2\Sigma^+$ state of CO^+ , $\Delta G_{1-0}=2184\text{ cm}^{-1}$,²⁵ while the $3p\sigma$, $C\ ^1\Sigma^+$ and $3p\pi$, $E\ ^1\Pi$ Rydberg states have values for ΔG_{1-0} of 2146 and 2153 cm^{-1} , respectively.²⁴ The observed band occurs at $\approx 2150\text{ cm}^{-1}$ to the higher-energy side of the $c-X(0-0)$ band.^{9,12} Hence, this provides a case for a $c-X(1-0)$ band assignment. However, the new band has a very different shape compared to the $c-X(0-0)$ band. Whereas the $c-X$

TABLE I. Term values derived from Berden *et al.* (Ref. 20) for the $k(v=5)$ state. All values are in units of cm^{-1} and term values are referenced to the $X\ ^1\Sigma^+(v=0)$ ground vibronic state. Values between parentheses are estimated errors. *o-c* signifies observed-calculated value for the final fit, see Table IV. Note that the extra line of $44\,223.51(08)$ given in Table III of Ref. 20, corresponding to a term value of $94\,416.56(11)\text{ cm}^{-1}$ is consistent with an assignment to the $^3\Pi_0[f_{1f}(J=0)]$ level with an *o-c* of -0.02 cm^{-1} . The $^3\Pi_0[f_{1f}(J=2)]$ and $^3\Pi_0[f_{1e}(J=1)]$ levels could not be identified from the extra lines given in Table III of Ref. 20.

Level	Term value	<i>o-c</i>
$^3\Pi_1[f_{2e}(J=1)]$	94 443.44(11)	0.05
$^3\Pi_1[f_{2f}(J=2)]$	94 448.67(11)	-0.08
$^3\Pi_2[f_{3f}(J=2)]$	94 469.20(11)	0.03

TABLE II. Line positions for the $k^3\Pi(v=5)-X^1\Sigma^+(v=0)$ transition. All values are in units of cm^{-1} . Values between parentheses are estimated errors. *o-c* signifies observed-calculated value for the final fit, see Table IV.

J	sR	<i>o-c</i>	$^R R$	<i>o-c</i>	$^Q Q$	<i>o-c</i>	$^O P$	<i>o-c</i>
0								
1			94 444.67(60) ^a	-0.20	94 439.69(50) ^a	0.13		
2			94 445.19(60) ^a	-0.01	94 436.91(50) ^a	-0.30	94 406.94(60)	-0.10
3	94 467.10(80) ^b	0.00	94 444.67(60) ^a	0.22	94 433.45(50)	-0.28	94 400.72(40)	0.24
4			94 442.74(40)	0.07	94 428.99(40)	-0.18	94 392.61(40)	0.02
5			94 439.69(50) ^a	-0.25	94 423.70(50)	0.13	94 383.37(40)	-0.05
6			94 436.30(60) ^a	-0.04	94 417.35(60)	0.33	94 373.08(40)	0.07
7			94 431.83(50)	-0.16	94 409.58(60) ^a	0.00	94 361.44(40)	0.02
8			94 426.78(50)	-0.23			94 348.69(40)	-0.06
9			94 421.79(50)	0.23			94 335.25(40)	0.17
10							94 320.56(40)	0.04
11			94 409.58(60) ^a	-0.38			94 305.33(50)	0.13
12							94 289.41(50)	0.14
13								

^aOverlapped lines.

^bFrom bandhead.

(0–0) band has one observable bandhead and is slightly blue degraded, the new band is significantly red degraded with three bandheads.

The rotational constants of the $v=0$ and 1 levels of the $X^2\Sigma^+$ ground state of CO^+ , representing the ionic core of these Rydberg states, are 1.967 46 and 1.948 46 cm^{-1} , respectively,²⁵ which are similar to but slightly greater than the rotational constant of 1.922 53 cm^{-1} for the $X^1\Sigma^+$ ground state of CO .²⁶ The rotational constants for the $v=1$ levels of the $3p\sigma$, $C^1\Sigma^+$ and $3p\pi$, $E^1\Pi$ Rydberg states are 1.923 90 and 1.939 89 cm^{-1} , respectively. Hence a ground-state transition to an unperturbed $3p\pi$, $c^3\Pi(v=1)$ state would be expected to form a band that was slightly blue degraded or not significantly degraded. If the new band was the $c-X(1-0)$ band, the $c^3\Pi(v=1)$ state would need to be significantly perturbed. The presence of the $k^3\Pi(v=5)$ state at higher energy will be shown to be the cause of this perturbation.

