# Laser Absorption Spectroscopy of the $d^3\Pi_g \leftarrow c^3\Sigma_u^+$ Transition of C_2

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Ⓢ *Supporting Information*

ABSTRACT: High-resolution laser absorption spectroscopy using concentration modulation has been applied to record the near-infrared spectrum of C_2 in an AC hollow-cathode discharge of acetylene/helium mixtures. The (2,1) and (1,0) vibronic bands of the $d^3\Pi_g - c^3\Sigma_u^+$ system have been observed in the spectral region between 12 010 and 12 540 cm^{-1}. While the analysis of the (1,0) band was straightforward, the (2,1) band was found to be perturbed. Using the effective Hamiltonians for $^3\Pi$ and $^3\Sigma^+$ states, molecular constants for the vibrational levels of the $c^3\Sigma_u^+$ state were retrieved in least-squares fits of the observed spectral lines. The experimental conditions, detailed analysis of the perturbations, and the determined molecular constants are reported.
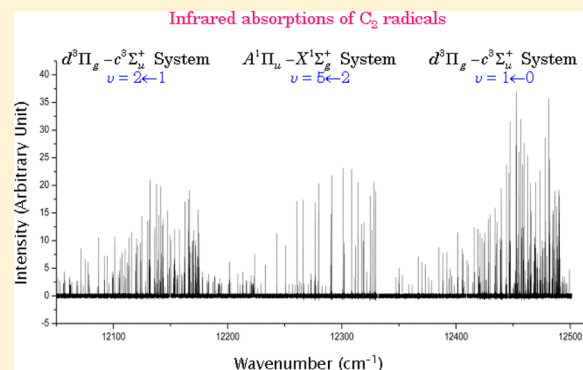
I. INTRODUCTION

Diatomic carbon molecules, C_2, have been known and extensively studied for over two centuries. With all valence orbitals from the carbon atoms half-filled, C_2 possesses a wealth of low-lying electronic states that are grouped into singlet and triplet manifolds. While transitions across the manifolds are spin-forbidden and have yet to be observed, various electronic band systems within each manifold have been studied over the years using mostly emission spectroscopy in the near-infrared, visible, and ultraviolet regions.[1]

In the singlet manifold, up to the $E^1\Sigma_g^+$ electronic states have been observed by spectroscopists.[1,2] Electronic band systems involving the two lowest electronic states $X^1\Sigma_g^+$ and $A^1\Pi_u$, respectively, with higher states have been reported. The Phillips[3] and Mulliken[4] systems connect the $A^1\Pi_u$ and the $D^1\Sigma_u^+$ states, respectively, with the $X^1\Sigma_g^+$ ground state. Transitions between the $A^1\Pi_u$ state and various upper states including the $B^1\Delta_g$,[5] $B'^1\Sigma_g^+$,[5] $C^1\Pi_g$,[6] $C'^1\Pi_g$,[7] and $E^1\Sigma_g^+$ states,[8] respectively, have also been investigated. In addition, the LeBlanc system[9] covers the transition between the $B'^1\Sigma_g^+$ state and the $D^1\Sigma_u^+$ state. These studies provide the spectroscopic data to show the existence of C_2 in astronomical objects. For instance, both the Phillips and Mulliken systems have been observed in interstellar spectra.[10,11]

The lowest state in the triplet manifold is the metastable $a^3\Pi_u$, which is about 700 cm^{-1} above the $X^1\Sigma_g^+$ ground state. The $d^3\Pi_g - a^3\Pi_u$ transition (also known as the Swan system) was first observed about 200 years ago[12] due to its prominent intensity that led to the mistake of proposing the $a^3\Pi_u$ state as the ground state of C_2 in the early days. Transitions $b^3\Sigma_g^- - a^3\Pi_u$ and $e^3\Pi_g - a^3\Pi_u$ have also been observed, respectively, by Ballik and Ramsay[13] in 1958 and Fox and Herzberg[14] in 1937. The $c^3\Sigma_u^+$ excited state of C_2 has been known from the

perturbation of the $A^1\Pi_u$ state since the 1960s.[15] On the basis of the perturbation, Ballik and Ramsay[15] estimated its rotational parameters and energy. Nevertheless, the $c^3\Sigma_u^+$ state was considered a metastable dark state since its relaxation to lower states is symmetry forbidden by dipole selection rules.

