

Analysis of the $c^3\Pi(v=0, 1)$ State on the Basis of the 3A Band System in the $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{14}\text{C}^{16}\text{O}$ Molecules

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Six bands of the 3A system ($c^3\Pi$ – $a^3\Pi$) in the CO molecule have been photographed as an emission spectra by the Geissler tube. The conventional technique of spectroscopy has been implemented. It was the first attempt to analyze the 1–3 band in the $^{13}\text{C}^{16}\text{O}$ molecule as well as the 1–2 band in the $^{12}\text{C}^{16}\text{O}$ molecule at high resolution. The Th lines were used as a standard along with the interferometric comparator equipped with a photoelectric scanning device. The 0–2 and 0–3 bands in $^{12}\text{C}^{16}\text{O}$ and the 0–3 band in $^{13}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{16}\text{O}$ were reanalyzed. The total number of lines studied within this project amounts to 3071. Due to complicated and not totally described perturbations which appeared in the upper state $c^3\Pi(v=0, 1)$, the effective rovibronic structure constants for this state were calculated (for the first time in the case of $v=1$ level in the $^{12}\text{C}^{16}\text{O}$). Global merging of the rotational constants of the $a^3\Pi(v=0, 1, 2, 3)$ and $c^3\Pi(v=0, 1)$ levels in $^{13}\text{C}^{16}\text{O}$, as well as $a^3\Pi(v=2, 3)$ and $c^3\Pi(v=0, 1)$ in $^{12}\text{C}^{16}\text{O}$, made it possible to obtain $c^3\Pi$ vibrational differences $\Delta v_{1-0} = 1742.0944$ (22) cm^{-1} in $^{13}\text{C}^{16}\text{O}$ as well as 1775.7665 (41) cm^{-1} in $^{12}\text{C}^{16}\text{O}$ for the first time. The so far unknown band origins of the $0-v''$ and $1-v''$ progressions of the 3A system in the molecules under consideration have also been determined. The first attempt to specify the equilibrium molecular constants for the $c^3\Pi$ state, along with the new values for the $a^3\Pi$ state, on the basis of the obtained values of merged rovibronic constants has been undertaken. The vibrational constants of the $c^3\Pi$ state in the $^{13}\text{C}^{16}\text{O}$ molecule as well as in the $^{12}\text{C}^{16}\text{O}$ molecule were thus obtained for the first time. The 1–2 band of $^{12}\text{C}^{16}\text{O}$ and Dunham's isotopic relationship were implemented for that purpose. The analysis of anomalously small values of the centrifugal distortion constant D of the $c^3\Pi$ state and the global character of perturbations in the observed isotopes of the CO molecule suggest homogeneous interaction between $c^3\Pi(v=0, 1)$ and the $k^3\Pi$ state. Simultaneously, the analysis of the comparatively large values of the Λ -doubling parameter q and the analysis of the shifts of the term values caused by perturbations presuppose a significant influence of a heterogeneous nature of any of the $^3\Sigma$ states (most probably the $j^3\Sigma^+$ state) on the $c^3\Pi(v=0, 1)$ state. The article also presents the first attempt to calculate RKR potentials, r -centroids, and Franck–Condon factors for the 3A system. © 2001 Academic Press

INTRODUCTION

The 3A band system was first observed by Asundi *et al.* (1) in 1929. Schmid (2) interpreted the upper state c of the 3A system as $^3\Sigma^+$. Schmid and Gerö (3) obtained short bands (up to $J_{\text{max}} = 19$) of the $c(v' = ?)$ – $a^3\Pi(v = 1, 2, 3)$ transitions with small resolution (about 0.13 nm/mm) and small precision (about 0.05 cm^{-1}). The first attempt at a rotational analysis of the previously obtained bands of the 3A system was conducted by Gerö (4). Nevertheless, Gerö and his predecessors regarded the c state as the $^3\Sigma$ state characterized by unmeasured spin splitting. This interpretation was accepted till the year 1969 when Tilford (5) obtained the 0–0 band in the c – X system. He suggested that the state in question is probably the $^3\Pi$ state. That same year Tilford and Ginter (6) proved the assumption that the upper state is not the state of the $^3\Sigma^+$ type. It was noted that the upper rotational levels ($N > 10$) of the c state are characterized by perturbations and caused an anomalous sign of the centrifugal distortion con-

stant ($D = -36.2 \text{ cm}^{-1}$). They also assumed that, if the c state belongs to $^3\Pi$, we have every reason to believe that comparatively large Λ -doubling ($q = -0.016 \text{ cm}^{-1}$) arises as a result of interaction with the $j^3\Sigma^+$ state. A similar result was previously specified by Tilford *et al.* (7) for the $E^1\Pi$ state.

Danielak *et al.* (8) undoubtedly stated that the observed v' level of the c state is equal to 0. Danielak *et al.* and their predecessors did not notice the multiple splitting of this state. The preliminary observation of the triplet splitting of the $c^3\Pi$ state was conducted by Siwiec-Rytel (9) for the $^2P_{32}$ and $^2R_{12}$ branches and Rytel *et al.* (10, 11). They also discovered an additional perturbation for the low J values, which the authors interpreted as the only one for the $c^3\Pi(v=0)$ level. It was also suggested that the perturbation is homogenous and is caused by the unknown c' triplet state. Its vibrational quantum number was evaluated as $v = 1$.

Nevertheless, the precise specification of the fine structure splitting of the $c^3\Pi$ state using two-step vacuum-ultraviolet visible excitation spectroscopy was presented by Kłopotek and Vidal (12) only in 1985. They also amply demonstrated the great increase of triplet splitting of the $N = 1$ term in respect of the further terms ($2 \leq N \leq 5$). According to Kłopotek and Vidal

Supplementary data for this article are available on IDEAL (<http://www.idealibrary.com>) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).



(12, p. 875), it may arise due to the perturbation caused by one of the $^3\Sigma^+$ states. Hence, the fine-structure splitting for $N = 1$ ($A = 1.49 \text{ cm}^{-1}$) was calculated using the method presented in Hougen's monographic study (13).

The subsequent specifications of numerous perturbations of the $c^3\Pi(v = 0)$ state revealed in noticeable displacements of the molecular lines for $N > 10$ and considerable increase of the triplet splitting for original values N were presented by Dabrowski *et al.* (14). The effective value of molecular constants of the $c^3\Pi(v = 0)$ state enabled them to draw the conclusion that the observed perturbations may arise due to the $c'^3\Pi$ state and any of the neighboring states of the aforementioned $^3\Sigma$ type. In addition, it was stated that there are more unidentified states interacting with the $c^3\Pi(v = 0)$ state, since all the components of the $c^3\Pi$ are affected. They also proved that the $c^3\Pi$ state is regular.

