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Perturbation study via rotational-resolved spectrum in the triplet band $d^3\Delta - a^3\Pi$ (2, 1) of CO*

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The triplet band $d^3\Delta - a^3\Pi$ (2, 1) of the CO molecule in the near infrared region of 12350–12850cm^{-1} has been observed and analysed by taking into account the perturbation interaction between the $d^3\Delta$(v= 2) and $a^3\Pi$ (v= 9) states. The most perturbed lines and most precise perturbation parameters, α_2 and β_2, and electronic perturbation constants, ξ_e and η_e, for the $d^3\Delta$ (v= 2) and $a^3\Pi$ (v= 9) states have been obtained.

Keywords: CO molecule, triplet band, perturbation
PACC: 3310J, 3320E

1. Introduction

The CO molecule has been found in extraterrestrial sources and in a variety of experiments, indicating that it plays significant roles in chemical reaction process, plasma, interstellar matter, biomedicine, environmental science and other fields. Its metastable state $a^3\Pi$, 6eV above the ground state $X^1\Sigma^+$, is the lowest excited state which has been studied by spectroscopy for many years, and its configuration is known to be $(\pi 2p)^4(\sigma 2p)^1(\pi^* 2p)^1$. The next-higher configuration, $(\pi 2p)^3(\sigma 2p)^2(\pi^* 2p)^1$, yields the $a'^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$, $I^1\Sigma$ and $D^1\Delta$ electronic states. The three triplet states of this configuration form the well-known band systems with the $a^3\Pi$ state, namely $a'^3\Sigma^+ - a^3\Pi$ (Asundi band), $d^3\Delta - a^3\Pi$ (Triplet band) and $e^3\Sigma^- - a^3\Pi$ (Herman band) of the CO molecule. As the $\pi 2p$ and $\sigma 2p$ orbitals have similar energies, the triplet states will interact with each other, giving rise to extensive perturbations. Due to its long mean radioactive lifetime of about 7.5ms[1] and high excitation energy, the metastable state $a^3\Pi$ plays an important role in various chemical reactions. Spectroscopic studies on the state $a^3\Pi$ have been reported in various wavelength regions. However, it is difficult to observe the triplet band system by conventional absorption spectroscopy due to the small transition probability. The $d^3\Delta$ and $a^3\Pi$ states were usually studied via the $d^3\Delta - X^1\Sigma^+$ and $a^3\Pi - X^1\Sigma^+$ transitions instead of the direct transition between these two states. The forbidden transition of Cameron band ($a^3\Pi - X^1\Sigma^+$) has been observed in both absorption and emission. A comprehensive review of the published papers concerning this transition was given by Krupenie *et al*[2] in 1966. The forbidden $d^3\Delta - X^1\Sigma^+$ transition was observed in the absorption at high resolution in the vacuum ultraviolet region by using a large spectrograph in 1970, and the bands involving the $d^3\Delta$ state, v=0–8, 10, 15, 19 and 22 levels, were observed and analysed by Herzberg *et al.*[3] Based on these results, Field *et al*[4] gave extensive analyses and derived the molecular constants for three more states of v=9, 12 and 29 in the $d^3\Delta$ state in 1972, accompanying with those of Carroll *et al*[5] and Gerö *et al.*[6] The perturbation studies between the $d^3\Delta$ (v=2) and $a^3\Pi$ (v=9) states were carried out from systematic rotational analysis incorporating with $a^3\Pi - X^1\Sigma^+$[3] and

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$d^3\Delta - X^1\Sigma^+$[4] spectral data. The obtained molecular constants including perturbation parameters between these two states were reasonable. In 1993, an important contribution to understand the perturbed levels was made by Momona *et al*[7] in the study of the triplet band system by analysing the perturbation between the $d^3\Delta_2(v{=}2)$ and $a^3\Pi_2(v{=}9)$ states with $J{=}6$ and 7. Unfortunately, they could not analyse all the perturbed positions because the J values of the observed lines were less than 12. Lu *et al* first directly studied the (5, 0) band[8] in the $d^3\Delta - a^3\Pi$ transition of CO using Zeeman modulation magnetic rotation spectroscopy and obtained fairly good results, and Li *et al*[9] further studied the (5, 0) and (4, 0) bands by taking the perturbation into account and obtained precise molecular constants of the levels involved.