Attempts at direct observation of transitions involving the $c^3\Sigma_u^+$ state have not been successful over the years until very recently. Several vibronic bands of the $\Delta v = 3$ and 4 sequences of the $d^3\Pi_g - c^3\Sigma_u^+$ system were observed by Schmidt and co-workers using fluorescence spectroscopy of a supersonic free jet expansion to obtain the corresponding spectroscopic constants for the first time.[16,17] However, the absorption spectrum of the $d^3\Pi_g - c^3\Sigma_u^+$ system was observed in our laboratory and reported as unidentified bands in 2004.[18] In hollow cathode discharges of methane/helium mixtures, two new vibronic bands buried in the $\Delta v = 3$ sequence of the Phillips system were observed. A preliminary analysis of the two bands at 12 140 and 12 450 cm^{-1} indicated that they were due to two carbon species but did not fit into any previously observed band systems. Since the signal-to-noise ratio of the two bands were inadequate for a detailed analysis, experimental attempts at improving the signals were made. By switching the gas plasmas from methane/helium to acetylene/helium, the unidentified bands were greatly enhanced together with the Swan system.[19] With reference to the observation by Joester et al.,[17] it was found that these two bands fit into the (2,1) and (1,0) bands of the $d^3\Pi_g - c^3\Sigma_u^+$ system. Since the d–c system is a $^3\Pi - ^3\Sigma$ transition, a total
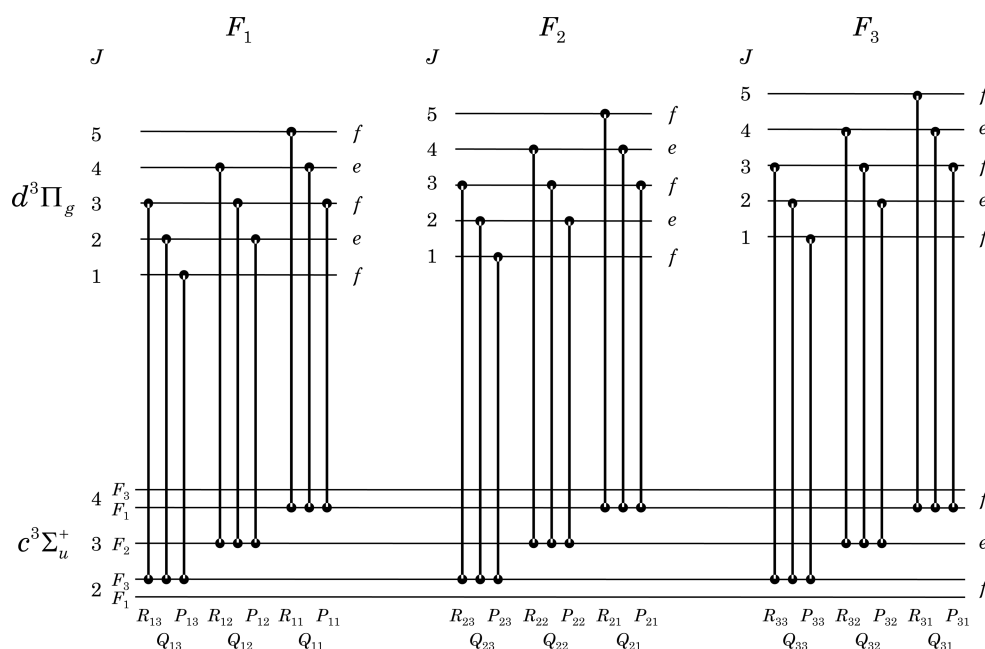
Figure 1. Schematic energy level diagram for the $d^3\Pi_g-c^3\Sigma_u^+$ system of C_2, illustrating the origins of the 27 branches allowed by the selection rule of $\Delta J = 0, \pm 1$.

of 27 branches are expected (shown in Figure 1) that makes the spectrum exceedingly intricate. Compared to experiments by Joester et al.,[17] the rotational temperature was much higher (at about 260 K) in our case. As a result, most branches with rotational progression up to about $J = 20$ were observed in our spectrum to exhibit complex pattern that made the analysis difficult. Nevertheless, the unprecedented resolution afforded by Doppler-limited laser spectroscopy allowed the rotational lines to be fully resolved. By analyzing the spectrum, structural parameters for the c state have been determined at high accuracy. In this article, the details of our study will be reported.