At this point it is worthwhile considering two previous studies that report the observation of the $c^3\Pi(v=1)$ state. The $c-X(1-0)$ assignment of this new band is consistent with the electron-energy-loss study of Mazeau *et al.*¹³ They assign a feature with a term value of $94\,285 \pm 81 \text{ cm}^{-1}$ to the $c^3\Pi(v=1)$ state, which compares with the location of the band at $\approx 94\,225 \text{ cm}^{-1}$ observed in our study. We do note, however, that their study lacked rotational resolution and the feature was overlapped with the electron-energy-loss feature associated with the $C^1\Sigma^+(v=1)$ state. Mazeau *et al.*¹³ also identified another feature at $94\,245 \pm 81 \text{ cm}^{-1}$ ($11.685 \pm 0.01 \text{ eV}$ —their feature *b*), under different electron energy and scattering angles, which can now be associated with the $k^3\Pi(v=5)$ state.^{16,20} The difference between their term value and the location of the $k-X(5-0)$ observed in this study at $\approx 94\,437 \text{ cm}^{-1}$ lies somewhat outside of the estimated experimental error by Mazeau *et al.*

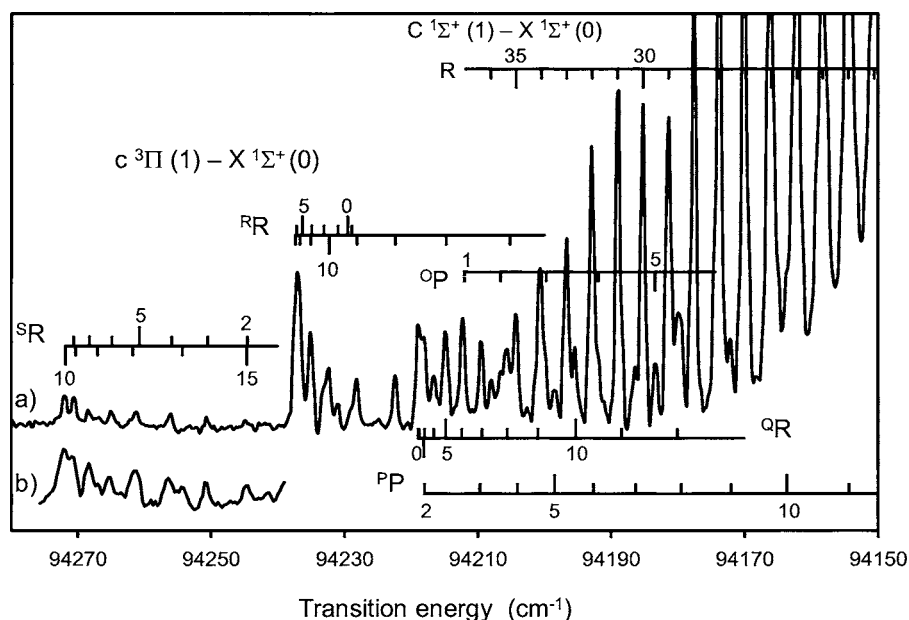


FIG. 3. Densitometer recording for the 94 150–94 280 cm^{-1} energy region recorded at (a) 0.5 Torr and (b) 1.5 Torr, showing the lower-energy band with the final branch assignments. Line positions that were not measured but are predicted (see later text) are indicated by dotted lines. This band is overlapped by the strong $C-X(1-0)$ band at lower transition energies.