In this paper the $d^3\Delta - a^3\Pi$ (2, 1) absorption spectral band of CO in the near infrared region was directly observed by employing the optical heterodyne magnetic-rotation-enhanced concentration modulation spectroscopy (OH-MR-CMS) technique[10] with a high signal-to-noise ratio, typically over 100, and thus, a set of more precise molecular constants was obtained, the comprehensive perturbation analysis about the $d^3\Delta$ ($v{=}2$) and $a^3\Pi$ ($v{=}9$) states was given as well.

2. Experiment

Concentration modulation spectroscopy for detecting weak absorption of molecules has been improved by optical heterodyne detection and a magnetic rotation effect. The experimental setup for OH-MR-CMS used in this work has been described in detail elsewhere.[10,11] Briefly, a ring Ti:sapphire laser (Coherent Ring 899-29), pumped by a compact laser-diode-pumped Nd:YVO_4 laser (Coherent Verdi 10 @ 532nm), was used as the excitation source and its wavenumber was measured by an attached wavemeter and meanwhile calibrated by the absorption spectrum of I_2 with an uncertainty of about 0.007cm^{-1}. The laser beam was first phase modulated by an electro-optical modulator (EOM) and then passed through an absorption cell. The metastable state $a^3\Pi$ of CO was produced by an AC glow discharge (200mA at 37kHz) of the mixture of CO (20Pa) and He (650Pa) gases. The signal of concentration modulation could be realized by $2f$ demodulation at the lock-in amplifier after the optical phase demodulated by a double-balanced mixer (DBM). Additionally, the whole absorption cell was located inside a water-cooled solenoid driven by a dc power supply to provide a longitudinal magnetic field of 40mT, and at each end of the cell a pair of nearly crossed polarizers was located. The molecular spectrum can be linearly enhanced by the longitudinal magnetic field[12] due to the Faraday effect. Finally, over one thousand lines were recorded in the near infrared region 12350–12850cm^{-1}.

3. Results and discussion

3.1. Theoretical model

The CO triplet band corresponds to the transition between the lower state $a^3\Pi$ and the upper state $d^3\Delta$. The $^3\Delta$ is an inverted state close to Hund's case (a) coupling at lower J values. In the $a^3\Pi$ state with a coupling intermediate between Hund's case (a) and Hund's case (b), the splitting of the Λ-type doubling can be observed. In the $d^3\Delta$ state, on the other hand, the Λ-type doubling is theoretically predicted to be too small to detect, however, it becomes noticeable in our observations because of the heavy perturbation between the $d^3\Delta(v{=}2)$ and $a^3\Pi$ ($v{=}9$) states, especially at the crossing points of potential curves. The triplet band of CO consists of 9 principal subbands, and each subband consists of 3 supplementary branches. Moreover, each rotational line has a Λ-type doubling to form a complicated spectrum. The Hamiltonians and their matrix elements for the $a^3\Pi$ and $d^3\Delta$ states used in the present work are taken from Ref.[9], and the interaction matrix elements between the $d^3\Delta(v{=}2)$ and $a^3\Pi$ ($v{=}9$) states from Ref.[7], which will be described in detail in section 3.2.

3.2. Spectrum and perturbation analysis

The Rydberg–Klein–Rees (RKR) potential-energy curves, as shown in Fig.1, are constructed for the $d^3\Delta$ and $a^3\Pi$ states using standard computer programs proposed by LeRoy.[13] For the equilibrium constants of the lower state $a^3\Pi$ we adopt the latest data of Wada *et al*[14] and those of the upper state $d^3\Delta$ are taken from Ref.[4]. The vibrational states, $v{=}2$ in $d^3\Delta$ and $v{=}9$ in $a^3\Pi$, lie approximately at the same height; furthermore, they are in a position near the intersection of the potential curves. A favourable mutual overlapping of the eigenfunctions of the two states gives a large value to the integral $W_{12}^v = \int \Psi_1^v W^v \Psi_2^v \mathrm{d}r$ of perturbation matrix. Both states have the same multiplicity and the Λ values differ only by 1. As a result,