The unknown $c'(v = 1)$ state was unambiguously identified as the $k^3\Pi(v = 1)$ valence state by Baker *et al.* (15), which was proved in Baker and Launay (16) and Baker (17). It was determined that the aforementioned $k^3\Pi(v = 1)$ state is located approximately 100 cm^{-1} below the $c^3\Pi(v = 0)$ level and is responsible for the indirect predissociation obtained for the $E^1\Pi$ state as well as a strong homogeneous perturbation of the $c^3\Pi(v = 0)$ level. On the basis of reanalysis of the data presented in Wan and Langhoff (18), Baker *et al.* (15) stated that the transitions, which were attributed to $c^3\Pi(v = 1, 2) - a^3\Pi(v = 0, 1)$ by Mazeau *et al.* (19) after electron impact spectroscopy, are, in fact, the $j^3\Sigma^+(v = 0, 1) - a^3\Pi(v = 2)$ transitions.

The $j^3\Sigma^+$ state was unambiguously identified by Mellinger and Vidal (20) at $90\,833 \text{ cm}^{-1}$. They suggested that the $j^3\Sigma^+(v = 0)$ level is responsible for some perturbations in the $c^3\Pi$ state. They proved that the $k^3\Pi(v = 1)$ level causes only a fraction of the whole perturbation of the $c^3\Pi(v = 0)$ level. Berden *et al.* (21) presented an exhaustive reinterpretation of vibrational levels of the $k^3\Pi$ valence state. It was suggested that one of the perturbants of the $c^3\Pi(v = 0)$ level can be the $k^3\Pi(v = 2)$ level, contrary to a widespread belief that it is the $k^3\Pi(v = 1)$ level that is responsible for that. Those assumptions were verified by Baker and Launay in their recently published article (22) dealing with the $c-X$ transition.

Due to the fact the properties of the $3A$ system had not been fully specified, it was decided to obtain the 0–0 and 0–1 bands for the first time and reanalyze the 0–2 band in the $3A$ system in the $^{13}\text{C}^{16}\text{O}$ molecule under high resolution even up to 0.029 nm/mm with maximum precision of approximately 0.010 cm^{-1} (Hakalla *et al.* 23). It enabled us to increase the number of observable rotational levels up to $J_{\text{max}} = 25$ in the main branches as well as to determine and interpret four new branches of the $3A$ system. Hakalla (24) observed and analyzed for the first time the $1-v''$ progression (the bands 1–0, 1–1, and 1–2 in the $^{13}\text{C}^{16}\text{O}$ molecule), which allowed to obtain the first data concerning previously unknown $c^3\Pi(v = 1)$ level. The set of effective molecular constants and terms values of the aforementioned level were provided. The preliminary rotational analysis

of this level showed a strong and multistate perturbations similar to the one observed for the $c^3\Pi(v = 0)$ level.

Baker *et al.* (25) have recently published a reanalysis of the 0–0 band in the $c-X$ system of the $^{12}\text{C}^{16}\text{O}$ molecule. A noticeable increase of intensities for low J values has been noted. It was proved that the increase is caused by the interaction between the $c^3\Pi(v = 0)$ state and the $a^1\Sigma^+$ state—the most probable candidate being the $C^1\Sigma^+(v = 0)$ state. The anomalously small value of the centrifugal distortion constant was attributed to a homogeneous perturbation by the $k^3\Pi(v = 2)$ state, whereas the interaction between the $c^3\Pi$ state and the $E^1\Pi$ state was ruled out.

The contemporary state-of-the-art in the field shows that numerous and complex perturbations of the $c^3\Pi$ state are yet unknown to a considerable extent, which warrants further interest to the state in question as well as to the $3A$ system as a whole. For this very reason the major aims of the present paper are as follows:

- (a) to excite and register a larger number of emission spectra of the $c^3\Pi - a^3\Pi$ transition in $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{14}\text{C}^{16}\text{O}$ molecules;
- (b) to reanalyze the perturbations of the $c^3\Pi(v = 0)$ and $c^3\Pi(v = 1)$ levels;
- (c) to obtain the equilibrium rotational and vibrational constants and vibrational energy differences, as well as the potential curve, on the basis of experimental data for the $c^3\Pi$ state;
- (d) to determine the Franck–Condon factors and the r -centroids for the $3A$ system.

EXPERIMENTAL DETAILS

The emission spectrum of the $c^3\Pi - a^3\Pi$ band system has been obtained in the water-cooled Geissler tube. The tubes were filled with $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, or $^{14}\text{C}^{16}\text{O}$ molecular gases. The pressure in the tubes was about 10 Torr. The tubes were operated at about 3 kV and 50 mA ac. The spectra were observed in the 10th order for the 0–2 and 0–3 bands in the $^{12}\text{C}^{16}\text{O}$ molecule and for the 0–3 band in the $^{14}\text{C}^{16}\text{O}$ molecule (previously photographed in our laboratory under the same experimental conditions) and 0–3 in the $^{13}\text{C}^{16}\text{O}$ and 1–2 in the $^{12}\text{C}^{16}\text{O}$ molecule, as well as in the 9th order for the 1–3 band in the $^{13}\text{C}^{16}\text{O}$ (recently photographed). Those bands have been obtained using the 2-m Ebert spectrograph (PGS-2) furnished with a 651 grooves/mm grating blazed at $1.0 \mu\text{m}$ (the total number of grooves equals 45 600). The 1–2 band of the $^{12}\text{C}^{16}\text{O}$ molecule has been obtained in the course of photographing the 1–2 band of the $^{13}\text{C}^{16}\text{O}$ molecule. For this very reason it is less intensive, hence shorter (up to $J_{\text{max}} = 13$), than other bands. Reciprocal linear dispersion was equal to $0.037\text{--}0.055 \text{ nm/mm}$ and theoretical resolving power was about 500 000. The exposure of ORWO UV-1 plates varied from 3 to 25 hr.

The standard thorium lines (26) calculated from a number of orders and emitted by the water-cooled, hollow-cathode tube

TABLE 1
Summary of Observations and Analyses of the 3A Bands
of the $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{14}\text{C}^{16}\text{O}$ Isotopic Molecules

| Molecule | Band | Remarks | Total number of lines | J_{max} | f^a | $\sigma_f \cdot 10^2^b$ (in cm^{-1}) |
|------------------------------|------|-------------------|-------------------------|-----------------------|-------|---|
| $^{12}\text{C}^{16}\text{O}$ | 0-2 | reanalysis | 609 (348 ^c) | 25 (19 ^c) | 323 | 1.70 |
| | 0-3 | reanalysis | 609 (336 ^c) | 25 (19 ^c) | 332 | 2.03 |
| | 1-2 | first observation | 116 | 13 | 48 | 2.83 |
| $^{13}\text{C}^{16}\text{O}$ | 0-3 | reanalysis | 587 (304 ^c) | 25 (18 ^c) | 324 | 2.09 |
| | 1-3 | first observation | 545 | 25 | 225 | 2.87 |
| $^{14}\text{C}^{16}\text{O}$ | 0-3 | reanalysis | 605 (318 ^c) | 25 (18 ^c) | 377 | 1.76 |

^a Number of degrees of freedom of the fit.

^b Standard deviation of the fit.

^c The previously obtained data concerning the bands under consideration.

were used as the calibration spectrum. Next, the plates were measured by an automatic comparator assembled in our laboratory. The positions of the line-centers were calculated by means of an interactive graphic computer program using a least-squares procedure and assuming Gaussian profiles for the lines. Repeatability of the measurements was tested to be 0.25–0.5 μm according to the grain of the plates.