II. EXPERIMENTAL DETAILS

The experimental setup for this work has been described elsewhere.[18] It was composed of a set of home-built apparatus including an AC high-voltage discharge power supply, a 2 m hollow cathode cell with a Roots pump station, and a high-resolution tunable near-infrared laser spectrometer. The AC power supply with two discharge channels was assembled using a function generator, an audio amplifier, and a pair of audio transformers. While the maximum peak-to-peak discharge current of about 2.5 A at AC frequency of ~5 kHz was possible, a typical discharge current of 1 A was used to avoid overheating. The cathode of the discharge cell was made of a stainless steel tube of 51 cm in diameter and 2 m in length. Each end of the tube was fitted with an anode housed in a Pyrex glass tube. A Roots pump station was used to maintain the cathode tube at a steady pressure during experiments with a constant gas flow. In order to reduce the discharge noise, the cathode tube was cooled by ethanol circulation at 200 K. The spectrometer was equipped with a Ti:sapphire laser source covering the range of ~9900−14 200 cm^{-1} and a silicon PIN diode detector. The Ti:sapphire laser, which was pumped by a 15 W Ar$^+$ laser operated at multiline configuration, exhibited a spectral purity of ~1 MHz. A small portion of the near-infrared radiation was sent to a wavelength meter with a resolution of 0.001 cm^{-1} for frequency calibration. A combination of an I_2

reference cell and a thermally stabilized spectrum analyzer with a free spectral range of 300 MHz was also used occasionally for calibration purposes. The uncertainty in frequency measurement was about 0.003 cm^{-1}. The absorption signals from the silicon detector were processed using a lock-in amplifier and then stored in a personal computer. An in-house program written in Lab-View for frequency calibration, data acquisition and processing, and data storage was used in this experiment.

C_2 radicals were generated using AC discharges at 5 kHz of the precursor gas mixtures of C_2H_2 and He at a ratio of 1:170. The typical pressure of the gas plasmas in the cell was ~850 mTorr so that stable operation for about 10 h was possible before the discharges became noisy due to the coating of the cathode surface with carbon soot. The stability of the discharges was resumed after removal of the soot followed by polishing the surface of the hollow cathode tube. A spectral region from about 12 000 to 12 500 cm^{-1} was scanned using the Ti:sapphire spectrometer to cover the two vibronic bands. In order to improve the signal-to-noise ratio, a pair of multitraversal mirrors were used to increase the effective optical path to about 64 m. The signals detected by the PIN diode detector were processed using a lock-in amplifier referenced at the AC discharge frequency. Since discharges were turned on in half of each AC cycle, the concentration of C_2 varied synchronously with the AC discharge frequency to give periodic modulation of absorption signals. The demodulation of C_2 absorption signals according to the AC discharge frequency allowed the removal of most background noise at random frequencies to achieve a detection limit of about 2×10^{-6} in fractional absorption.[18] Our observation of the $d^3\Pi_g-c^3\Sigma_u^+$ system was made possible because of this unprecedented sensitivity.