the perturbation can be quite considerable when the total angular momenta J of the two states equals each other because the Kronig selection rules are fulfilled. The vibrational energies of the $d^3\Delta$ (v=2) and $a^3\Pi$ (v=9) levels lie close together (about 55cm^{-1} separation), giving rise to a strong perturbation that must be treated explicitly. However, the rotational constant of the $d^3\Delta$ (v=2) state is larger than that of the $a^3\Pi$ (v=9) state ($B_\Pi - B_\Delta \approx 0.24\text{cm}^{-1}$). The rotational energy level difference at the same J between two unperturbed states is $E_\Delta - E_\Pi + (B_\Delta - B_\Pi)J(J+1) \approx 55 - 0.24J(J+1)\text{cm}^{-1}$, which decreases as J increases. The perturbing interaction depends inversely on the separation of the two levels, and it becomes the strongest at a given J to cause level shift and lead to a "repulsion" effect. In addition, each of the two states assumes the properties of the other and both states form a kind of *hybrid*. The analysis of the perturbation between the $d^3\Delta$ (v=2) and $a^3\Pi$ (v=9) states was accomplished by Field *et al*[4] and seven positions of perturbation in the $d^3\Delta - a^3\Pi$ (2, 1) transition were predicated.

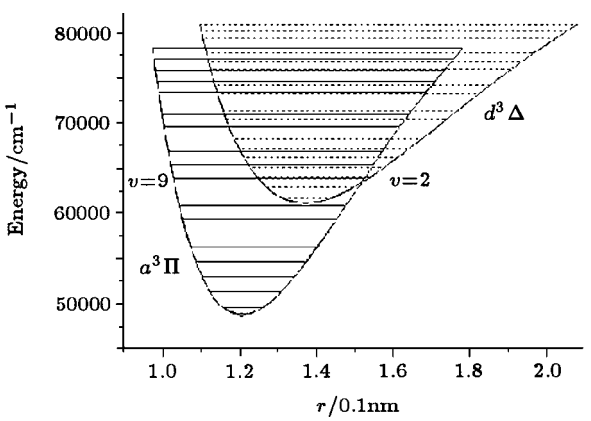


Fig.1. RKR potential energy curves of the $d^3\Delta$ and $a^3\Pi$ states of CO.

The severe perturbation, resulting in anomalous line positions and intensities, complicates the assignment of individual lines. For tentative assignments, we have composed a program to calculate the frequencies of the $d^3\Delta - a^3\Pi$ (2, 1) transition. As for the upper state $d^3\Delta$, the Λ-type doublet splitting is negligible when J is small without perturbation. Therefore, the Hamiltonian matrix consisting of 3×3 elements for both e and f components can be employed. When considering the perturbation from the a state, the energy level of the $d^3\Delta(v=2)$ state is affected by both e and f components of the $a^3\Pi$ (v=9) state. Consequently, the Hamiltonian matrix containing the perturbation of the $a^3\Pi$ (v=9) states, which consists of two 6×6 elements for e component and f component in each, was used to determine the rotational term values of the $d^3\Delta(v=2)$ state. There are five non-zero matrix elements, which are $\langle\Delta_3|H|\Pi_2\rangle$, $\langle\Delta_2|H|\Pi_1\rangle$, $\langle\Delta_1|H|\Pi_0\rangle$, $\langle\Delta_2|H|\Pi_2\rangle$ and $\langle\Delta_1|H|\Pi_2\rangle$ according to Ref.[7]. For the unperturbed $a^3\Pi$ (v=1) state, the rotational term value of each J level was calculated by diagonalizing the e/f Hamiltonian matrix comprising 3×3 matrix elements. Thus, the elementary frequencies of this transition could be computed according to the selection rules given by Brown *et al*.[15]

The observed lines were assigned and analysed sequentially based on the calculated frequencies, with the intensity distribution and the intrinsic phase character of magnetic rotation spectroscopy[16] as an assistant way. Furthermore, the central frequencies of those overlapped lines were determined more accurately by deconvolution method. Altogether 562 lines were assigned to the (2, 1) band of the CO $d^3\Delta - a^3\Pi$ system with J values up to 22. Considering the second difference $\Delta^2\nu$ (m) of some successive lines being varied significantly, 45 perturbed lines were observed for the first time, which allowed us to investigate the perturbation further. The spectral atlas of this band can be reached by contacting the corresponding author. A nonlinear least-squares fitting procedure based on the experimental data gives more precise perturbation constants, α_2 and β_2, and electronic perturbation constants, ξ_e and η_e, for both the $d^3\Delta$ and the $a^3\Pi$ states of CO molecule. The standard error of the fit is 0.0046cm^{-1}, which is the best one obtained so far.