The other study requires a more detailed consideration as it appears to be inconsistent with our study. This other study, by Hakalla, reported new but weak rotationally resolved bands in the 3A emission band system of $^{12}\text{C}^{16}\text{O}$ and its isotopomer $^{13}\text{C}^{16}\text{O}$, recorded in the ninth or tenth order of a 2 m Ebert spectrograph.^{14,15} The upper state of these bands was assigned to the $c^3\Pi$ ($v=1$) state but only a partial rotational analysis was given, where it was reported that the state had an unidentified perturbation. An energy difference of $\Delta G_{1-0}=1775.7665\pm 0.0041\text{ cm}^{-1}$ for $^{12}\text{C}^{16}\text{O}$ was reported (Table 6 of Ref. 15) from which a $c^3\Pi$ ($v=1$) state term value of $93\,852\text{ cm}^{-1}$ can be derived. However, we query this assignment as Hakalla's value of ΔG_{1-0} for the $3p\pi$, $c^3\Pi$ Rydberg state is significantly lower than what might be expected for such a Rydberg state, where a ΔG_{1-0} value in the range of $2100\text{--}2200\text{ cm}^{-1}$ would be expected. Although Hakalla does not consider this apparent discrepancy, it seems possible that a very strong homogeneous perturbation might explain such a low ΔG_{1-0} value, significantly shifting the $v=1$ level of the $c^3\Pi$ state relative to the $v=0$ level. If Hakalla's assignment was correct we might expect to observe a weak absorption band at around $93\,852\text{ cm}^{-1}$ which would place it to the lower-energy side of the $C\text{--}X$ ($1\text{--}0$) band which has a band origin of $94\,065.6\text{ cm}^{-1}$.²⁴ At such a location although part of the band might be overlapped with high- J lines of the P branch of the $C\text{--}X$ ($1\text{--}0$) transition, the majority of the band would be free from overlap and so we might have expected to observe it. However, under the experimental conditions of this study no new absorption lines in this region could be identified. Only the high- J P branch lines of the $C\text{--}X$ ($1\text{--}0$) band of $^{12}\text{C}^{16}\text{O}$ and its isotopomer $^{13}\text{C}^{16}\text{O}$ were clearly identifiable as well as an ArI absorption line at $106.665\,99\text{ nm}$ ($93\,750.60\text{ cm}^{-1}$) which was used as part of the calibration. Our lack of observation does not necessarily mean that the band does not exist as it would be a forbidden transition and its intensity would depend on the degree of "intensity borrowing" from neighboring allowed transitions. However, we shall show that the band that we observe at $\approx 94\,225\text{ cm}^{-1}$ is the $c\text{--}X$ ($1\text{--}0$) band and we therefore conclude that the new 3A band reported by Hakalla¹⁵ for $^{12}\text{C}^{16}\text{O}$ is not associated with the $c^3\Pi$ ($v=1$) state.

A $c\text{--}X$ ($1\text{--}0$) assignment for the new band at $\approx 94\,225\text{ cm}^{-1}$ would imply that the $c^3\Pi$ ($v=1$) state is significantly perturbed such that its effective rotational constant is reduced to a value significantly below that of the $X^1\Sigma^+$ ($v=0$) ground state. The $k^3\Pi$ ($v=5$) valence state, which would be at higher energy to the $c^3\Pi$ ($v=1$) state, could give rise to this effect. In this case a homogeneous perturbation would give rise to an increase in the effective rotational constant of the $k^3\Pi$ ($v=5$) state and a decrease in the effective rotational constant of the $c^3\Pi$ ($v=1$) state. This will be shown more clearly below. Berden *et al.*²⁰ determined a rotational constant for the $k^3\Pi$ ($v=5$) state and although only few lines were measured (three for $^{12}\text{C}^{16}\text{O}$ and eight lines for the $^{13}\text{C}^{16}\text{O}$ isotopomer), the effective rotational constants were shifted upwards by about 0.11 and 0.15 cm^{-1} for $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$, respectively, when compared to neighboring vibrational levels of the $k^3\Pi$ state.

Rotational assignment of the $94\,225\text{ cm}^{-1}$ band was, as for the $k\text{--}X$ ($5\text{--}0$) band, a nontrivial matter. Past spectroscopic studies of the $v=0$ level of the $c^3\Pi$ state show the state to be approximately of Hund's case b coupling and branches of the $c\text{--}X$ ($1\text{--}0$) band will be characterized by ΔN and ΔJ , where N and J are the electron spin and total, rotational quantum numbers, respectively, and the rotational branches are labeled as $^{\Delta N}\Delta J$. Considering the $94\,225\text{ cm}^{-1}$ band, it would be expected that the branch at highest transition energy would be the S -type ($\Delta N=2$) branch followed by R -type and Q -type branches (see Figs. 1 and 3). The branches appearing at lower transition energy (Q , P , and O -type branches) would be heavily overlapped with the $C\text{--}X$ ($1\text{--}0$) band. Assignment of branch lines was difficult due to this overlap with the $C\text{--}X$ ($1\text{--}0$) band and the perturbations in the upper state.

For both bands single rotational branches were first identified through basic Loomis-Wood-type procedures.²⁷ Then assuming upper-state assignments to the $k^3\Pi$ ($v=5$) and $c^3\Pi$ ($v=1$) states, based on the arguments presented above, a combined molecular fit was attempted (described in the next section). The final rotational assignments of branch lines were ultimately obtained through an iterative process involving fitting of the transition energies by weighted least-square variation of upper-state molecular constants. Figures 1–3 indicate these final assignments. Table III gives the measured line positions and final assignments for the $c\text{--}X$ ($1\text{--}0$) band.