III. RESULTS AND ANALYSIS

Compared to the CH_4/He plasmas, the (1,0) and (2,1) bands of the $d^3\Pi_g-c^3\Sigma_u^+$ system were observed with much more prominent intensities in C_2H_2/He plasmas. In addition, many more transitions of the Swan system were also observed in the
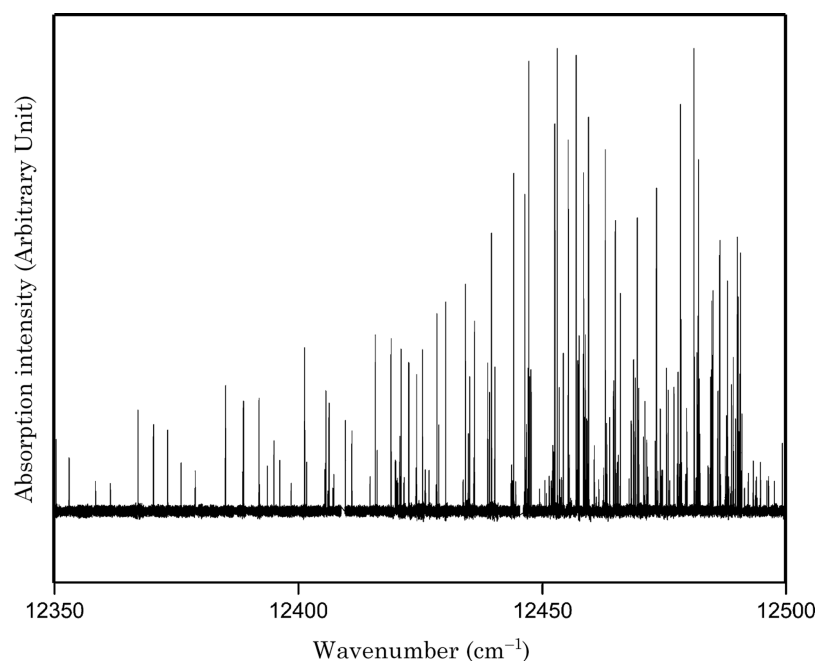
Figure 2. Absorption spectrum of the (1,0) band of the $d^3\Pi_g - c^3\Sigma_u^+$ system of C_2. The overall appearance is very intricate due to the 27 allowed branches.
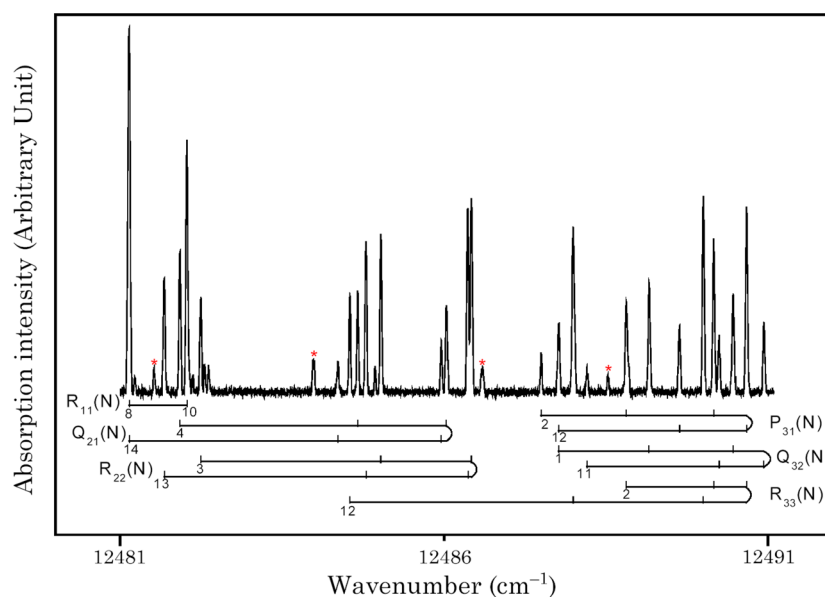
Figure 3. Band head region of the (1,0) band of the $d^3\Pi_g - c^3\Sigma_u^+$ system of C_2 under high resolution. The unassigned weak absorption features marked with asterisks may be due to the (4,9) band of the Swan system.

spectral region of 12 000−14 200 cm^{-1}. For instance, the $\Delta v =$ −4 sequence was observed in the region around 13 750 cm^{-1}.[19] The (1,0) and (2,1) bands of the $d^3\Pi_g - c^3\Sigma_u^+$ system were observed in spectral regions 12 300−12 500 and 12 010−12 210 cm^{-1}, respectively, with good signal-to-noise ratio.

Since C_2 is a homonuclear diatomic molecule, the symmetry considerations require that even J levels in the $^3\Sigma_u^+$ state are only allowed for the F_1 and F_3 components and odd J levels for the F_2 component. However, the $d^3\Pi_g$ state has only one component for each J level. According to the scheme of angular momentum coupling, the $c^3\Sigma_u^+$ state belongs to the Hund's case (b), while the $d^3\Pi_g$ state belongs to the Hund's case (a). Combining these considerations, a total of 27 allowed branches,

as shown in Figure 1, are expected for this specific $^3\Pi(a)-^3\Sigma$-(b) band system of C_2 molecules. The overall appearance of the (1,0) absorption band is depicted in Figure 2. The intricate structure is a result of the number of allowed branches for the $d^3\Pi_g - c^3\Sigma_u^+$ system.

