The observed perturbations in $v'=11$ of $A^1\Pi$ state at $^{13}\text{C}^{16}\text{O}$ molecule

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Abstract. The rotational structure of the bands with $v'=11$ belonging to Fourth Positive System of $^{13}\text{CO}$ molecule is given here. The perturbations caused by $d^3\Delta$ state were analysed, and the perturbational parameters were evaluated. The inversion of $d^3\Delta$ state was confirmed.

1. Introduction
Perturbation phenomena in $A^1\Pi$ state are the rich source of molecular data connected with others electronic states of CO molecule. An analysis of these perturbations can bring some information on quantum properties of the several electronic states. This possibility occurs in $A^1\Pi$ state of CO molecule and we can investigate many electronic states in this way. Spectral image of the perturbations by several states is described in the classical literature [1,2]. We can investigate the physical properties of these electronic states by the studies of this image. Carrol [3] has been mentioned about very specific properties of $d^3\Delta$ state in CO molecule. Some of them are accessible by the observations of perturbations in $v'=11$ of $A^1\Pi$ state at the spectra of Fourth Positive System for $^{13}\text{C}^{16}\text{O}$ molecule, where $d^3\Delta$ state occurs his properties.

Very important circumstance here, is the fact that an application of the isotopic molecules allows to analyze the quantum properties of the perturbing states quite precisely. Especially, the isotopic shifts appear very specific properties of $d^3\Delta$ state.

2. Experimental details
The Fourth Positive System of $^{13}\text{C}^{16}\text{O}$ molecule was excited in the water-cooled Geissler’s lamp filled up with $^{13}\text{C}^{16}\text{O}$ gas compound containing 95% of $^{13}\text{C}$ isotope. Spectrum was photographed with Ebert 2-m spectrograph (PGS-2, Carl Zeiss, Jena GmbH) in $X^{th}$ and $XI^{th}$ orders. To receive a spectrum at so high orders, the standard monochromator was used as a preliminary separator of the spectral orders.

The thorium atomic lines from a hollow – cathode type lamp were used as the standard spectrum.

The received accuracy for wave numbers of this molecular spectrum is about 0.1 cm$^{-1}$.

3. Analysis
An examination of the band perturbations in origins at $v'=6$ at $^{13}\text{C}^{16}\text{O}$ molecule [4] inclined us to analyze the perturbations at $v'=11$ of $A^1\Pi$ state. Additionally, according to Carrol suggestions [3] and Tilford and all [5], we were inspired to more exact analysis of perturbations caused by $d^3\Delta$ state. Also some previous observations [5,6] appeared very extraordinary behavior of $d^3\Delta$ state, visible in a perturbation image at the several bands.
An emission spectrum of The Fourth Positive System of $^{13}\text{C}^{16}\text{O}$ molecule in our experiment occurs just two bands: (11,21) and (11,22) with vibrational level $v'=11$ of $A^1\Pi$ state. Their rotational structure is very clear and rotational assignment is not too difficult. Moreover if the ground state is quite regular and spectroscopic data are very completed for this state [7-13], so McKeller – Jenkins method [1] can be the excellent test for an exactness of the established rotational structure. In this way we just prepared a rotational structure of these bands to continue a perturbation analysis. The rotational structure of these bands is given in Table 1.

Table 1. Band (11, 21) [cm$^{-1}$].

| J | R(J) | Q(J) | P(J) |
|---|------|------|------|
| 0 | 40091.975 |      |      |
| 1 | 94.537 | 40089.642 |      |
| 2 | 96.772 | 88.823 | 40083.736 |
| 3 | 97.807 | 87.524 | 80.033 |
| 4 | 40098.480 | 85.802 | 75.591 |
| 5 | 99.199 | 40083.736 | 70.969 |
| 6 | 99.199 | 81.159 | 40065.839 |
| 7 | 98.480 | 77.975 | 60.245 |
| 8 | 96.772 | 74.634 | 54.333 |
| 9 | 99.199 | 69.936 | 47.908 |
| 10 | 96.772 | 69.476 | 39.956 |
| 11 | 94.537 | 63.994 | 36.596 |
| 12 | 91.975 | 58.659 | 28.151 |
| 13 | 89.089 | 53.152 | 19.829 |
| 14 | 85.802 | 47.256 | 11.362 |
| 15 | 82.024 | 40.978 | 02.468 |
| 16 | 77.975 | 34.277 | 39993.226 |
| 17 | 73.160 | 27.205 | 983.554 |
| 18 | 68.403 | 19.829 | 973.521 |
| 19 | 62.940 | 11.729 | 963.115 |
| 20 | 57.263 | 03.460 | 952.162 |
| 21 | 51.026 | 39994.708 | 940.870 |

According to a behavior of $d^3\Delta$ state mentioned previously [3,5,6], one can observe an intermediate coupling between Hund’s case (a) and (b). For this reason at lower rotational levels we have a-case with $\Delta\Omega = 0$ selection rule, whereas for higher rotational levels (b-case) we have $\Delta\Omega = \pm 1$ selection rules. These quantum conditions guide to the run of perturbations observed in Table 1.