FINAL ANALYSIS AND DISCUSSION

The transition energies of the absorption lines of the two new bands were fitted simultaneously. The two upper $^3\Pi$ states were each represented by the $^3\Pi$ Hamiltonian of Brown and Merer forming a 6×6 Hamiltonian in total for both e and f parity levels.²⁸ The homogeneous interaction between the two states was represented by the interaction term $\langle c^3\Pi_i(v=1)|H|k^3\Pi_i(v=5)\rangle = W$, where $i=0\text{--}2$.^{9,29} The three term values derived from Berden *et al.*²⁰ and given in Table I were included in the molecular fit in addition to the transition energies of the absorption lines measured and assigned in this study for the $k\text{--}X$ ($5\text{--}0$) and $c\text{--}X$ ($1\text{--}0$) bands and given in Tables II and III, respectively. The ground-state $X^1\Sigma^+$ molecular constants are well known, where $B=1.922\,528\,9\text{ cm}^{-1}$, $D=6.12\times 10^{-6}\text{ cm}^{-1}$, and $H=5.74\times 10^{-12}\text{ cm}^{-1}$, and were derived from Ref. 26.

The results of the weighted least-squares molecular fit are given in Table IV. The last column gives the final fit with the homogeneous perturbation taken into account. Columns A and B are for comparison purposes only and are the results of single band fits where the homogeneous perturbation was neglected. Consequently the parameters obtained in those fits represent effective molecular constants, whereas the parameters given in the last column represent the deperturbed molecular constants. Without including the homogeneous perturbation the molecular fit was poor, with many observed-calculated values falling significantly outside the estimated measurement error. When the homogeneous perturbation between the states was included, all observed-calculated values

TABLE III. Line positions for the $c^3\Pi(v=1)-X^1\Sigma^+(v=0)$ transition. All values are in units of cm^{-1} . Values between parentheses are estimated errors. $o-c$ signifies observed-calculated value for the final fit, see Table IV.

J	$^S R$	$o-c$	$^R R$	$o-c$	$^P P$	$o-c$	$^Q R$	$o-c$	$^O P$	$o-c$
0							94 218.05(80) ^a	-0.08		
1			94 228.90(40)	0.00			94 218.85(80) ^a	-0.11		
2	94 244.41(60) ^a	-0.09	94 230.96(40)	-0.01			94 218.85(80) ^a	0.05	94 206.61(50) ^a	0.01
3	94 250.40(40)	-0.05	94 233.00(50)	-0.07			94 218.05(80) ^a	0.06	94 199.81(80) ^a	0.07
4	94 255.96(40)	0.10	94 235.01(60) ^a	0.11			94 216.55(50)	-0.11	94 191.95(80) ^a	0.06
5	94 260.88(40)	0.20	94 236.85(70) ^a	0.55	94 198.37(40)	-0.10	94 214.82(50)	0.01	94 183.40(50)	0.01
6	94 264.78(40)	-0.05	94 237.15(70) ^a	0.00			94 212.25(50)	-0.15		
7	94 268.22(40)	0.03	94 237.15(70) ^a	-0.18	94 186.38(40)	0.05	94 209.38(50)	0.01		
8	94 270.47(60) ^a	-0.13	94 236.85(70) ^a	0.16			94 205.48(50) ^a	-0.12		
9	94 271.82(60) ^a	-0.07	94 235.01(60) ^a	-0.05	94 172.00(40)	0.01				
10	94 271.82(60) ^a	-0.04	94 232.31(40)	0.04	94 163.60(40)	-0.07	94 195.46(50)	0.16		
11	94 270.47(60) ^a	0.17	94 228.12(40)	0.02						
12	94 266.91(50)	-0.07	94 222.27(40)	-0.07	94 143.69(60) ^a	-0.22	94 179.88(50)	-0.19		
13	94 262.34(80)	0.63	94 214.82(70)	0.05						
14	94 254.16(60)	-0.14	94 205.48(50)	0.27						
15	94 244.41(60) ^a	-0.21								
16										

^aOverlapped lines.

fell within the estimated measurement error (these are given in Tables I–III). The second column of Table IV gives the molecular parameters for the $k^3\Pi(v=5)$ state as determined by Berden *et al.*²⁰ for comparison.