In the initial stage of analyzing the (2,1) and (1,0) bands, we made use of the molecular constants published earlier by Tanabashi et al.[20] for the $d^3\Pi_g$ state and by Joester et al.[17] for the $c^3\Sigma_u^+$ state to predict the energies of the rovibronic states based on the effective Hamiltonian by Brown and Carrington[21] for, respectively, the $^3\Pi$ state

$$\hat{H}_{\text{eff}} = B\hat{\mathbf{R}}^2 - D\hat{\mathbf{R}}^4 + A\hat{\mathbf{L}}_z\hat{\mathbf{S}}_z + \frac{2}{3}\lambda(3\hat{\mathbf{S}}_z^2 - \hat{\mathbf{S}}^2)$$
$$+ \gamma(\hat{\mathbf{J}} - \hat{\mathbf{S}})\cdot\hat{\mathbf{S}} \qquad (1)$$

and the $^3\Sigma$ state

$$\hat{H}_{\text{eff}} = B\hat{\mathbf{R}}^2 - D\hat{\mathbf{R}}^4 + \gamma\hat{\mathbf{R}}\cdot\hat{\mathbf{S}} + \frac{2}{3}\lambda(3\hat{\mathbf{S}}_z^2 - \hat{\mathbf{S}}^2) \qquad (2)$$

The parameters in eqs 1 and 2 have the usual meaning, i.e., B and D are, respectively, the rotational constant and centrifugal distortion constant, A is the spin–orbit constant, λ is the spin–spin constant, and γ is the spin–rotation constant. Using the matrix elements in the corresponding Hamiltonian matrixes for the $^3\Pi$ and $^3\Sigma$ states found in Brown and Merer[22] and Cheung et al.,[23] respectively, the transition frequencies for the two bands were then calculated for all 27 allowed branches.

Our analysis began with assigning spectral lines with $J < 5$ for both (1,0) and (2,1) bands. On the basis of the predicted frequencies, we attempted to locate from our spectrum the corresponding lines in the vicinity that matched with the prediction. The analysis of the (1,0) band was straightforward and the branches were generally well behaved. Figure 3 shows the assigned lines in the band head region of the (1,0) band between 12 481 and 12 491 cm^{-1}. Those lines marked in red have yet been assigned. According to estimate from published vibrational molecular constants, it is likely that they belong to the (4,9) band of the Swan system. We subsequently extended the assignment to the high J lines. Among the 27 branches, we were able to identify 21 of them for the (1,0) band. However, the $v = 1$ level of the $c^3\Sigma_u^+$ state has long been known to be perturbed.[15] The line positions in the (2,1) band were therefore affected. In general, lines exhibited greater difference between the predicted and observed frequencies. Among the 27 branches predicted for the (2,1) band, 20 branches were identified. Since the $c^3\Sigma_u^+$ is a metastable state, it is quite probable that the $v = 0$ level has higher population to give rise to more observed lines for the (1,0) band. The full list of lines assigned to the (1,0) and (2,1) bands of the $d^3\Pi_g{-}c^3\Sigma_u^+$ system is available as Supporting Information.

Molecular constants for the $c^3\Sigma_u^+$ state were retrieved from the observed lines by performing least-squares fittings separately for the (1,0) and (2,1) bands using effective molecular Hamiltonians shown in eqs 1 and 2. Since the molecular constants measured by Tanabashi et al.[20] for the $v = 1$ and 2 levels of the $d^3\Pi_g$ state were determined accurately, these constants were held fixed in our fit so that only the molecular constants for the $c^3\Sigma_u^+$ state were allowed to float. A total of 129 rotational lines for the (1,0) band were measured and fitted to give a root-mean-square (rms) error of 0.019 cm^{-1}. In the case of the (2,1) band, allowing the centrifugal distortion constant D to float in the fit always ended in obtaining a negative value, suggesting it could be affected by perturbations in the $v = 1$ level. This irregularity was removed by setting and fixing the D constant to the value of the $v = 0$ level. For the (2,1) band, 87 lines were measured and fitted to give an error of 0.057 cm^{-1}, which is slightly worse compared to the case of the (1,0) band. Because of various minor perturbations in the $v = 1$ level, there were individual lines with residues as large as 0.1 cm^{-1} in our fit. Nevertheless, all assigned lines except those with $J > 12$ of the F_3 component were used in the least-squares fitting with equal weight. The value of $\Delta G_{1/2}$ determined for the $c^3\Sigma_u^+$ state is 2031.812 cm^{-1}, within the experimental error of the value of 2031.845 cm^{-1} by Joester et

