**Report Title:** Spectroscopic Determination of Intermolecular Potentials of Gas Laser Components and of Major Atmospheric Constituents

**Authors:** William Klemperer

**Performing Organization:** Harvard University
Department of Chemistry
Cambridge, MA 02138

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**Abstract:**

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we have completed the detailed structural study of a number of complexes of carbon dioxide. The structure of molecular complexes of carbon dioxide may be of considerable importance in developing a better complete understanding of energy transfer processes in the important carbon dioxide laser and especially in our understanding of the earth's (and other planetary) atmosphere.

Earlier studies performed under the support of APOSFR produced structural results for the CO₂ HF complex. This together with the study of SCO HF and N₂O HF showed a problem of considerable complexity. The structures of CO₂ HF and SCO HF are linear hydrogen bonded structures with atomic arrangement written. The structure N₂O HF, a species iso-electronic to CO₂ HF, has a highly nonlinear arrangement. The prediction of the geometry of CO₂ complexes is clearly likely to be complicated.

In pursuing the detailed structure of carbon dioxide complexes the system CO₂ HCl (J. Chem. Phys. 77, 4344 (1982)) has been shown to be similar to CO₂ HF. We have recently completed the study of the system HCN CO₂. Although HCN is well known to form hydrogen bonds the structure of this system is not hydrogen bonded. The results of this study are:
HCN CO₂

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>DGN CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>11861.5(10) MHz</td>
<td>12133.1 MHz</td>
</tr>
<tr>
<td>B</td>
<td>2226.51(10) MHz</td>
<td>2093.9 MHz</td>
</tr>
<tr>
<td>C</td>
<td>1861.60(11) MHz</td>
<td>1764.9 MHz</td>
</tr>
<tr>
<td>uₐ</td>
<td>3.2005(60) D</td>
<td>3.2235(55) D</td>
</tr>
<tr>
<td>eqQₐ</td>
<td>-4.068(41) MHz</td>
<td>----</td>
</tr>
<tr>
<td>rₐbb</td>
<td>-38 (18) kHz</td>
<td>----</td>
</tr>
<tr>
<td>rₐbab</td>
<td>-570(475) kHz</td>
<td>----</td>
</tr>
</tbody>
</table>

kₛ = 0.0489 mdyne/Å

r_cm = 3.60 Å ; rₐ-N-C = 3.01 Å

0 = C = 0 + 3.01 Å

A-1
Of great general interest is the complex of $\text{CO}_2$ and $\text{H}_2\text{O}$. The importance of this species in the earth's atmosphere is not clear presently. We are in the process of completing the rotational spectrum of the three isotopic species $\text{H}_2\text{O} \text{CO}_2$, $\text{D}_2\text{O} \text{CO}_2$ and $\text{HDO} \text{CO}_2$. The results at the present stage of research are the rotational constants and electric dipole moment components. These are listed in Table I.

**TABLE I**

Average Rotational Constant and Electric Dipole Moment for Water Carbon Dioxide Complexes

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}_2\text{O} \text{CO}_2$</th>
<th>$\text{D}_2\text{O} \text{CO}_2$</th>
<th>$\text{HDO} \text{CO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B+C$ (MHz)</td>
<td>7979.2</td>
<td>7265.7</td>
<td>7608.5</td>
</tr>
<tr>
<td>$B-C$ (MHz)</td>
<td>1361.5</td>
<td>1166.4</td>
<td>1254.7</td>
</tr>
<tr>
<td>$A$ (MHz)</td>
<td>11374</td>
<td>11236</td>
<td>11349</td>
</tr>
<tr>
<td>$\mu_a$ (D)</td>
<td>1.849</td>
<td>1.925</td>
<td>1.899</td>
</tr>
</tbody>
</table>

The structure of the complex is \( \text{linear} \) with structure

$$
\begin{array}{c}
\text{O} = \text{C} = \text{O} \\
\text{O} \\
\text{H} \\
\end{array}
\quad \text{with} \quad \text{length} \quad 2.83 \ \text{Å}
$$

The primary uncertainty presently is the knowledge of the barrier hindering the internal rotation about the C-O axis.
Earlier research emphasized complexes of HF. The present research which initiates studies of complexes with \( \text{H}_2 \text{O} \) shows that the structural and dynamical behaviour of these two species HF and \( \text{H}_2 \text{O} \) can be quite different. In this sense our early optimism that studies of HF binding would likely be adequate for understanding \( \text{H}_2 \text{O} \) binding is certainly unwarranted. It is clear that the \( \text{H}_2 \text{O} \) systems require much spectroscopic research to place them in a securely understood position. Complete manuscripts on these two problems, \( \text{CO}_2 \) HCN and \( \text{CO}_2 \) \( \text{H}_2 \text{O} \) are in the process of preparation.

Prof. William Klemperer
Harvard University