Including the homogeneous interaction results in significant changes to the molecular constants. For the $c^3\Pi(v=1)$

$=1$) state the rotational constant is increased from an effective value of $1.6\text{--}1.8\text{ cm}^{-1}$ (dependent on whether the centrifugal distortion constant is also fitted) to a deperturbed value of 1.921 cm^{-1} , while the term origin, T_{10} , is increased from an effective value of $\approx 94\,223\text{ cm}^{-1}$ to a deperturbed value of $94\,267.9\text{ cm}^{-1}$. For the $k^3\Pi(v=5)$ state the rota-

TABLE IV. Molecular constants of the $c^3\Pi(v=1)$ and $k^3\Pi(v=5)$ states. All units are in cm^{-1} except for N , which gives the number of transitions included in the fit. For the $k^3\Pi(v=5)$ state the term values derived from Berden *et al.* (Ref. 20) and given in Table I were also included in the fit. σ corresponds to the standard deviation of the overall weighted fit. Values between parentheses are errors, to one standard deviation, in the least significant figure. Values in the final fit that were fixed could not be determined to within the fitting error and so were fixed to their respective values for the $c^3\Pi(v=0)$ state (Ref. 12) for $c^3\Pi(v=1)$ and for the $k^3\Pi(v=3)$ state (Ref. 17) for $k^3\Pi(v=5)$. Note the molecular constants determined by Ref. 20 were obtained using a slightly different form of $^3\Pi$ Hamiltonian. Columns A and B correspond to single band fits where the homogeneous perturbation between the two states was neglected. For fit A the centrifugal distortion constants were fixed to their expected values (see above) while for fit B they were allowed to vary.

Molecular parameter	Previous studies	A	B	Final fit
$c^3\Pi(v=1)$				
T_{10}		94 225.37(70)	94 220.87(29)	94 267.93(11)
B		1.6252(62)	1.7633(61)	1.9212(15)
$D \times 10^6$		11.76 fixed	581(24)	11.76 fixed
A		-3.2(20)	9.27(53)	1.62(12)
$o+p+q$		0.0893 fixed	0.0893 fixed	0.0893 fixed
$p+2q$		0.019 69 fixed	0.019 69 fixed	0.019 69 fixed
q		0.009 938 fixed	0.009 938 fixed	0.009 938 fixed
W		0 fixed	0 fixed	88.96(5)
N		48	48	48
$k^3\Pi(v=5)$				
	(Ref. 20)			
T_{50}	94 439.12(22)	94 437.36(42)	94 437.78(16)	94 391.06(10)
B	1.344(40)	1.428(13)	1.382(12)	1.192 62(97)
$D \times 10^6$	0 (fixed)	9.35 fixed	-396(97)	9.35 fixed
A	25.32(12)	24.85(64)	24.60(20)	31.247(59)
$o+p+q$...	0.297 fixed	0.297 fixed	0.297 fixed
N	3	32	32	32
σ	...	2.451	0.720	0.122

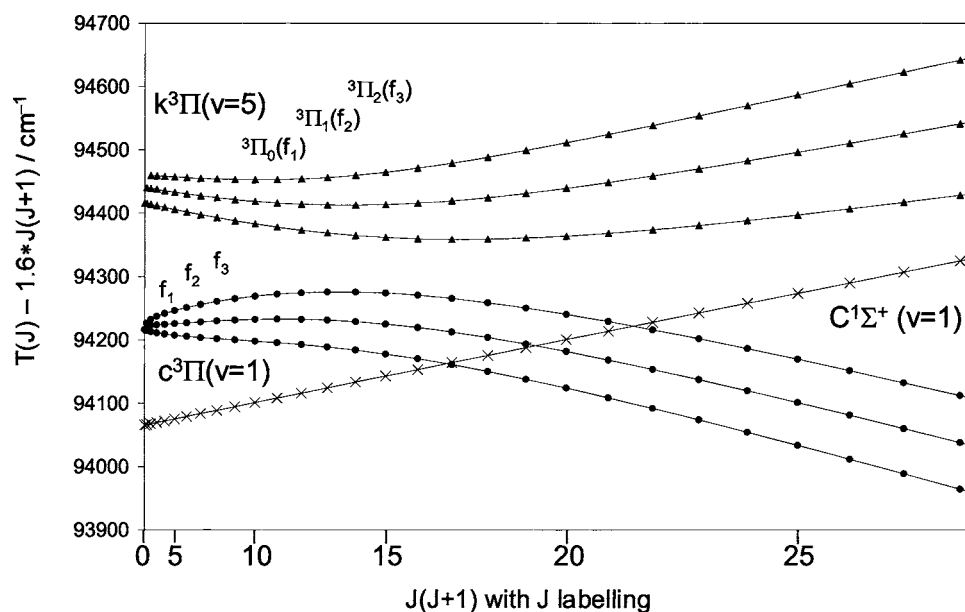


FIG. 4. Reduced term value plot of the calculated rotational levels of the $c^3\Pi(v=1)$ and $k^3\Pi(v=5)$ states showing the avoided crossing. Also included are the reduced term values of the $C^1\Sigma^+(v=1)$ state.

tional constant is reduced from an effective value of about 1.4 cm^{-1} to a deperturbed value of 1.193 cm^{-1} , the spin-orbit constant is increased from an effective value of about 25 cm^{-1} to a deperturbed value of 31.2 cm^{-1} , and the term origin, T_{50} , is reduced from an effective value of about $94\,437\text{ cm}^{-1}$ to a deperturbed value of $94\,391.1\text{ cm}^{-1}$. It is important to note that the effective molecular constants considered here refer to the lowest rotational levels of the states ($J < 17$) which were the only levels observed in this study.

