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THE BONDING IN THE INERT GAS-HALOGEN COMPOUNDS—THE LIKELY EXISTENCE OF HELIUM DIPROXIDE

Sir:

In 1951, Pimentel discussed the bonding in trihalide ions in terms of a simple molecular orbital description. In this widely ignored paper, the applicability of the bonding scheme to other molecular species was recognized and, in fact, the existence of inert gas—halogen compounds was predicted. "It is to be expected that a rare gas could form complexes with halogens." At about the same time, Hach and Rundle discussed bonding of trihalides in similar terms, though without any reference to possible inert gas compounds.

Since then there has appeared significant support for this molecular orbital description of the trihalides through electric quadrupole resonance studies and infrared studies. The quadruple coupling constants both IC\textsuperscript{-} and I\textsuperscript{-} confirm the proposal that d orbitals do not contribute significantly to the bonding.

The case of inert gas compounds has naturally stimulated much interest in their bonding.

Among these discussions, there has appeared a revival of the molecular orbital description proposed by Pimentel and we feel, the model provides a simple and sufficient basis for explaining the existence of such compounds as XeF\textsubscript{2}. The case of extension of the scheme to such compounds as ICl\textsuperscript{-} and XeF\textsubscript{2} has been amply pointed out by others and need not be reproduced here.

There is, however, one other aspect of the molecular orbital description offered by Pimentel that deserves attention. The essential similarity of the molecular orbital descriptions of HF\textsubscript{2} and F\textsuperscript{-} was noted and remarked upon by Pimentel and McClellan. Experimental support for this connection has also appeared and we are encouraged to explore its implications in reference to inert gas chemistry. In particular, the compound HeF\textsubscript{2} can be expected to be stable.

The molecular orbital description of HF\textsubscript{2}, based upon the halogen axial 2p orbitals and the hydrogen 1s orbital, need not be repeated here and its applicability to the isoelectronic molecule HeF\textsubscript{2} is obvious. We can, however, make some comparisons between HF\textsubscript{2} and HeF\textsubscript{2} that may aid in searching for this interesting molecule. A rough estimate of the infrared spectrum of HeF\textsubscript{2} can be based upon that of HF\textsubscript{2}. The vibrational frequencies and a set of force constants for HF\textsubscript{2} are shown in Table 1.

<table>
<thead>
<tr>
<th>Frequency, cm\textsuperscript{-1}</th>
<th>Force constant*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1$</td>
<td>$r_2$</td>
</tr>
<tr>
<td>HF\textsubscript{2}</td>
<td>600</td>
</tr>
<tr>
<td>HeF\textsubscript{2}</td>
<td>600</td>
</tr>
<tr>
<td>HeF\textsubscript{2}</td>
<td>585</td>
</tr>
</tbody>
</table>

The quadrupole coupling constants in the second row of Table 1. Smith has concluded that the ratio $r_1/r_2$ is much smaller for XeF\textsubscript{2} than for the trihalide ions. We do not take this view that this difference violates the molecular orbital bonding description, for a reasonable rationale can be formulated to explain it. The molecules XeF\textsubscript{2} and ICl\textsuperscript{-}, though isoelectronic (in bonding electrons), involve quite different formal charge distributions. The proposed molecular orbitals tend to place somewhat less than one electron charge on the central atom and somewhat more than 1/2 electron charges on the terminal atoms. In the case of ICl\textsuperscript{-}, the formal charge implication is that the excess charge of the ion is distributed on the chlorine atoms and the iodine atom has a charge near zero. The case of XeF\textsubscript{2} contrasts since the central atom must have a significant positive formal charge to balance the negative charge placed on the terminal atoms. This difference can be expected to tend to strengthen the bond somewhat because of the electrostatic attractions, raising $f_r$. At the same time, the interaction force constant should be reduced, because an asymmetric displacement is no longer energetically favored over a symmetric displacement. In the symmetric mode, the terminal atom repulsions that tend to raise the energy are counteracted by the central atom positive charge.

In view of these considerations, we feel that a more educated guess of the force constants for HeF\textsubscript{2} is possible. In the last row of Table 1, we propose a more likely potential function (and an appropriately shortened bond length) together with the implied frequencies.

Though the two sets of predicted frequencies are discordant, they show that the infrared absorptions should fall in a readily accessible region. A search for this species, HeF\textsubscript{2}, is in progress here.

References: