NEW BANDS IN THE TRIPLET CARBON SYSTEM

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The triplet carbon bands were discovered by Merton and Johnson\(^1\) in the spectrum of an uncondensed discharge through a tube with carbon electrodes and containing helium at a pressure of about 20 mm. of Hg. Birge\(^2\) gave the vibrational quantum analysis of the bands and suggested that their final electronic state is very probably identical with that of the third positive bands of carbon. Following the discovery of Cameron bands\(^3\) and their analysis and interpretation by Johnson\(^4\), the third positive carbon bands and consequently the triplet carbon bands, could be definitely attributed to CO. These bands are more easily developed in the presence of a rare gas than in its absence and not only helium\(^1\) but argon\(^5\) and neon\(^6\) also favour their production.

Recently, L. Gerô with F. Szabo\(^6\) has done the rotational analysis of some of these bands and shows that they are due to the transition \(d^2\Pi_{\text{un}} \rightarrow a^3\Pi_{\text{reg}}\), the latter being also the final level of the third positive bands of CO. Assuming the band at \(\nu = 15540\) cm.\(^{-1}\) to be the \((0, 0)\) band, the following equation is deduced to represent the null lines of the bands of \(v'' = 0\) progression:

\[
\nu = 14987.66 + 1105.82 u' - 8.272 u'^2 - 0.1125 u'^3
\]  

(1)

where, \(u' = (\nu' + \frac{1}{2})\). The position of the \(d^3\Pi_1\) level relative to the ground level is also calculated as \(\nu = 64013.3\) cm.\(^{-1}\), the origin of the system being observed at \(\nu = 15538.5\) cm.\(^{-1}\).

A further study of the bands shows, however, that the band at \(\nu = 15540\) cm.\(^{-1}\) is not the \((0, 0)\) band of the system. Three new bands on the higher wave-length side have been photographed on suitable far-red sensitive plates from the spectrum of a discharge tube showing the triplet system as developed in the presence of helium. The resolving instrument used was a Littrow type Hilger E\(_4\) glass spectrograph having an average dispersion of 31 A/mm. between \(\lambda\lambda\) 6850 and 7550 A.U. These new bands fit into the existing \(v', v''\) table but necessitate an increase of two units in the present \(v'\) quantum numbers. The wave-numbers of the band heads \textit{in vacuo}, probably accurate to \(\pm 3\) cm.\(^{-1}\) are displayed in the following
table which shows their connection to the band at $15540 \text{ cm}^{-1}$ and forms therefore, the extension of the existing table.

<table>
<thead>
<tr>
<th>$\nu''$</th>
<th>0</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13326</td>
<td></td>
</tr>
<tr>
<td></td>
<td>303 †</td>
<td></td>
</tr>
<tr>
<td></td>
<td>346</td>
<td></td>
</tr>
<tr>
<td></td>
<td>374</td>
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</tr>
<tr>
<td></td>
<td>387</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>dif.</th>
<th>1129, 1139, 1148, 1159, 1169, 1179</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14355</td>
</tr>
<tr>
<td></td>
<td>436</td>
</tr>
<tr>
<td></td>
<td>471</td>
</tr>
<tr>
<td></td>
<td>503</td>
</tr>
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<td></td>
<td>516</td>
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</table>

<table>
<thead>
<tr>
<th>dif.</th>
<th>1110, 1140, 1148, 1158, 1170, 1177</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(15465) 1715 13825</td>
</tr>
<tr>
<td></td>
<td>(15540) 1712 867</td>
</tr>
<tr>
<td></td>
<td>(15661) 1720 901*</td>
</tr>
<tr>
<td></td>
<td>(15622) 1728 911</td>
</tr>
</tbody>
</table>

† Indicates a probable perturbation.

* Confused with other bands.

(1) The new bands here reported are those not included in brackets.

(2) Incidentally, it may be mentioned that four heads have been recorded by Merton and Johnson for most of the bands of this system but an additional head for some of them is clearly shown on the present plates. This extra head, third in the above table in each of the bands is probably due to the branch designated by Ger6 as $^9R_{12}$.

It should be mentioned that it is not certain whether the band at $\nu = 13303 \text{ cm}^{-1}$ is definitely the (O, O) band as shown here. It is likely that the origin may be higher up in the near infra-red region beyond the range of the present investigation. Assuming, however, that the one shown
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here is the (O, O) band and that there are no perturbations, equation (1) transforms, on extrapolation, to,

\[ v = 12743.8 + 1137.79 u' - 7.624 u'^2 - 0.1125 u'^3. \]

Hence also the position of the \( d^3\Pi_1 \) level from the ground level of the CO molecule is calculated as 61785.5 cm\(^{-1}\), the origin of the system, on extrapolation, being at \( v = 13310.7 \) cm\(^{-1}\).

Summary

A few new band heads belonging to the triplet carbon band system of CO are reported. These necessitate an increase of two units in the existing \( \nu' \) numbering. The origin of the system may be still further in the region of longer waves but is definitely shifted at least to \( v = 13310.7 \) cm\(^{-1}\) according to these new results, thus locating the \( d^3\Pi_1 \) level at 61785.5 cm\(^{-1}\) from the ground level of the CO molecule.

REFERENCES

1. T. R. Merton and R. C. Johnson
2. R. T. Birge
3. W. H. B. Cameron
   Phil. Mag., 1926, 1, 405.
4. R. C. Johnson
5. L. Gerö with F. Szabo
6. L. Gerö with F. Szabo