Hence the effect of the homogeneous perturbation is to shift downwards in energy the origin of the $c^3\Pi(v=1)$ state by about 45 cm^{-1} and to shift upwards in energy by the same amount the origin of the $k^3\Pi(v=5)$ state. Similarly the rotational constant of the $c^3\Pi(v=1)$ state is decreased by about 0.22 cm^{-1} , whereas that of the $k^3\Pi(v=5)$ state is increased by about 0.21 cm^{-1} . The former is the reason why the $c^3\Pi-X^1\Sigma^+(1-0)$ band appears to be red degraded whereas the unperturbed band would be essentially undegraded.

Figure 4 gives the reduced term value plot of the calculated rotational levels of the $c^3\Pi(v=1)$ and $k^3\Pi(v=5)$ states. Included in this figure are the reduced term values of the $C^1\Sigma^+(v=1)$ state. The effect of the homogeneous interaction between the two states is to give rise to an avoided crossing. The avoided crossing region has its maximum effect in the $J=14-18$ region. Below this avoided crossing region the states have eigenvector characteristics dominated by their state labels, i.e., the lower triplet state has a dominant $c^3\Pi(v=1)$ eigenvector character and the upper state has a dominant $k^3\Pi(v=5)$ eigenvector character. Above the avoided crossing region (i.e., above the diabatic crossing region), $J > 20$, the characteristics of the states swap so that the lower state has mainly $k^3\Pi(v=5)$ character and the upper state has $c^3\Pi(v=1)$ character. The transition lines observed in this study correspond to the region essentially below the avoided crossing point.

Incidentally, the $C^1\Sigma^+(v=1)$ state is predicted to cross the lower triplet state in the $J=16-22$ rotational quantum number region, with nearest crossings for $J=17, 19$, and 22

($\approx 3.1, 5.8$, and 11.9 cm^{-1} , respectively). Ubachs *et al.*³⁰ observed the $C-X(1-0)$ band of $^{12}\text{C}^{16}\text{O}$ for rotational levels up to about $J=30$ in both $2+1$ and $1\text{ vuv}+1$ UV REMPI with a resolution of about 0.1 cm^{-1} and reported no line shifts. This would indicate that the interaction between the $C^1\Sigma^+(v=1)$ and lowest triplet state (which would be of mixed $c^3\Pi(v=1)-k^3\Pi(v=5)$ character in this region) is small and possibly not significant.

Inclusion of the homogeneous perturbation between the $c^3\Pi(v=1)$ and $k^3\Pi(v=5)$ states enables a satisfactory assignment and fit to all the measured transition energies of the rotational absorption lines identified for the two new bands. The deperturbed molecular constants for the assigned $c^3\Pi(v=1)$ state are consistent with their expected values. The T_{10} term origin of $94\,267.9 \pm 0.2\text{ cm}^{-1}$ yields a deperturbed value of the vibrational energy separation, $\Delta G_{1-0} = 2194.8 \pm 0.5\text{ cm}^{-1}$.¹² This is very close to the $X^2\Sigma^+ \text{CO}^+$ ionic core value of $\Delta G_{1-0} = 2184\text{ cm}^{-1}$ (Ref. 25) and the iso-electronic $3p\pi, E^1\Pi$ Rydberg state value of 2153 cm^{-1} .²⁴ The rotational constant for the $c^3\Pi(v=1)$ state of 1.9212 cm^{-1} compares with the rotational constants of the $v=1$ levels of the $X^2\Sigma^+ \text{CO}^+$ ionic core and the $E^1\Pi$ Rydberg state of $1.948\,46$ and $1.939\,89\text{ cm}^{-1}$, respectively.^{24,25} The rotational constant of the $c^3\Pi(v=0)$ state¹² is $1.9717 \pm 0.0002\text{ cm}^{-1}$, which when combined with the value for the $c^3\Pi(v=1)$ state determined in this study enables the following minimum-energy potential constants to be determined: $B_e = 1.9970\text{ cm}^{-1}$, $\alpha_e = 0.051\text{ cm}^{-1}$, and $r_e = 1.1096\text{ \AA}$. Finally the small spin-orbit constant of $A = 1.6 \pm 0.1\text{ cm}^{-1}$ seems consistent with the small spin-orbit constant previously determined¹² for the $c^3\Pi(v=0)$ state of $0.45 \pm 0.02\text{ cm}^{-1}$. Hence in summary the deperturbed molecular constants are consistent with the $c^3\Pi(v=1)$ state assignment.