Due to the severe perturbation, the intensity is abnormally small for some lines in this band, e.g. the observed lines of P_{12e} branch at J=6 and 7 shown in Fig.2. The projection of the eigenvector from diagonalizing the effective Hamiltonian matrix of the basic vector was calculated in order to know the mixing complexion in these two perturbed energy levels more clearly. For each J the eigenvector of $d^3\Delta_3$ can be represented as

$$\begin{aligned}|\Delta_3, e/f\rangle =& c_{31}|\Delta_1, e/f\rangle + c_{32}|\Delta_2, e/f\rangle \\ &+ c_{33}|\Delta_3, e/f\rangle + c_{34}|\Pi_0, e/f\rangle \\ &+ c_{35}|\Pi_1, e/f\rangle + c_{36}|\Pi_2, e/f\rangle, \quad (1)\end{aligned}$$

where c_{3j}, derived from the measured frequencies of correctly assigned lines, is the expansion coefficient with $\sum_{j=1}^{6}|c_{3j}|^2 = 1$. ρ_{3j}, equal to $|c_{3j}|^2$, is the mixing

coefficient of the eigenvector. The mixing coefficient of the $d^3\Delta_3$ level shown in Fig.3 decreases to 50% at $J(J+1)$=42 where the $d^3\Delta_3$ and $a^3\Pi_1$ levels cross each other because the $d^3\Delta_3$ level is composed 50% of basis functions, leaving 50% to be distributed in other basis functions of $a^3\Pi_1$. Eventually, the intensity of the corresponding lines shows abnormally small due to the transition strength "lending" to the (9, 1) transition in the $a^3\Pi_1$ state at $J(J+1)$=42. However, they still follow the conservation of total intensity, $I_{+0} + I_{-0} = I^0_{10}$. If the energy level separation of the $d^3\Delta$ (v=2) and $a^3\Pi$ (v=9) states is extremely small or even nearly equals zero, they will nearly be degenerate at the crossing points.

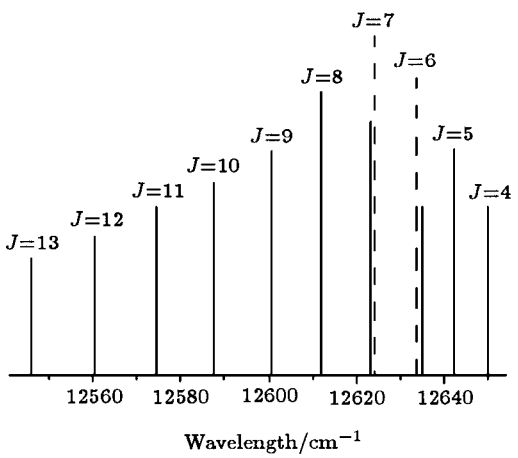


Fig.2. Intensity distribution for P_{12e} lines of $d^3\Delta - a^3\Pi$ (2, 1) band. Experimental intensity (solid lines) calculated intensity (dashed lines) without perturbation when J=6, 7.