The typical standard deviation of the least-squares fit for the 80–170 calibration lines was about $(3.6\text{--}5.4) \times 10^{-3} \text{ cm}^{-1}$. The final calculations of the position of molecular line centers were backed up by an earlier set of sorted wavenumbers of the CO lines in measured regions obtained from preliminary measurements.

Finally, the precision of single lines with a good line/background ratio was evaluated to be about 0.010–0.020 cm^{-1} . However, many lines were blended due to (a) the complexity of the triplet spectrum; (b) 12 bandheads in each band; (c) overlapping by the third positive system; and (d) strong overlapping by the fourth positive system. Blended lines of less precision are asterisked in the tables and have not been used to calculate molecular constants.

Tables of the observed wavenumbers of lines, along with rotational assignments for the 0–2, 0–3, and 1–2 bands for $^{12}\text{C}^{16}\text{O}$, the 0–3 and 1–3 bands for $^{13}\text{C}^{16}\text{O}$ and the 0–3 band for $^{14}\text{C}^{16}\text{O}$, respectively, have been deposited as supplementary data. A measurement summary of the analyzed bands of the 3A system in several isotopic molecules can be found in Table 1.

ANALYSIS AND CALCULATIONS

A preliminary analysis of the observed bands and J numbering of lines in the $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{14}\text{C}^{16}\text{O}$ molecules was conducted on the basis of the previously obtained molecular spectra description of the 3A bands system (23, 24).

The previous analyses of the $c^3\Pi(v=0)$ level presented in Ref. (6, 9–12, 14, 20) and that of the $c^3\Pi(v=1)$ level conducted by Hakalla (24) made it possible to specify the location

of perturbations on those levels. They are strongest for the $J=1$ and $10 \leq J \leq 20$ rotational levels. The other levels are slightly perturbed, but within one standard deviation of the individual bands fit.

Due to those perturbations as well as others which have not been yet specified, the reduction of wavenumbers to rovibronic parameters was calculated within the framework of an individual band-by-band analysis using the nonlinear least-squares method suggested by Curl and Dane (27) and Watson (28), later elaborated on by Rytel and Rytel (29). This method enables us to separate molecular information about the $c^3\Pi$ upper state from that concerning the $a^3\Pi$ lower state. In the method under consideration the $a^3\Pi$ state is represented by the effective Hamiltonian from Brown *et al.* (30). Direct matrix elements of this Hamiltonian for the $^3\Pi$ state and for the basis functions of the Hund's case (a) were taken from Brown and Merer (31), which made it possible to obtain individual molecular constants for the $a^3\Pi(v=2, 3)$ state in $^{12}\text{C}^{16}\text{O}$, for the $a^3\Pi(v=3)$ state in $^{13}\text{C}^{16}\text{O}$, and for the $a^3\Pi(v=3)$ state in $^{14}\text{C}^{16}\text{O}$, as well as term values of the rotational structure for the $v=0$ and $v=1$ levels of the $c^3\Pi$ state.

The individual effective rotational constants were determined in connection with the aforementioned complicated and not quite clear perturbations of the $c^3\Pi$ state ($v=0, 1$). In this case both states under consideration were represented by effective Hamiltonians from Brown *et al.* (30, 31). As for the $c^3\Pi$ state, this model was simplified to the version in which additional perturbing matrix elements were disregarded. Only the unperturbed lines with $1 < J < 10$ and $J > 20$ as well as the well-determined values of molecular constants of the lower $a^3\Pi$ state have been considered in the least-squares fit using a computer program described in Ref. (32). In the case of the 1–2 band of the $^{12}\text{C}^{16}\text{O}$ molecule the values of molecular parameters of the $a^3\Pi(v=2)$ level were constrained to the values determined for the 0–2 band of the same molecule.

Calculations of the final molecular parameters for the observed levels in $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}$ were conducted by the least-squares merge fit described by Albritton *et al.* (33) and Coxon (34). All the rovibronic constants values from bands analyzed in Refs. (23, 24), as well as those described in the present paper, i.e., 0–0, 0–1, 0–2, 0–3, 1–0, 1–1, 1–2, 1–3 in the $^{13}\text{C}^{16}\text{O}$ molecule and 0–2, 0–3, and 1–2 in the $^{12}\text{C}^{16}\text{O}$ molecule have been applied. The estimated variance of the merging and the number of degrees of freedom were $\sigma_M = 1.98$ and $f_M = 83$ for $^{13}\text{C}^{16}\text{O}$ and $\sigma_M = 2.46$ and $f_M = 16$ for $^{12}\text{C}^{16}\text{O}$. The final molecular constants output as a result of the merge fit are represented in Table 2 for the $c^3\Pi$ state and in Tables 3 and 4 for the $a^3\Pi$ state. The rovibronic constants calculated for the singular 0–3 band in the $^{14}\text{C}^{16}\text{O}$ molecule were also introduced into those tables.

The 12 previously unknown band origins are presented in Table 5. The vibrational energy differences of the $c^3\Pi$ state in $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}$ as well as those determined for the $a^3\Pi$ state in $^{13}\text{C}^{16}\text{O}$ were calculated in the course of those mergings and are featured in Table 6.

TABLE 2
**Merged^a Molecular Constants (in cm⁻¹) for the *c*³Π State of the ¹²C¹⁶O, ¹³C¹⁶O,
and ¹⁴C¹⁶O Isotopic Molecules^b**

| Constant | <i>v</i> = 0 (¹² C ¹⁶ O) | <i>v</i> = 1 (¹² C ¹⁶ O) | <i>v</i> = 0 (¹³ C ¹⁶ O) | <i>v</i> = 1 (¹³ C ¹⁶ O) | <i>v</i> = 0 (¹⁴ C ¹⁶ O) |
|---|--|--|--|--|--|
| <i>B_v</i> | 1.955425(38) 1.9469 [*] 1.96019(19) ^e 1.9484(7) ^h 1.97504(63) ^j | 1.94199(12) | 1.873986(64) 1.87522(18) ^g | 1.857052(63) 1.85719(11) ^k | 1.802809(21) 1.80224(16) ^d |
| <i>D_v · 10⁶</i> | - 14.669(48) - 36.2 [*] 3.68(54) ^e - 60(6) ^h 15.01(69) ^j | - 6.28(89) | - 6.009(84) 4.25(60) ^g | - 5.617(81) - 5.64(13) ^k | - 2.146(34) 4.42(46) ^d |
| <i>A_v</i> | 1.5907(37) 1.430(25) ^e 1.49(3) ^f 1.504(12) ^h - 0.13(13) ^j | 1.057(16) | 1.0664(51) 1.109(27) ^g | 1.0594(70) 1.0684(86) ^k | 0.9800(45) 0.956(21) ^d |
| <i>A_{D_v} · 10²</i> | 0.826(22) | 0.956(52) | 0.763(32) | 0.931(25) 1.043(41) ^k | 0.607(24) |
| <i>λ_v</i> | 0.0517(12) 0.064(7) ^h | 0.3486(23) | 0.0294(20) | 0.1319(24) 0.1310(30) ^k | 0.0289(18) |
| <i>o_v · 10²</i> | 7.27(23) | - 1.61(30) | 6.29(33) | - 1.72(38) - 1.63(59) ^k | - 0.19(22) |
| <i>p_v · 10³</i> | 0.41(13) | 5.42(39) | 0.44(27) | 4.68(30) 4.58(40) ^k | - 0.59(17) |
| <i>q_v · 10³</i> | 10.010(21) 13. ^c 9.88(13) ^h 12. ^g 9.770(59) ^j | 9.929(36) | 9.063(23) | 9.095(23) 9.118(37) ^k | 8.4116(69) |

^a The calculation conducted for the ¹⁴C¹⁶O molecule is an exception, since there is only one known band.

