The $D^1\Delta \to X^1\Sigma^+$ Transition in $^{13}C^{16}O$ Molecule

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Abstract. $D^1\Delta \to X^1\Sigma^+$ forbidden transition in $^{13}C^{16}O$ molecule was observed here. The resolved structure of $10 - 17$ band was analyzed and new spectroscopic data were received for $D^1\Delta$ state. These data are in a good agreement with other authors referring this upper state of $^{13}C^{16}O$ molecule. Some perturbations in the rotational structure were observed also.

1. Introduction
Several rovibronic states of CO molecule were investigated by many researches [1]–[5]. Most of the accuring band systems in this molecule were referrd in Herzberg’s monography [1] and also by Simmons and Tilford [3]. The first report on $D^1\Delta \to X^1\Sigma^+$ transition in absorption was published by Tiford and Simmons [6], as a forbidden band system. More detailed investigations were realised lately by Kittrell et al [7]–[9]. Now we just mention an observation of $10 - 17$ band in $^{13}C^{16}O$ molecule. The registration of this band took a place during the realisation of a research project of IV-th Positive System [10] for this molecule.

2. Experimental
An emission spectrum in the near ultraviolet region was excited in a water-cooled Geissler’s tube filled up with $^{13}C^{16}O$ molecule containing 95% of $^{13}C$ isotope. The spectrum was photographed with PGS-2 spectrograph at $X^{th}$ spectral order. To separate the overlapping spectral orders, a standard monochromator was used for this spectrograph. The thorium lines excited in a water–colled lamp known as the hollow–cathode type lamp were used as the standard spectrum [11].

Spectral analysis
Registration of a single band belonging to $D^1\Delta \to X^1\Sigma^+$ transitions give a chance us for more detailed quantum description of the upper state. Up to now, this description is not satisfactory because the optical transitions from this state are not too probable. Additionaley the perturbations of the neighbouring states are some source of data [9] for $D^1\Delta$ state.

An analysis of the registered band classified as $10 - 17$ band of $D^1\Delta \to X^1\Sigma^+$ electronic transition was rather difficult. Just one circumstance which makes easier this analysis is a fact that $X^1\Sigma^+$ ground state is very well known and spectroscopic parameters for this state have an excellent precision. For these reasons a reconstruction of the vibrational levels in the ground state is possible with very high accuracy. So combination relations can be used for ground state for a rotational analysis of our registered band. Unfortunately some strong perturbation is observed in this band. However the combination differences $\Delta_2F(J)$ are not influenced by...
the perturbations in $X^1\Sigma^+$ ground state. The knowledge of these values for $^{13}C^{16}O$ molecule [12] allows to perform the rotational analysis. The rotational structure of our band is listed in Table 1. This structure consists of three branches: P, Q and R, and it seems to be surprising circumstance, because $D^1\Delta \rightarrow X^1\Sigma^+$ transition is attributed to electric–quadrupole transition. However such rotational assignment corresponds quite well with discoussion proposed by Tilford in his first report about [6].

**Table 1.** Observed wavenumbers (in $cm^{-1}$) and rotational assignments for the 10-17 band of the $D^1\Delta \rightarrow X^1\Sigma^+$ system of the $^{13}C^{16}O$ molecule

| $J$ | $R(J)$ | $Q(J)$ | $P(J)$ |
|-----|-------|--------|-------|
| 0   |       |        |       |
| 1   | 43135.590 | 43125.904 | 43114.234 |
| 2   | 43134.905 | 43121.226 | 43098.804 |
| 3   | 43133.978 | 43115.128 | 43090.564 |
| 4   | 43132.096 | 43111.694 | 43099.939 |
| 5   | 43125.904 | 43106.620 | 43097.177 |
| 6   | 43124.700 | 43109.939 | 43070.544 |
| 7   | 43123.100 | 43106.620 | 43097.177 |
| 8   | 43121.200 | 43099.939 | 43070.544 |
| 9   | 43121.200 | 43093.333 | 43062.764 |
| 10  | 43114.239 | 43087.177 |       |
| 11  | 43109.064 | 43079.177 | 43056.333 |
| 12  | 43104.092 | 43070.540 | 43043.960 |
| 13  | 43098.116 | 43061.004 | 43032.740 |
| 14  | 43096.769 |            | 43021.990 |
| 15  | 43083.779 |            | 43009.953 |
| 16  |        |            | 42997.503 |
| 17  |        |            | 42984.658 |
| 18  |        |            | 42971.370 |
| 19  |        |            | 42957.664 |

Having the rotational assignment for our band we could determine the band origin by an extrapolation of Q branch, which seems to be more regular than P and R branches. This value can by estimated also from Deslandres table:

\[
\sigma_0 = 43128.65 \text{cm}^{-1} \text{ (Q - branch)}
\]
\[
\sigma_0 = 43128.94 \text{cm}^{-1} \text{ (Deslandres table)}
\]

These two values have a sufficient convergence. The first one from an extrapolation of Q branche seems to be slightly shifted by perturbation. An estimation on the second value was performed on the basis of the completed vibrational constants (of the Kittrell [8] and also our estimation) for $D^1\Delta$ state:

\[
T_e = 65975.84 \text{cm}^{-1}
\]
\[
\omega_c = 1038.007 \text{cm}^{-1}
\]
\[
\omega_c x_c = 9.4275 \text{cm}^{-1}
\]
\[
\omega_c y_c = 0.5075 \text{cm}^{-1}
\]
Taking into account the divergence between Tilford [6] and Kittrell [8] the next investigations are necessary to receive an accuracy comparable with other electronic states in $^{13}C^{16}O$ molecule.

Also the identification of the accruing perturbations actually is not possible. Some existing data [10] concerning $^{13}C^{16}O$ molecule could be a basis for the first trial of the identification. All these aspects will be undertaken in next our research efforts.

3. Conclusion

Observation of the 10-17 band belonging to $D^1\Delta \rightarrow X^1\Sigma^+$ system permits to receive additional vibrational constants, that is $\omega_{e,y}$ for $D^1\Delta$ state. Now, this molecular set of parameters allows to reconstruct the vibronic terms in $D^1\Delta$ state. In this way we can try to complete $D^1\Delta \rightarrow X^1\Sigma^+$ system and in the consequence to achieve a typical spectroscopic data set for $D^1\Delta$ state. Moreover an evidence of the accruing perturbations caused by $D^1\Delta$ state [9] will be completed.

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