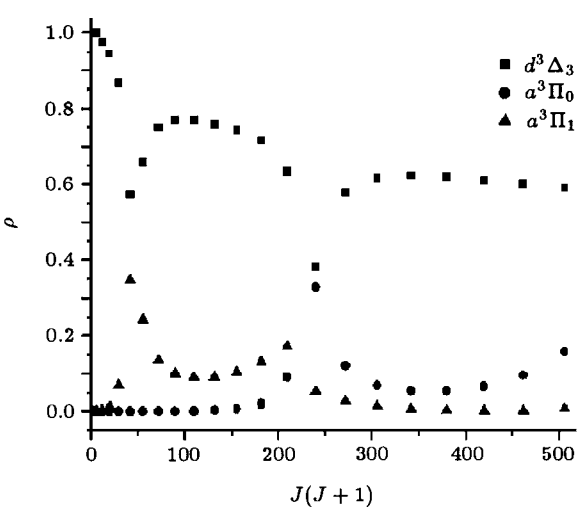


Fig.3. A plot of the squared eigenvector coefficient of $d^3\Delta_3$ (v=2),$a^3\Pi_0$ and $a^3\Pi_1$ (v=9) states.

In addition, perturbation also affects the Λ-doubling. Generally, the Λ-type doubling of the $d^3\Delta$ state is too small to be observed, thus, it is usually neglected in the level diagram, as shown in Fig.2 of Ref.[8]. Due to the interaction with the $a^3\Pi$ (v=9) state, the Λ-type doublet splitting of the $d^3\Delta_3$(v=2) state cannot be ignored any more and presents clearly as shown in Fig.4, especially at J values of 6, 7 and 15.

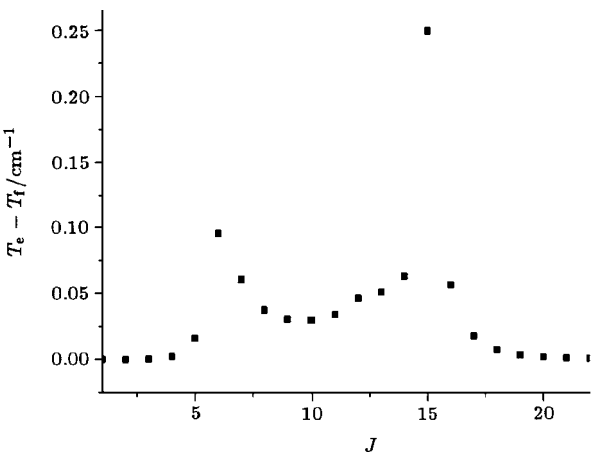


Fig.4. Λ-type doubling of $d^3\Delta_3$ state.

Figure 5 illustrates the relation between the reduced term values and $J(J+1)$ of the $d^3\Delta$ (v=2) and $a^3\Pi$ (v=9) states, using the molecular constants T and B fitted from the observed lines. The lower $d^3\Delta_3$ level is displaced downward because of the apparent repulsions between the $d^3\Delta_3$ and $a^3\Pi_1$ states at $J(J+1)$ = 56, the $d^3\Delta_3$ and $a^3\Pi_0$ states at $J(J+1)$=240 where they are close. Therefore, the reduced term value of the $d^3\Delta_3$ state decreases suddenly at $J(J+1)$=56 and 240 . On the contrary, this value increases suddenly at $J(J+1)$=42 when the higher $d^3\Delta_3$ level is repulsed by $a^3\Pi_1$ states. A few lines shift from their expected positions. The magnitudes of the perturbations are sometimes considerable. Deviation up to 18cm^{-1} from the normal position has been observed. Figure 5 shows that when the perturbations appear for a number of successive J values, they usually have a resonance-like behaviour. The deviation from the normal course increases rapidly to a maximum with increasing J and then decreases rapidly back to zero.

In conclusion, from the analysis of the spectra, the positions of the perturbation are located in the $d^3\Delta_3$ and $a^3\Pi_1$ states at J=6 and 7, in the $d^3\Delta_3$ and $a^3\Pi_0$ states at J=15, in the $d^3\Delta_2$ and $a^3\Pi_1$ states at J= 14, in the $d^3\Delta_2$ and $a^3\Pi_2$ states at J= 6 and 7, and in the $d^3\Delta_1$ and $a^3\Pi_2$ states at J= 13 and 14. It is worthy of noting here that these positions are

observed directly in the experiment for the first time except the first one. The results we obtained are in close agreement with the results predicted by Field *et al*[4] at relatively low J, less than 23. However, a small discrepancy in two analyses is the weak perturbation between the $d^3\Delta_3$ and $a^3\Pi_1$ states when J is 7, which was not predicted by Field *et al.*[4]