^b Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. The underlined values are discussed in detail in the body of the paper. The values written in the bold type are obtained in the course of the present research.

^c After Ginter *et al.* (6) (* in this paper two values were given, one of the substate Π⁻ and the other for the Π⁺. The number reported here is their arithmetic average).

^d After Siwec-Rytel (9).

^e After Rytel *et al.* (10).

^f After Klopotek *et al.* (12).

^g After Rytel *et al.* (11).

^h After Dabrowski *et al.* (14).

ⁱ After Mellinger *et al.* (20).

^j After Baker *et al.* (22).

^k After Hakalla (24).

Next, the unperturbed term values were determined for each band by means of the nonlinear least-squares method in the Curl–Dane–Watson version (27, 28). Only the unperturbed lines $1 < J < 10$ and $J > 20$ were implemented for the calculation in question. The values of the perturbed terms were then compared to those of the unperturbed ones. The results are highlighted in Fig. 1.

The equilibrium rotational constants were determined for the *c*³Π state (for the first time) and for the *a*³Π state. Those computations were performed using the weighted least-squares method on the basis of the merged rovibronic constant values, assuming their traditionally recognized polynomial dependence on the vibrational quantum number. In order to determine equilibrium molecular constants with greater precision, the rotational

TABLE 3
Merged Molecular Constants (in cm^{-1}) for the $a^3\Pi$ State
of the $^{13}\text{C}^{16}\text{O}$ Molecule^a

| Constant | $v = 0$ | $v = 1$ | $v = 2$ | $v = 3$ |
|------------------------|--------------|--------------|--------------|--------------|
| B_v | 1.607797(74) | 1.590044(75) | 1.572525(67) | 1.553915(68) |
| $D_v \cdot 10^6$ | 5.74(11) | 5.96(11) | 7.097(91) | 5.132(91) |
| A_v | 41.4562(26) | 41.2951(26) | 41.1201(23) | 40.9479(21) |
| $A_{D_v} \cdot 10^4$ | -1.93(27) | -1.61(25) | -2.50(22) | 0.13(21) |
| $\lambda_v \cdot 10^2$ | 3.78(23) | 3.01(24) | 2.66(21) | 3.03(18) |
| o_v | 0.8580(32) | 0.8487(34) | 0.8269(29) | 0.8108(27) |
| $p_v \cdot 10^3$ | 5.69(40) | 5.54(43) | 4.64(36) | 5.18(38) |
| $q_v \cdot 10^4$ | 0.77(37) | -0.11(36) | 1.45(36) | -0.84(37) |

^a Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

constants of the $a^3\Pi(v = 0, 1)$ levels obtained by Hevenith *et al.* (35) for the $^{12}\text{C}^{16}\text{O}$ molecule, as well as some constants of the $a^3\Pi$ state determined by Amiot *et al.* (36) for the $^{13}\text{C}^{16}\text{O}$ molecule, were additionally used. The results are featured in Table 7.

On the basis of the band origins of $^{13}\text{C}^{16}\text{O}$ the equilibrium vibrational constants for the $c^3\Pi$ and $a^3\Pi$ states of this molecule were obtained using the weighted least-squares method. The constant $w_e x_e$ for the $c^3\Pi$ state in the $^{13}\text{C}^{16}\text{O}$ molecule was constrained to the value determined by the band origins 1–2 of the $^{12}\text{C}^{16}\text{O}$ molecule and by means of Dunham's isotopic relationship. The appropriate formulas were given by Dunham

TABLE 4
Merged^a Molecular Constants (in cm^{-1}) for the $a^3\Pi$
State of the $^{12}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{16}\text{O}$ Isotopic Molecules^b

| Constant | $v = 2$ ($^{12}\text{C}^{16}\text{O}$) | $v = 3$ ($^{12}\text{C}^{16}\text{O}$) | $v = 3$ ($^{14}\text{C}^{16}\text{O}$) |
|------------------------|---|---|---|
| B_v | 1.643399(38) | 1.624007(50) | 1.494275(67) |
| $D_v \cdot 10^6$ | 6.497(49) | 6.463(72) | 5.647(97) |
| A_v | 41.1096(12) | 40.9480(18) | 40.9587(18) |
| $A_{D_v} \cdot 10^4$ | -2.09(17) | -2.86(16) | -0.74(21) |
| $\lambda_v \cdot 10^2$ | 3.494(94) | 4.69(17) | 3.80(15) |
| o_v | 0.8344(15) | 0.7852(23) | 0.8102(29) |
| $p_v \cdot 10^3$ | 6.11(21) | 7.13(29) | 5.49(29) |
| $q_v \cdot 10^4$ | 1.37(56) ^c | 1.36(66) ^c | 1.00(58) |

^a The calculation conducted for the $^{14}\text{C}^{16}\text{O}$ molecule is an exception, since there is only one known band.

^b Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

^c This work (individual results).

TABLE 5
Band Origins (in cm^{-1}) for the 3A ($c^3\Pi$ – $a^3\Pi$) System
of the $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{14}\text{C}^{16}\text{O}$ Isotopic Molecules^a

| Band | $^{12}\text{C}^{16}\text{O}$ | $^{13}\text{C}^{16}\text{O}$ | $^{14}\text{C}^{16}\text{O}$ |
|-------|------------------------------|------------------------------|------------------------------|
| 1 – 0 | | 45341.4967(22) | |
| 1 – 1 | | 43664.5044(22) | |
| 1 – 2 | 41981.5140(30) | 42015.4655(23) | |
| 1 – 3 | | 40394.2821(22) | |
| 0 – 0 | | 43599.4023(25) | |
| 0 – 1 | | 41922.4100(33) | |
| 0 – 2 | 40205.7475(11) | 40273.3711(31) | |
| 0 – 3 | 38549.4971(18) | 38652.1877(30) | 38742.1756(12) |

^a Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

(37) and by Brown *et al.* (30). The results are represented in Table 7 too.

The equilibrium constants from Table 7 were then used to draw the RKR potential curves for the $a^3\Pi$ state as well as for the $c^3\Pi$ state for the first time. Those curves can be found in Fig. 2, whereas the values of RKR turning points are presented in Table 8. The Franck–Condon factors, r -centroids, and relative intensities have been determined for the 3A system for the first time, and are represented in Table 9.