The deperturbed molecular constants for the $k^3\Pi(v=5)$ state can be compared with the molecular constants determined for other known vibrational levels of this state. Previously, vuv absorption corresponding to the $k^3\Pi(v=$

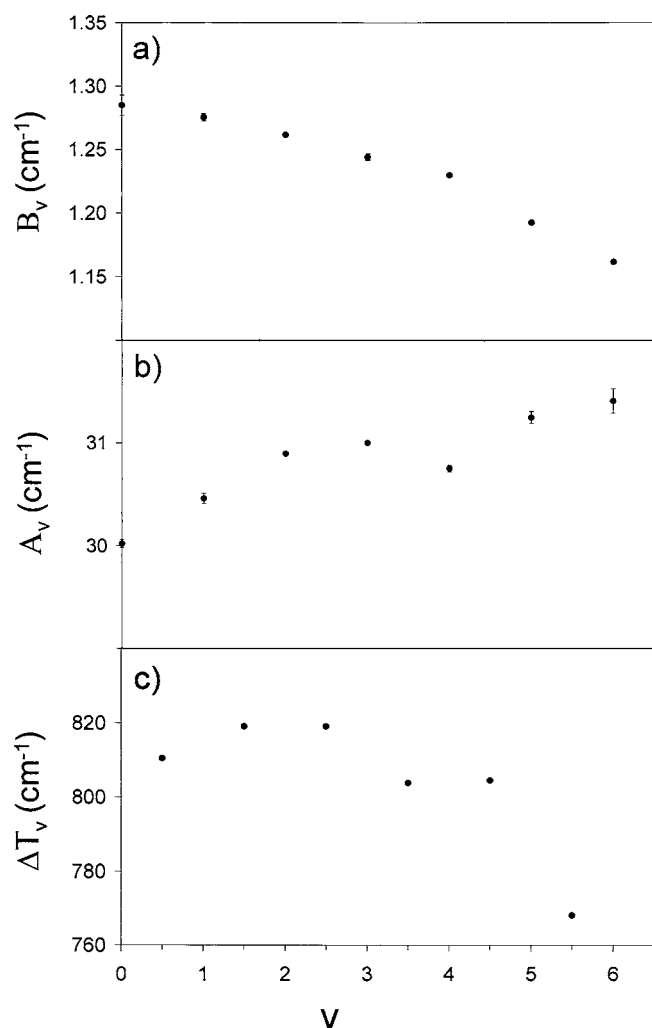


FIG. 5. Molecular constants of the $k^3\Pi$ state as a function of vibrational quantum number v . Shown are the vibrational trends in (a) the rotational constant B_v , (b) the spin-orbit constant A_v , and (c) the vibrational energy separation $\Delta T_{v+1/2} = T_{v+1} - T_v$, where T_v corresponds to the T_{v0} term origin. Data were taken from this study (for $v=5$) and from Refs. 12 and 17–20 for the other vibrational levels—see text for further details.

$=1, 3, 4, 6) - X^1\Sigma^+(v=0)$ transitions has been identified and analyzed.^{17,18} Data for the $k(3,4) - X(0)$ bands are the most extensive, giving rise to more precisely determined molecular constants.¹⁷ Six rotational levels of the $k^3\Pi$ ($v=2$) state have been observed by Berden *et al.*,²⁰ up to $J=2$, while Mellinger and Vidal¹⁹ in a double-resonance study observed rotational levels up to $J=5$. The $k^3\Pi$ ($v=2$) state is perturbed by the $c^3\Pi$ ($v=0$) state,^{9,12} and recently a set of deperturbed molecular constants for the $k^3\Pi$ ($v=2$) state has been generated.¹² Molecular constants for the $v=0$ level were obtained from the study of Berden *et al.*²⁰

Figure 5 compares the molecular constants of the $k^3\Pi$ ($v=5$) state obtained in this study with the molecular constants of the other known vibrational levels reported in the above previous studies. This figure is similar to Fig. 4 of Berden *et al.*²⁰ but shows that the deperturbed molecular constants of the $k^3\Pi$ ($v=5$) state fall within the general trends indicating that the perturbation with the $c^3\Pi$ ($v=1$) state essentially explains all the observed shifts within the $k^3\Pi$ ($v=5$) state. The rotational constants B_v appear to fol-

low the expected smooth trend of decreasing values with vibrational quantum number. The spin-orbit constant A_v appears to increase smoothly with v apart from perhaps the $v=4$ level. The successive vibrational energy separation with v is plotted as $\Delta T_{v+1/2} = T_{v+1} - T_v$ in Fig. 5(c) and generally decreases with v , although not smoothly indicating relative shifting of some of the levels. In summary the deperturbed molecular constants of the $k^3\Pi$ ($v=5$) state obtained in this study are consistent with the available data.