Just two maxima of the observed perturbations shown here are the consequence of a fact, that third component of triplet $d^3\Delta$ state occurs in the origins of bands and there we can observe the slight influence only. Taking into account the selection rules mentioned here and also the received perturbation parameters we got a confirmation of the inversion effect at $d^3\Delta$ state.

For perturbational analysis we used least squares routine to evaluate the perturbational parameters $W$ and $\Delta$. These parameters are listed in Table 2. The calculation for both components of $d^3\Delta$ state was performed quite separately, because we expect that the perturbation parameters will be different for each spin component of this state. We can perceive that the received parameters for both component of $d^3\Delta$ state have a good agreement, comparing the results from both bands. The values listed in Table 2 are the averaged means.

The rotational constant $B$, for upper electronic state with $v'=11$, is listed in Table 3. This parameter is in good agreement with those published previously [6].
Table 1. (continued) Band (11, 22) [cm$^{-1}$].

| J  | R(J)       | Q(J)       | P(J)       |
|----|------------|------------|------------|
| 0  | 38513.493  | 38510.490  | 38505.084  |
| 1  | 515.660    | 509.763    | 500.922    |
| 2  | 517.512    | 508.588    | 500.922    |
| 3  | 38519.480  | 506.971    | 496.673    |
| 4  | 520.230    | 38505.084  | 492.177    |
| 5  | 520.385    | 502.677    | 38488.328  |
| 6  | 519.822    | 499.757    | 482.053    |
| 7  | 518.786    | 496.673    | 476.415    |
| 8  | 521.620    | 492.177    | 469.939    |
| 9  | 519.480    | 492.177    | 462.592    |
| 10 | 517.512    | 486.967    | 459.571    |
| 11 | 515.342    | 482.053    | 451.522    |
| 12 | 512.860    | 476.968    | 443.644    |
| 13 | 509.984    | 471.504    | 435.597    |
| 14 | 506.798    | 465.735    | 427.232    |
| 15 | 503.186    | 459.571    | 418.499    |
| 16 | 499.229    | 453.066    | 409.377    |
| 17 | 494.835    | 446.249    | 399.914    |
| 18 | 490.084    | 438.817    | 390.066    |
| 19 | 484.950    | 431.129    | 379.840    |
| 20 | 479.423    | 423.088    | 369.199    |
| 21 | 473.446    | 414.570    | 358.233    |
| 22 | 467.077    | 405.749    | 346.822    |
| 23 | 460.084    | 396.447    | 335.037    |

Table 2. The parameters received from perturbation analysis.

| Triplet component | W       | Λ        |
|-------------------|---------|----------|
| Ω=2              | 0.111(12)| -0.13(2) |
| Ω=1              | 0.20(4) | 3.85(6)  |

If in the rotational structure of bands we observe the spectral lines belonging to higher rotational levels, so we must take into account centrifugal spectroscopic constants D for several electronic states. These parameters were used from the existing literature [14] using isotopic relations [1]. However an estimation of D rotational constants is rather problematic in our research, because of the appearing perturbations here.

Table 3. Rotational constant B for the observed vibrational level.

| v'  | B'     |
|-----|--------|
| 11  | 1.2791(2) |

4. Conclusion

Specific behaviour of d$^3\Delta$ state is a subject of the investigations by the rotational analysis of the triplet bands in CO molecule. Here we give some data describing this state received by the analysis of the singulet bands. Received spectroscopic constants for this state is not too precise, because of too small
statistic of the spectral lines. For this reason these constants is not published here, but the perturbations parameters only.

However, the received convergence between the fitting and experimental data is quite precise.

References
[1] Herzberg G 1954 *Spectra of Diatomic Molecules* (Van Nostrand)
[2] Kovač I 1969 *Rotational Structure in the Spectra of Diatomic Molecules* (London: Budapest and Adam Hilger)
[3] Carrol P K 1962 *J. Chem. Phys.* 36 2861
[4] Domin J, Fraň M, Ploskoň B 2003 *Proceedings os SPIE* Vol 5125 345
[5] Tilford S G and Simmons J D 1972 *J. Phys. Chem. Ref. Data* Vol 1 No 1
[6] Domin J 1986 *Acta Phys. Hung* 60 (1-2) 43
[7] Johns J W C, McKeller A R W and Weitz D 1974 *J. Mol. Spectr.* 51 539
[8] Kępa R, Knot – Wiśniwska M and Rytel M 1974 *Acta Phys. Polon.* A 48 818
[9] Ross A H M, Eng R S and Kidal H 1974 *Opt. Comm.* 12 433
[10] Tood T R, Clayton C M, Telfair W B, McCubbin T K and Pliva Ir J 1976 *J. Mol. Spectr.* 62 201
[11] Chen Da-Wun, Narahari Rao K and McDowell R S 1976 *J. Mol. Spectr.* 61 71
[12] Dale R M, Herrman M, Johns J W C, McKeller A R, Nagler S and McStarthy I K 1979 *Canad. J. Phys.* 57 677
[13] Rytel M 1970 *Acta. Phys. Polon* A 37 539
[14] Field R W, Wicke B G, Simmon J D and Tilford S G 1972 *J. Mol. Spectr.* 44 383