DISCUSSION

Merged effective rotational constants of the $c^3\Pi$ state of the $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}$ molecules as well as rotational constants

TABLE 6
Vibration Energy Differences (in cm^{-1}) of the $c^3\Pi$ State in the
 $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ Molecules and of the $a^3\Pi$ State in the $^{13}\text{C}^{16}\text{O}$
Molecule^a

| State | Remarks | Vibration energy difference |
|----------|-------------------|--------------------------------|
| $c^3\Pi$ | $G(1') - G(0')$ | 1775.7665(41) ^b |
| | | 1742.0944(22) |
| $a^3\Pi$ | $G(1'') - G(0'')$ | 1676.9923(33) |
| | | 3326.0312(31) |
| | | 4947.2146(30) |

^a Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

^b Vibration energy difference of the $c^3\Pi$ state in the $^{12}\text{C}^{16}\text{O}$ molecule.

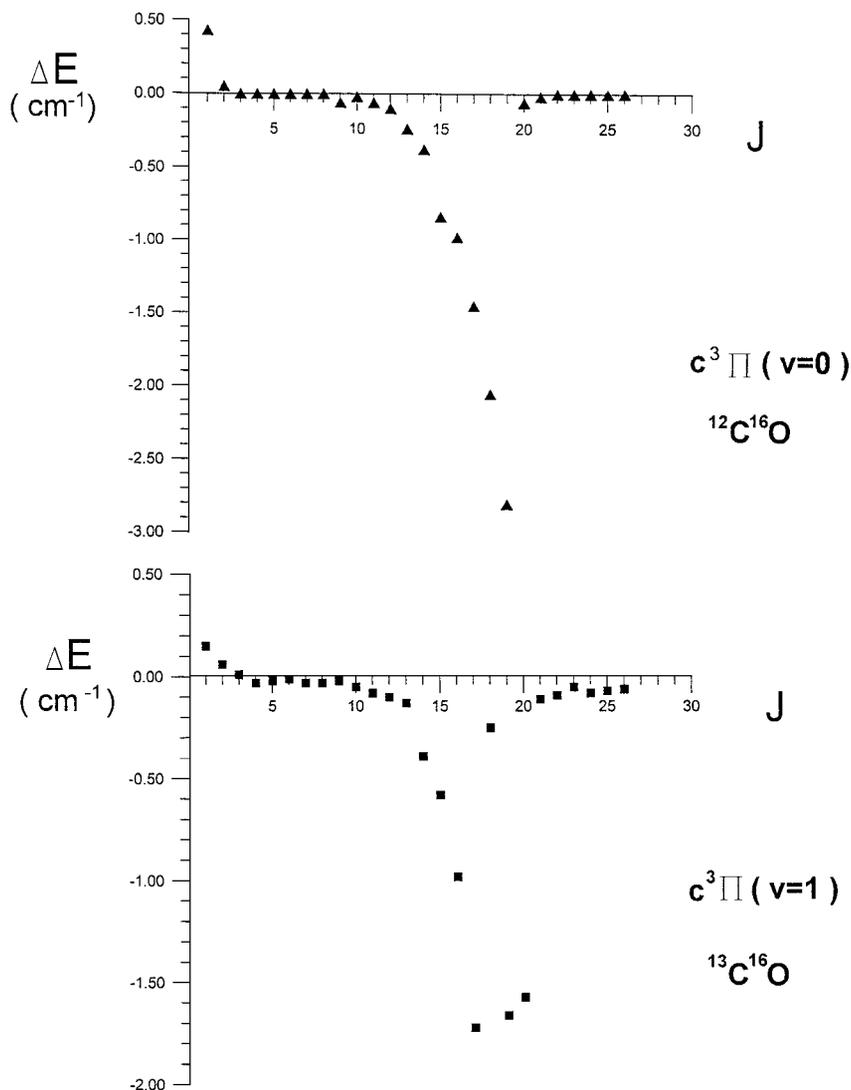


FIG. 1. Calculated energy shifts of the $c^3\Pi$ terms caused by the complex, multistate, and not fully identified perturbation. Displacements are demonstrated using the examples of the $F_{1e}(J)$ terms for the $c^3\Pi_0(v=0)$ level in the $^{12}\text{C}^{16}\text{O}$ molecule and for the $c^3\Pi_0(v=1)$ in the $^{13}\text{C}^{16}\text{O}$ molecule.

from the individual fits of the 0–3 band of the $^{14}\text{C}^{16}\text{O}$ molecule are represented in Table 2. The $c^3\Pi(v=1)$ constants in the $^{12}\text{C}^{16}\text{O}$ molecule have not been noted in specialized publications before, whereas the rest of the constants are well determined, are more precise, and are in reasonable agreement with the previously published results.

Of primary importance for the analysis of the $c^3\Pi$ state are three constants. They will be discussed below.

The Λ -doubling constant q directly represents the $^3\Pi\text{--}^3\Sigma$ interaction (31). Its relatively large values for the $c^3\Pi(v=0)$ and 1) $3p\Pi$ levels in all the analyzed molecules (e.g., the well-determined $q_{c^3\Pi(v=0)}^{^{12}\text{C}^{16}\text{O}} = 10.010(21) \cdot 10^{-3} \text{ cm}^{-1}$) amply demonstrate that the interaction is very intensive. The most probable cause of this perturbation is the $j^3\Sigma^+(3p\sigma)$ Rydberg state because, of all the states of $^3\Sigma$ type, it is the closest to the

$c^3\Pi$ state. Moreover, the $j^3\Sigma^+$ state possesses a similar value $q_{j^3\Sigma^+(v=0)}^{^{12}\text{C}^{16}\text{O}} = 0.012 \text{ cm}^{-1}$ in the pure precession model (20). As has been noted by Mellinger *et al.* (20), the $c^3\Pi(v=0)$ level ($T_{00}^{c^3\Pi\text{--}X^1\Sigma^+} = 92\,072.04 \text{ cm}^{-1}$ (22)) appears to be perturbed by the $j^3\Sigma^+(v=0)$ level ($T_{\Sigma_{\text{eff}}} = 90\,833.233 \text{ cm}^{-1}$ (20)). In the $^{12}\text{C}^{16}\text{O}$ molecule, this interaction is slightly weaker for the $c^3\Pi(v=1)$ level ($9.929 \cdot 10^{-3} \text{ cm}^{-1}$) as compared to the $c^3\Pi(v=0)$ level ($10.010 \cdot 10^{-3} \text{ cm}^{-1}$), whereas in the $^{13}\text{C}^{16}\text{O}$ molecule this interaction is similar for the $c^3\Pi(v=1)$ level and $c^3\Pi(v=0)$ level and equals $9.095(23) \cdot 10^{-3} \text{ cm}^{-1}$ and $9.063(23) \cdot 10^{-3} \text{ cm}^{-1}$, respectively. The least impact of this interaction is noticeable in the $^{14}\text{C}^{16}\text{O}$ molecule ($8.4116 \cdot 10^{-3} \text{ cm}^{-1}$).