al.[17] The molecular constants obtained in our fits are shown in Table 1. The band origins for the (2,1) and (1 0) bands of the $d^3\Pi_g{-}c^3\Sigma_u^+$ system were determined, respectively, to be 12153.653 and 12469.189 cm^{-1}.

Table 1. Derived Molecular Constants for the $c^3\Sigma_u^+$ State of C_2 (cm^{-1})^a

state	constants	this work	ref 17	ref 24
	$T_0{}^b$	8662.950	8662.925(3)	8691.2
	$\Delta G_{1/2}$	2031.812	2031.845	2048.6
$v = 1$	B	1.8985(1)	1.8975(3)	1.9022
	10^6D	2.84^c		
	λ	−0.218(1)	−0.304(3)	
	γ	0.01372(1)	−0.014(1)	
$v = 0$	B	1.92238 (9)	1.9222(3)	1.9147
	10^6D	2.84(5)		
	λ	−0.3189(3)	−0.333(3)	
	γ	0.0108(3)	0.011(1)	

^{a}Numbers in parentheses are one standard deviation (in unit of the last figure). ^{b}Value referenced to the $v = 0$ level of the $a^3\Pi_u$ state. ^{c}Value fixed to D_0.

Even without direct observation, structural constants of the $c^3\Sigma_u^+$ state have been estimated for a long time based on the perturbation study of other band systems. For instance, in studying the Phillips ($A^1\Pi_u{-}X^1\Sigma_g^+$) system, Davis et al.[24] identified 5 perturbations due to interactions of the $c^3\Sigma_u^+$ state with the $A^1\Pi_u$ state. Parameters T_0, $\Delta G_{1/2}$, B_0, and B_1 for the $c^3\Sigma_u^+$ state were thus deduced. As shown in Table 1, these values compare favorably with our results.

IV. DISCUSSION

The molecular constants for the $v = 0$ level of the $c^3\Sigma_u^+$ state determined in this work are in excellent agreement with those recently reported by Joester et al.[17] However, constants for the $v = 1$ level exhibit some discrepancies, in particular, the λ and γ constants between both work. While a negative γ was obtained by Joester et al.,[17] we found that only a positive γ could give a satisfactory fit of our data. In addition, the value of λ from our study was only ~70% of the value from Joester et al.[17] Since λ and γ are small constants, they will be easily changed by the fitting equations as well as the sets of transitions observed in experiments. Considering the resolution of our instrument and the number of transitions used in our fit, the parameters derived from this work are expected to be statistically more representative.

The B constants obtained in this work are in excellent agreement with those by Joester et al.[17] As pointed out in ref 17, the B constant for the $v = 1$ level in the $c^3\Sigma_u^+$ state appeared to be unexpectedly small due to perturbation that appears to have the same affect on all rotational levels to give rise to a smaller B. The consistency of the B constants in both experiments supports this proposition. As far as the perturbing states for the $v = 1$ level of the $c^3\Sigma_u^+$ state, the $v = 2$ level of the $A^1\Pi_u$ state has long been suggested by Ballik and Ramsey[15] and Joester et al.[17] In addition, Tanabashi and Amano[25] speculated that the $v = 7$ level of the $a^3\Pi_u$ state could also be a perturbing state. In order to understand the situation better, we have plotted the term values of these three states using the best available experimental data to determine the perturbation. Figure 4 shows the term values of the $v = 1$ level of the $c^3\Sigma_u^+$, the $v = 7$ level of the $a^3\Pi_u$,[25] and the $v = 2$ level of $A^1\Pi_u$ states[24]
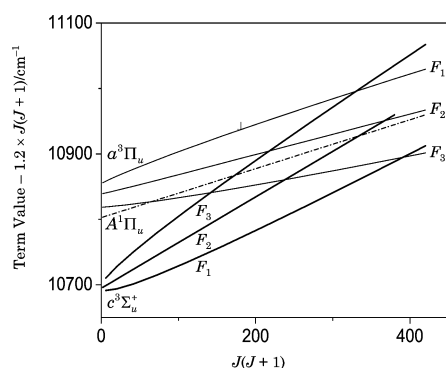
Figure 4. Term values of the $c^3\Sigma_u^+$, $a^3\Pi_u$, and $A^1\Pi_u$ states plotted as a function of $J(J + 1)$. A quantity of $1.2 \times J(J + 1)$ has been subtracted from each term value to expand the scale.

