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CHARACTERIZATION OF XENON (II) FLUORIDE COMPLEXES

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Laser Raman spectroscopy offers a number of advantages over infrared spectroscopy in the vibrational characterization of rare-gas compounds. Perhaps most importantly, sampling problems are greatly reduced, as Raman spectra are routinely obtained from the solid materials in glass or Kel-F containers of various shapes and sizes. A particularly convenient procedure is to place a sample in a quartz X-ray capillary, so that both powder photographs and Raman spectra may be obtained from the same sample. Solid-state infrared spectra on the other hand are usually harder to obtain because of difficulties associated with sample dispersion and chemical interactions of the compounds with the window materials.

Another usual advantage of the Raman spectra, both for "fingerprinting" and structural purposes, is that spectra are almost always sharper, better resolved, and more characteristic than the corresponding infrared spectra. This provides for more certain identification and differentiation of related samples.

Raman spectroscopy has been applied to the study of a number of complexes of xenon (II) fluoride, and representative spectra of some of these are shown. The vibrational features allow the complexes to be classified into several types:
a. Molecular adducts, exemplified by XeF$_2$· IF$_5$ and XeF$_2$· XeOF$_4$.

For these complexes the Raman spectra (Figures 1 and 2) are very nearly the simple sums of the Raman spectra of the respective components. In particular, the presence of an essentially unperturbed XeF$_2$ moiety in each case is demonstrated by the appearance of an intense line within a few cm$^{-1}$ of 497 cm$^{-1}$, the symmetric stretching frequency for pure XeF$_2$ (solid). For XeF$_2$· IP$_5$, a crystal structure determination has confirmed these conclusions.$^3$

b. XeF$^+$ salts, exemplified by XeF$^+$IrF$_6$.

Although the compounds XeF$_2$· MF$_5$, where M is a noble metal, are formally analogous to XeF$_2$· IF$_5$, (see above), the Raman results require different formulations.$^4$ XeF$_2$· IrF$_5$, for example, shows no feature attributable to XeF$_2$ near 500 cm$^{-1}$. The XeF$_2$· IrF$_5$ spectrum is, however, similar to that of NO$^+$IrF$_6$ (Figure 3), suggesting the approximate formulation XeF$^+$IrF$_6^-$ with the doublet at 602-608 cm$^{-1}$ assigned to Xe-F stretching. A recent crystal structure determination$^5$ for XeF$_2$· RuF$_5$, which is isomorphous with the iridium analog, confirms this formulation, as well as an interaction between the cation and anion predicted by the analysis of the Raman data. Similar considerations hold for the compounds XeF$_2$· 2MF$_5$$^4$$^6$ so that these may be formulated at least approximately as XeF$^+$M$_2$F$_{11}$.

c. Xe$_2$F$_3^+$ salts, exemplified by Xe$_2$F$_3^+$AsF$_6^-$ and Xe$_2$F$_3^+$RuF$_6^-$.

Raman spectra show that the compound 2XeF$_2$· AsF$_5$ is different from either type of complex considered above. An X-ray structure determination established the formulation Xe$_2$F$_3^+$AsF$_6^-$, with the cation a V-shaped F-Xe-F-Xe-F grouping.$^7$ The noble metal analogs 2XeF$_2$· MF$_5$ are not isomorphous with the arsenic compound, but the similarity of the Raman spectra (Figure 4) confirm the presence of the Xe$_2$F$_3^+$ ion, characterized by (terminal) Xe-F stretching frequencies in the range 575-600 cm$^{-1}$.
In summary, we have found Raman spectroscopy, in conjunction with conventional X-ray techniques, to be a very powerful tool in the identification of species present in XeF₂ complexes. The Xe-F frequencies are easily assigned and found to be quite sensitive to the respective Xe-F bond lengths as indicated in Table 1.
REFERENCES

### TABLE 1

#### The Xe-F Bond

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond Length (Å)</th>
<th>Bond Order*</th>
<th>v(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-Xe-F</td>
<td>2.01</td>
<td>0.5⁺</td>
<td>497</td>
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<tr>
<td>F-Xe···F</td>
<td>1.90</td>
<td>0.76</td>
<td>588</td>
</tr>
<tr>
<td>XeF⁺</td>
<td>2.14</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>FXe··FMF₅</td>
<td>1.88</td>
<td>0.83</td>
<td>604</td>
</tr>
<tr>
<td>FXe··FSbF₄FSbF₅</td>
<td>2.35</td>
<td>0.13</td>
<td>621</td>
</tr>
<tr>
<td>XeF⁺</td>
<td>1.83</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

*From the Pauling equation \( r(n/2) = r(1) - 0.60 \log n/2 \).

⁺Assumed value.
### IF₅ BANDS (l):

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>VS</td>
<td>696 (υ₁)</td>
</tr>
<tr>
<td>VS</td>
<td>593 (υ₂)</td>
</tr>
<tr>
<td>VS</td>
<td>575 (υ₄)</td>
</tr>
<tr>
<td>W</td>
<td>374 (υ₈)</td>
</tr>
<tr>
<td>W</td>
<td>315 (υ₃)</td>
</tr>
<tr>
<td>W</td>
<td>273 (υ₆)</td>
</tr>
</tbody>
</table>

### XeF₂ BANDS (s):

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>VS</td>
<td>497 (υ₅)</td>
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<tr>
<td>W</td>
<td>385</td>
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<tr>
<td>W</td>
<td>329</td>
</tr>
<tr>
<td>W</td>
<td>292</td>
</tr>
<tr>
<td>W</td>
<td>213 (ω₄)</td>
</tr>
</tbody>
</table>

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THE RAMAN SPECTRUM OF THE ADDUCT XeF₂,IF₅
Figure 2

THE RAMAN SPECTRUM OF XeF₂ · XeOF₄
Figure 3

$\nu_1(\text{IrF}_6^-)$

$\nu_2(\text{IrF}_6^-)$

$\nu_3(\text{IrF}_6^-)$

$\nu_4(\text{XeF})$

$\nu_5(\text{IrF}_6^-)$

RAMAN SPECTRA OF NO$^+$IrF$_6^-$ AND XeF$^+$IrF$_6^-$
Figure 4
The Raman Spectra of $\text{Xe}_2\text{F}_3^{+}\text{AsF}_6^-$ and $\text{Xe}_2\text{F}_3^{+}\text{RuF}_6^-$
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