Of a considerable interest also is the centrifugal distortion constant D . Its small values (e.g., $D_{c^3\Pi(v=0)}^{^{12}\text{C}^{16}\text{O}} = -14.669 \times$

TABLE 7
Equilibrium Molecular Constants (in cm^{-1}) of the $c^3\Pi$ and $a^3\Pi$ States of the $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ Molecules^a

| Constant/State | $^{12}\text{C}^{16}\text{O}$ | | $^{13}\text{C}^{16}\text{O}$ | |
|---------------------------------|------------------------------|---------------------------------------|------------------------------|---------------------------------------|
| | $c^3\Pi$ | $a^3\Pi^d$ | $c^3\Pi$ | $a^3\Pi^e$ |
| σ_e | 43568.9644 ^f | | 43568.9644(61) | |
| ω_e | 1804.7244 ^f | | 1764.4944(18) | 1705.040(14) |
| $\omega_e x_e$ | 11.7 ^f | | 11.2 ^b | 14.0501(81) |
| $\omega_e y_e \cdot 10^2$ | | | | 1.6317(13) |
| B_e | 1.9649(14) | 1.691129(15) | 1.88245(11) | 1.6165660(48) |
| $\alpha_e \cdot 10^2$ | 1.8119 ^c | 1.8844(27) | 1.6934(90) | 1.77099(79) |
| $\gamma_e \cdot 10^5$ | | -9.61(78) | | -4.82(26) |
| $D_e \cdot 10^6$ | -14.64(46) | 6.344(46) | -6.21(14) | 5.80414(63) |
| $\beta_e \cdot 10^7$ | | 1.40(49) | 3.9(12) | 0.3548(37) |
| $\delta_e \cdot 10^8$ | | -3.1 ^c | | |
| A_e | 1.8576(98) | 41.5346(30) | 1.0699(85) | 41.53790(62) |
| α_{A_e} | -0.534(17) | -0.1754(30) | -0.0070(87) | -0.1602(11) |
| $\beta_{A_e} \cdot 10^3$ | | -2.20(70) | | -2.92(38) |
| $A_{D_e} \cdot 10^3$ | 8.46(47) | -0.286(45) | 8.67(82) | -0.3623(33) |
| $\alpha_{D_e} \cdot 10^4$ | | 0.121 ^c | | 0.113(22) |
| λ_e | -9.67(22) · 10 ⁻² | 3.69(59) · 10 ⁻² | -2.19(33) · 10 ⁻² | 4.54(33) · 10 ⁻² |
| $\alpha_{\lambda_e} \cdot 10^3$ | 0.2969(26) | -6.65 ^c · 10 ⁻³ | 0.1025(32) | -6.51 ^c · 10 ⁻³ |
| o_e | 0.1171(38) | 0.8811(66) | 0.1030(53) | 0.8804(39) |
| $\alpha_{o_e} \cdot 10^2$ | -8.88(38) | -2.23(46) | -8.01(51) | -2.18 ^c |
| p_e | -2.15(26) · 10 ⁻³ | 6.99(58) · 10 ⁻³ | -1.68(44) · 10 ⁻³ | 5.58(19) · 10 ⁻³ |
| α_{p_e} | 5.11(36) · 10 ⁻³ | -1.87 ^c · 10 ⁻⁴ | 4.24(41) · 10 ⁻³ | -1.75 ^c · 10 ⁻⁴ |
| $q_e \cdot 10^3$ | 9.989(36) | 0.05963(60) | 9.079(16) | 0.117(38) |
| $\alpha_{q_e} \cdot 10^6$ | | -2.88(85) | | -3.22 ^c |

^a Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

^b The value determined on the basis of the band origins of the $^{13}\text{C}^{16}\text{O}$ molecule (see Table 5) as well as Dunham's relationships using the band origin of the 1–2 band in the $^{12}\text{C}^{16}\text{O}$ molecule. The value was fixed during the evaluation of the equilibrium molecular constants.

^c Values constrained to reproduce original data with full accuracy.

^d In order to determine the equilibrium constants with greater precision, the rotational constant of the $a^3\Pi(v=0, 1)$ levels given by Havenith *et al.* (35) were implemented in calculations for the $^{12}\text{C}^{16}\text{O}$ molecule.

^e Some less exact rovibronic constants determined in this paper for the $^{13}\text{C}^{16}\text{O}$ molecule have been replaced by the constants given by Amiot *et al.* (36) in the course of evaluation of the equilibrium molecular constants.

^f Evaluated from the $^{13}\text{C}^{16}\text{O}$ parameters using Dunham's isotopic relationships.

10^{-6} cm^{-1} , which is negative, like those obtained by Ginter and Tilford (6) and Dabrowski *et al.* (14) indicate perturbations, rather than the centrifugal distortion. The rotational fit conducted by Baker *et al.* (25) explicitly encompasses possible homogeneous interactions (38) between the $c^3\Pi(v=0)$ and $k^3\Pi(v=2)$ states and yields a satisfactory result in the form of a more realistic value $D = 15.01 \times 10^{-6} \text{ cm}^{-1}$. This result shows that the $k^3\Pi(v=2)$ level which, according to Baker *et al.* (25), is located approximately 118 cm^{-1} below the $c^3\Pi(v=0)$ level, is one of the perturbers of the $c^3\Pi(v=0)$ level. A similar result was obtained by Siwiec-Rytel (9) and Rytel *et al.* (10, 11) with an erroneous interpretation of vibrational lev-

els of the $k^3\Pi$ state, which was corrected by Berden *et al.* (21). Nevertheless, those calculations took into consideration only one of numerous perturbers of the $c^3\Pi$ state. It is quite probable that a very similar, though weaker, perturbation ($D = -6.28 \times 10^{-6} \text{ cm}^{-1}$ and $D = -5.617 \times 10^{-6} \text{ cm}^{-1}$ for $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$, respectively) of the $c^3\Pi(v=1)$ level ($T_v^{c^3\Pi(v=1)} = 94\,663.1413 \text{ cm}^{-1}$ for $^{13}\text{C}^{16}\text{O}$ and $T_v^{c^3\Pi(v=1)} = 94\,696.8134 \text{ cm}^{-1}$ for $^{12}\text{C}^{16}\text{O}$ (the values calculated within the framework of this project)) is caused by a closely located $v=4$ vibrational level of the $k^3\Pi$ state ($T_v^{k^3\Pi(v=4)} = 94\,589.22 \text{ cm}^{-1}$ for $^{13}\text{C}^{16}\text{O}$ and $T_v^{k^3\Pi(v=4)} = 94\,669.37 \text{ cm}^{-1}$ for $^{12}\text{C}^{16}\text{O}$ (as specified by Berden *et al.* (21))).