with respect to the $v = 0$ level of the $a^3\Pi_u$ state, whose energy was taken to be zero. The effective term values (i.e., term values $-1.2 \times J(J + 1)$) were plotted to expand the energy scale. The energy separation between the $v = 0$ level of the $a^3\Pi_u$ state and the $v = 0$ level of the $X^1\Sigma_u^+$ state was taken to be 609.75 cm^{-1}.[1] It can be easily noticed that the $v = 1$ level of the $c^3\Sigma_u^+$ state is subjected to perturbations from both the $A^1\Pi_u$ and $a^3\Pi_u$ states. The two F_3 components of the $a^3\Pi_u$ and the $c^3\Sigma_u^+$ state cross at J value as low as 14, which confirmed the observed perturbation by Tanabashi and Amano.[25] For the $A^1\Pi_u$ state, the perturbation occurs at around $J = 18$ for the F_3 component of the $c^3\Sigma_u^+$ state. The exact locations of these perturbations are subjected to the accuracy of literature value for the separation between $v = 0$ levels of the $a^3\Pi_u$ and the $X^1\Sigma_u^+$ states. As noticed by Joester et al.,[17] the B value for the $v = 1$ level of the $c^3\Sigma_u^+$ state is smaller than expected. The depression of the B value can be interpreted as the resultant effect of interacting with both the $v = 7$ level of the $a^3\Pi_u$ and the $v = 2$ level of $A^1\Pi_u$ states. Since these two states are above the $c^3\Sigma_u^+$ state, the $c^3\Sigma_u^+$ state would be pushed down to some extent. A close examination of the B values for both the $v = 7$ level of the $a^3\Pi_u$ and the $v = 2$ level of $A^1\Pi_u$ states indicates that they are not significantly deviated or pushed up from their original values. This situation could be reasonable because the upward push from the $v = 1$ level of the $c^3\Sigma_u^+$ state is shared by these two levels, which becomes less severe for each level.

The multitraversal laser absorption technique with concentration modulation has been proven to be very successful in studying spectra of free radicals and ions due to the high sensitivity achieved by zero-background detection and the versatility in generating various molecular species. This sensitivity in general is a major advantage for recording weak molecular absorptions. In the case of studying perturbations, however, the sensitivity of this technique that allows detecting many more weak lines due to high J levels or different v sequence may introduce extra difficulty in identifying the perturbed transitions from the bush of weak absorption lines. In the case of the (2,1) band, only a portion of lines have been assigned and fitted, with a number of rotational lines remained unassigned. Because of many unidentified minor perturbations in the $v = 1$ level of the $c^3\Sigma_u^+$ state, the rms error of the least-squares fit for the (2,1) band was 0.059 cm^{-1}, slightly worse than the case of the (1,0) band. In order to further investigate these perturbations, one has to be confident with the lines identified. Because of the reasons mentioned above, however, some of the assignments for the (2,1) band might only be

partially correct. In view of the limited information available to date, we have not attempted to perform any deperturbation procedure.

In summary, the (1,0) and (2,1) bands of the $d^3\Pi_g \leftarrow c^3\Sigma_u^+$ system have been observed and assigned using Doppler-limited zero-background laser absorption spectroscopy. The molecular constants for the c state determined from this work are consistent with those by Joester et al.[17] and Davis et al.[24] The perturbation of the $v = 1$ level of the $c^3\Sigma_u^+$ state was investigated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

List of assigned absorption lines with measured frequencies is accessible for public use. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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