The $c^3\Pi(v=1) - k^3\Pi(v=5)$ interaction parameter W was determined to be 89.0 cm^{-1} . This can be compared to the interaction parameter determined for the $c^3\Pi$ ($v=0$) and $k^3\Pi$ ($v=2$) states of 21.1 cm^{-1} .¹² The homogeneous interaction term should be separable into electronic and vibrational factors, i.e., $W = H_e \langle v_c/v_k \rangle$.²⁹ For such a case the ratio $W_{c1-k5}/W_{c0-k2} = \sqrt{(\text{FCF}_{c1-k5}/\text{FCF}_{c0-k2})}$, i.e., the ratio of the interaction parameters is equal to the square root of the ratio of the Franck-Condon factors (FCFs). We calculated Franck-Condon factors from Rydberg-Klein-Rees (RKR) potentials.^{31,32} The following k -state potential parameters were first determined from the available experimental data: $B_e = 1.3067 \pm 0.0114 \text{ cm}^{-1}$, $\alpha_e = 0.0203 \pm 0.0028 \text{ cm}^{-1}$, $\omega_e = 791.6 \pm 1.4 \text{ cm}^{-1}$, $\omega_e x_e = -11.46 \pm 0.48 \text{ cm}^{-1}$, and $\omega_e y_e = -1.479 \pm 0.047 \text{ cm}^{-1}$, and then used to generate the k -state RKR potential.³¹ In determining the vibrational parameters the $v=4$ level was excluded in order to improve the observed-calculated differences of the vibrational energies (G_v) of the remaining levels to $<0.9 \text{ cm}^{-1}$. For the $c^3\Pi$ state an RKR potential was generated from available experimental data of the isoelectronic $E^1\Pi$ state, since the two potentials would be expected to be approximately parallel and there is more data available for the E state.²⁴ The following Franck-Condon factors were determined:³² $\text{FCF}_{c1-k5} = 7.823 \times 10^{-2}$ and $\text{FCF}_{c0-k2} = 4.147 \times 10^{-3}$, which yield a value of 4.34 for the predicted W_{c1-k5}/W_{c0-k2} ratio. This is in excellent agreement with the experimentally determined value of 4.22. Using the calculated Franck-Condon factors we determine the electronic interaction parameter between the $c^3\Pi$ and $k^3\Pi$ states to be $H_e = 323 \pm 40 \text{ cm}^{-1}$.

CONCLUSION

Two new red-degraded bands in the vuv absorption spectrum of carbon monoxide in the $94\,000\text{--}94\,500 \text{ cm}^{-1}$ energy region have been identified and analyzed. The lower-energy band at $\approx 94\,225 \text{ cm}^{-1}$ (106.1 nm), with three bandheads and partially overlapped with the $C^1\Sigma^+ - X^1\Sigma^+$ ($1-0$) band, is assigned to the $c^3\Pi - X^1\Sigma^+$ ($1-0$) transition. The higher-energy band at $\approx 94\,437 \text{ cm}^{-1}$ (105.9 nm), with one clear bandhead and weaker by about a factor of 10 than the lower-energy band, is assigned to the $k^3\Pi - X^1\Sigma^+$ ($5-0$) transition. A strong homogeneous perturbation was found to exist between the two upper states that strongly influences the line positions and shapes of these bands. A rotational deperturbation analysis was performed and molecular rotational constants for both upper states were determined. These deperturbed molecular constants are entirely consistent with the expected values for the $k^3\Pi$ valence and $c^3\Pi$ Rydberg states. The interaction term of the Hamiltonian was found to

be consistent with the interaction term previously determined for the $k^3\Pi(v=2)-c^3\Pi(v=0)$ perturbation¹² and was separable into vibrational and electronic factors ($W=H_e\langle v_c/v_k \rangle$). The electronic factor was determined to be $H_e=323\pm 40\text{ cm}^{-1}$. This study is inconsistent with a previous study by Hakalla¹⁵ and we conclude that the new 3A band reported in that study for $^{12}\text{C}^{16}\text{O}$ is not associated with the $c^3\Pi(v=1)$ state.

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