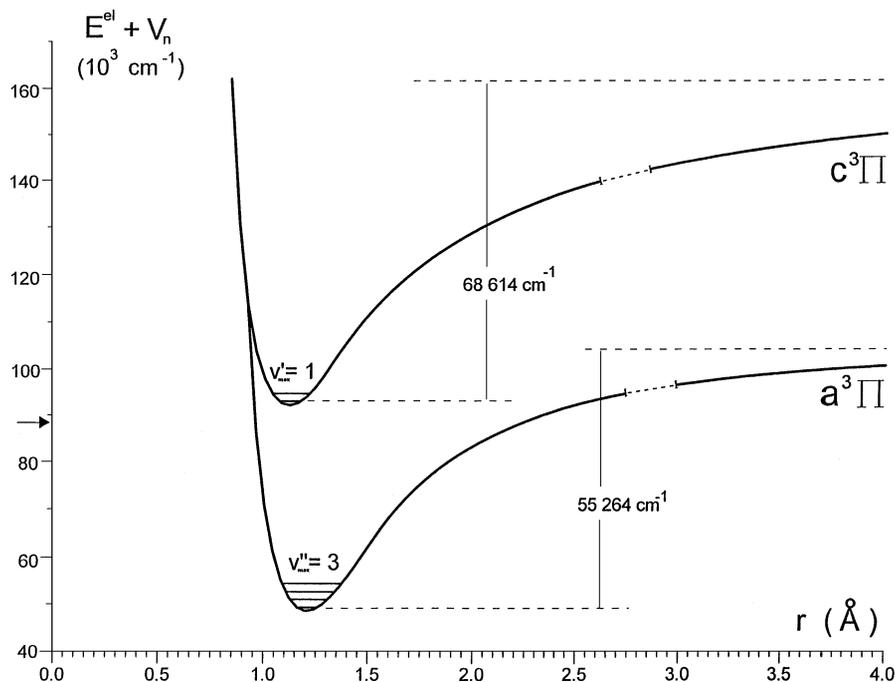


FIG. 2. RKR potential curves of the $c^3\Pi$ and $a^3\Pi$ states in the $^{13}\text{C}^{16}\text{O}$ molecule. The arrow marks the dissociation energy given by Mellinger and Vidal (20). The figure shows for the first time the dissociation energy of the $c^3\Pi$ state, which equals $68\,614\text{ cm}^{-1}$.

The impact of this perturbation weakens with the increase of molecular mass, and in each isotope under consideration it is less for the $v = 1$ level than for the $v = 0$ level. This discrepancy is, nevertheless, smaller in the $^{13}\text{C}^{16}\text{O}$ molecule than in an ordinary molecule.

A considerably smaller value of the D constant ($-60 \times 10^{-6}\text{ cm}^{-1}$), as specified by Dabrowski *et al.* (14, $c^3\Pi$ - $b^3\Sigma^+$ system), arises as a result of additional strong perturbation of the $b^3\Sigma^+$ state, whereas a smaller value of the same constant ($-36.2 \times 10^{-6}\text{ cm}^{-1}$), as given by Ginter and Tilford (6), may be attributed to their shorter bands (up to $J_{\text{max}} = 19$), since higher rotational levels have a greater influence on the centrifugal distortion constant.

The last parameter of primary importance for the analysis of the $c^3\Pi$ state is the spin-orbit interaction constant A . As compared to all the varieties of CO isotopes noted in Table 2, the aforementioned constant has values smaller than can be expected for the states close to Hund's (b) case (e.g., the greatest of the calculated values equals $A_{c^3\Pi(v=0)}^{12\text{C}^{16}\text{O}} = 1.5907\text{ cm}^{-1}$). In accordance with the suggestion put forward by Baker *et al.* (25), it is only the Rydberg electron that contributes to the spin-orbit splitting of the $c^3\Pi$ state and it is the Rydberg nature of the orbital that leads to the small value of the A constant. In the $^{12}\text{C}^{16}\text{O}$ molecule this constant is smaller for the $v = 1$ level (1.057 cm^{-1}) than for the $v = 0$ level (1.5907 cm^{-1}) of the $c^3\Pi$ state. As for the $^{13}\text{C}^{16}\text{O}$ molecule, the constants under consideration has a comparably small value ($1.0594(70)\text{ cm}^{-1}$ and $1.0664(51)\text{ cm}^{-1}$ for the $v = 1$ and $v = 0$ level, respec-

tively), which leads to considerable difficulties in the observation of the triplet splitting of the $c^3\Pi(v = 1)$ level. The least significant impact of this interaction can be found in the $^{14}\text{C}^{16}\text{O}$ molecule (0.9800 cm^{-1} for the $c^3\Pi(v = 0)$ level). Due to the very small value of the spin-orbit interaction constant, it was only in 1983 when the triplet splitting of the $c^3\Pi$ state was first observed by Siwiec-Rytele in the $^{14}\text{C}^{16}\text{O}$ molecule (9, $A = 0.956\text{ cm}^{-1}$). Nevertheless, it was rather a fragmentary observation, dealing only with two satellite branches: $^oP_{32}$ and $^oR_{12}$. The first clear observation of the triplet splitting ($A_{c^3\Pi(v=0)}^{12\text{C}^{16}\text{O}} = 1.49\text{ cm}^{-1}$) was performed by Klopotek and Vidal (12) in 1985.

This research has yielded the well-determined values of the A constant for the $c^3\Pi(v = 0)$ level of $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{14}\text{C}^{16}\text{O}$ as well as determined the A value for the $c^3\Pi(v = 1)$ level of $^{12}\text{C}^{16}\text{O}$ molecule ($1.057(16)\text{ cm}^{-1}$) which has never been noted in specialized literature. Those observations justify the conclusion drawn by Klopotek *et al.* (12) that the $c^3\Pi$ state electronic state is regular. Hence, the negative value ($A_{c^3\Pi(v=0)}^{12\text{C}^{16}\text{O}} = -0.13\text{ cm}^{-1}$) obtained by Baker *et al.* (25) may be attributed to the inclusion of only one perturbing state [$k^3\Pi(v = 2)$] in the deperturbation calculations, whereas those states are numerous.

Calculated energy shifts of the $c^3\Pi$ terms cause by perturbations are shown in Fig. 1. The graphic representation suggests that the main, the most forcible part of perturbations of the $c^3\Pi$ state causes a state which is characterized by a different multiplicity (39, Fig. 4.81). Hence, it is a heterogeneous perturbation that can be attributed to the action of the $^3\Sigma^+$ state (most

TABLE 8
Vibrational Levels and RKR Turning Points for the $c^3\Pi$ and $a^3\Pi$ States of the $^{13}\text{C}^{16}\text{O}$ Molecule^a

| | $c^3\Pi$ | | $a^3\Pi$ |
|---------|-----------------|------------------------------|------------------------|
| | Y_{00} | 0.0772 | 0.0026 |
| | r_e | 1.117388 | 1.205647 |
| $v = 0$ | $G(v) + Y_{00}$ | <u>879.3700</u> ^b | 849.0069 |
| | r_{min} | 1.06851 | 1.15634 |
| | r_{max} | 1.17201 | 1.26172 |
| $v = 1$ | $G(v) + Y_{00}$ | 2621.4644 | 2525.9997 |
| | r_{min} | 1.03595 | 1.12397 |
| | r_{max} | 1.21618 | 1.30776 |
| $v = 2$ | $G(v) + Y_{00}$ | 4341.1588 ^c | 4175.0392 |
| | r_{min} | 1.01496 ^c | 1.10333 |
| | r_{max} | 1.24890 ^c | 1.34227 |
| | B_V | 1.840115 ^c | |
| $v = 3$ | $G(v) + Y_{00}$ | | 5796.2233 |
| | r_{min} | | 1.08747 |
| | r_{max} | | 1.37220 |
| $v = 4$ | $G(v) + Y_{00}$ | | 7389.6498 ^d |
| | r_{min} | | 1.07438 ^d |
| | r_{max} | | 1.39958 ^d |

^a $G(v)$ values are in cm^{-1} ; all r -values are in Å .