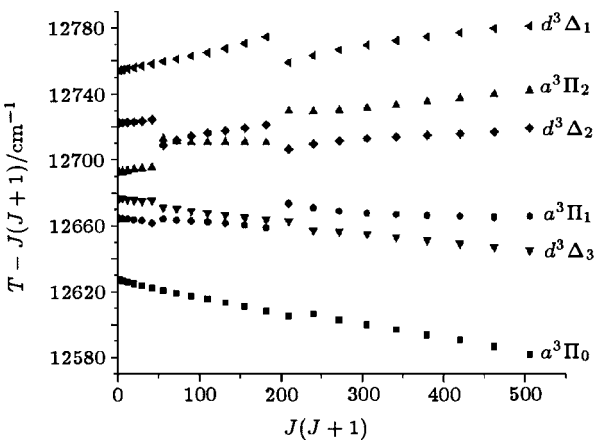


Fig.5. A plot of the reduced term values of $d^3\Delta$ (v=2) and $a^3\Pi$ (v=9) states.

The perturbation between the $d^3\Delta$ (v=2) and $a^3\Pi$ (v=9) states is mainly from the spin-orbital and rotational interactions. According to Born-Oppenheimer approximation the perturbation parameters α_2 and β_2 are related to the overlap integrals by the following expressions:

$$\begin{aligned}\alpha_2 &= \langle v, \Pi \,|(A(r)/2)\ L_+|\ v', \Delta\rangle \\ &= \langle \Pi \,|(A(r)/2)L_+\,|\Delta\rangle\,\langle v \mid v'\rangle \\ &= \xi_e\,\langle v \mid v'\rangle\,, \qquad (2)\\ \beta_2 &= \langle v, \Pi\,|B\ (r)L_+|\ v', \Delta\rangle \\ &= \langle \Pi \mid L_+\,|\Delta\rangle\,\langle v|\,B(r)\,|v'\rangle \\ &= \eta_e\,\langle v|\,B(r)\,|v'\rangle \\ &= \frac{h\eta_e}{8\pi^2 c\mu}\left\langle v\left|\frac{1}{R^2}\right|\ v'\right\rangle. \qquad (3)\end{aligned}$$

The product of vibrational matrix elements, $\langle v=1\ |v'=2\rangle$ and

$$\frac{h}{8\pi^2 c\mu}\left\langle v=1\left|\ \frac{1}{R^2}\right|v'=2\right\rangle,$$

were calculated by using the RKR potential and LEVEL7.1[17] computer program. The perturbation parameters α_2 and β_2 were divided by $\langle v=1\ |v'=2\rangle$ and

$$\frac{h}{8\pi^2 c\mu}\left\langle v=1\left|\ \frac{1}{R^2}\right|v'=2\right\rangle,$$

respectively, to obtain the electronic perturbation constants ξ_e and η_e, as listed in Table 1. There good agreements are shown among three sets of values; furthermore, the present data are the most accurate so far as we know. The electronic perturbation constant, normally determined by the electronic state, is approximately independent of the vibrational quantum number v. As a result, the perturbation between the vibrational energy levels can be judged more reliably on the basis of the perturbation parameters calculated from the electronic perturbation constants.

Table 1. Perturbation parameters between $d^3\Delta$ (v=2) and $a^3\Pi$ (v=9) states.

	Ref.[3]	Ref.[7]	This work
α_2	–9.241(21)	–9.1817(20)	–9.17188(70)
β_2	0.087	0.1039(5)	0.098840(74)
ξ_e	$-24.79(6)\mathrm{cm}^{-1}$		$-24.58542(18)\mathrm{cm}^{-1}$
η_e	0.217(7)		0.249126(21)

4. Conclusion

The absorption spectrum of CO in the near infrared region of 12350–12850cm^{-1} has been recorded by employing the OH-MR-CMS technique. 562 lines were assigned to the (2, 1) band of the CO triplet $d^3\Delta - a^3\Pi$ system, among which 45 perturbed lines were observed for the first time so far as we know. A perturbation analysis of this triplet band has been performed, yielding an improved set of perturbation parameters and electronic perturbation constants for the $d^3\Delta(v$=2) and $a^3\Pi$ (v=9) states.

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