^b The underlined value is simultaneously the value of the $c^3\Pi$ state zero-point energy.

^c Theoretically determined for the so far unobserved $c^3\Pi(v = 2)$ vibrational level.

^d Theoretically determined for the $a^3\Pi(v = 4)$ level, which has not been observed in the present research.

probably the $j^3\Sigma^+$). This assumption is justified by a relatively large value of the Λ -doubling constant q (see Table 2).

The global character of perturbations observed on the majority of rotational levels, particularly original ones, is evidence of homogenous interaction between the $c^3\Pi$ state and another forcible, lower located, perturbing state, namely the $k^3\Pi$ state, as has been shown by Baker *et al.* (25). This assumption is justified by the anomalous small values of the centrifugal distortion constants D (see Table 2).

Nevertheless, different kinds of perturbations are observable at the lines with low J value, which is manifested by the increase of intensity noted by Baker *et al.* (25), as well as a considerable increase of the triplet splitting for the original J values observed by Klopotek *et al.* (12).

Merging of all the individual rotational constants enables us to specify for the first time the vibrational differences between the $c^3\Pi(v = 1)$ level originally observed and analyzed by Hakalla (24) and the previously known $c^3\Pi(v = 0)$ level. Those differences are $G(1') - G(0') = 1742.0944$ (22) cm^{-1} and 1775.7665 (41) cm^{-1} for $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}$, respectively

(see Table 6). On the basis of the merged rotational constants of the $c^3\Pi$ state, its equilibrium molecular constants for both the $^{13}\text{C}^{16}\text{O}$ molecule and the $^{12}\text{C}^{16}\text{O}$ molecule have been determined (see Table 7). Those constants allowed to determine for the first time Dunham's factor ($Y_{00} = 0.0772 \text{ cm}^{-1}$), zero-point energy ($G(0) + Y_{00} = 873.3700 \text{ cm}^{-1}$), and Franck–Condon factors, r -centroids, and relative intensities for the $c^3\Pi$ state (see Tables 8 and 9). The data above justify the experimental results observed in our laboratory; namely, the 1–0, 0–1, 0–0, 0–2, and 0–3 bands of the 3A system have the greatest intensity, whereas the 1–1 and 1–2 bands are very weak in all the isotopic molecules under consideration.

Figure 2 represents the experimental RKR potential curve for the $c^3\Pi$ state. This curve was determined using (a) the $T_e^{c^3\Pi} = 92\,041.68 \text{ cm}^{-1}$ value above the CO ground state, which was calculated on the basis of the $T_{00}^{c^3\Pi-X^1\Sigma^+} = 92\,072.04 \text{ cm}^{-1}$ value given by Baker *et al.* (25); and (b) the zero-point energy value of the $c^3\Pi$ and $a^3\Pi$ states taken from Table 8. The previously unknown dissociation energy of the $c^3\Pi$ state, which equals $68\,614 \text{ cm}^{-1}$, was thus determined. The $c^3\Pi$ state is $13\,350 \text{ cm}^{-1}$ “deeper” than the $a^3\Pi$ state. The $c^3\Pi$ state also reveals a slight deviation from the asymptotic attraction to the dissociation energy, which can be attributed to the fact that only two vibrational levels of the $c^3\Pi$ state, $v = 0$ and $v = 1$, have been observed.

TABLE 9
Franck–Condon Factors, r -Centroids, and Relative Intensities for the 3A System ($c^3\Pi$ – $a^3\Pi$) of the $^{13}\text{C}^{16}\text{O}$ Molecule^a

| $v'' \setminus v'$ | 0 | 1 | 2 ^b |
|--------------------|------------------------|-------------------------|------------------------|
| 0 | 0.2342 | 0.4029 | 0.264 |
| | 1.1677 | 1.1989 | 1.236 |
| | 7.5690 | 10.0000 | 10.000 |
| 1 | 0.2774 | 4.5335·10 ⁻² | 0.106 |
| | 1.1376 | 1.1502 | 1.212 |
| | 10.0000 | 1.00487 | 3.603 |
| 2 | 0.2093 | 1.7915·10 ⁻² | 0.161 |
| | 1.1128 | 1.1601 | 1.164 |
| | 8.4017 | 0.4382 | 4.905 |
| 3 | 0.1298 | 9.3699·10 ⁻² | 3.045·10 ⁻² |
| | 1.0917 | 1.1204 | 1.122 |
| | 5.7689 | 2.5480 | 1.008 |
| 4 ^c | 7.253·10 ⁻² | 0.124 | 3.63·10 ⁻³ |
| | 1.073 | 1.096 | 1.16 |
| | 3.552 | 3.736 | 0.13 |

^a The values represented in sequence one under the other stand for the Franck–Condon factor, r -centroids (in Å), and relative intensities (in $\frac{\text{quantum}}{s}$ scaled to 10) for each band.

^b Theoretically determined for the so far unobserved $c^3\Pi(v = 2)$ vibrational level.

^c Theoretically determined for the $a^3\Pi(v = 4)$ level, which has not been observed in the present research.

CONCLUSIONS

This paper presents the first observations of the 1–2 and 1–3 bands of the 3A band system in the emission spectra of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$, respectively. It has also specified with higher precision the 0–2 and 0–3 bands in the $^{12}\text{C}^{16}\text{O}$ molecule, as well as the 0–3 band in the $^{13}\text{C}^{16}\text{O}$ and $^{14}\text{C}^{16}\text{O}$ molecules.

The analysis of the structure of the bands belonging to the 3A system suggests that the $c^3\Pi(v=0)$ level and the $c^3\Pi(v=1)$ level are subject to a complicated and multistate perturbation whose main part is caused by a $^3\Sigma$ (most probably the $j^3\Sigma^+$) state and by the $k^3\Pi$ state. Nevertheless, those are not the only perturbers of the $c^3\Pi$ state.

The values of the following parameters of the $c^3\Pi$ state have not been previously noted in specialized publications: (a) the rotational constants for the $v=1$ level in $^{12}\text{C}^{16}\text{O}$, (b) the vibrational energy differences in $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}$, (c) the equilibrium rotational and vibrational molecular constants in $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}$, (d) the 12 band origins of the 3A system in $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{14}\text{C}^{16}\text{O}$, and (e) the experimental RKR curve, FCF factors, and r -centroids. The data above are an important source of information concerning the aforementioned band system and considerably widen the scope of knowledge about the complicated most excited triplet state of the CO molecule.

Our previous publications (23, 24) and the present paper have increased by more than three times the experimental material concerning the 3A band system. Over 6600 molecular lines in 12 bands have been interpreted, whereas the previously observed data deal with no more than over 2000 lines in 9 bands.

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