

Electric deflection studies of halogen and interhalogen polymers^{a)}

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Electric deflection studies of the polymeric halogen species, $(\text{Br}_2)_2$, $(\text{ICl})_2$, $(\text{ICl})_3$, $(\text{ClF})_2$, and $(\text{F}_2)_2$ are reported. The dimeric species listed above are found to be polar. The trimeric species $(\text{ICl})_3$ is also observed to be polar, a relatively unusual occurrence. A comparison is made between the gas phase dimer orientations and the local crystal structure of these halogens.

INTRODUCTION

Molecular beam electric deflection experiments can indicate whether or not a given beam species has a polar structure. This information places constraints upon the molecular symmetry and therefore provides limited structural information. Thus, when the electric deflection technique is applied to weakly bound molecular complexes, it provides, through structural implications, a probe into the intermolecular forces between molecules in a given complex. It would, of course, be interesting to compare the qualitative structural results from deflection experiments with other structural data in which intermolecular interactions are also important. At present, the principal source of such information is provided through molecular crystal structures.

Chlorine dimer, $(\text{Cl}_2)_2$ was found, in a previous molecular beam electric deflection study,¹ to be a polar species. Nearest-neighbor Cl_2 molecules in crystalline chlorine form an L-shaped structure with the two Cl_2 units at approximately right angles to one another and with three of the four chlorine atoms almost collinear. This is, of course, consistent with a polar dimer structure and is at least suggestive of a similar interaction. In a recent theoretical study of $(\text{Cl}_2)_2$, Prissette and Kochanski² do indeed find an L-shaped structure to be the most stable free dimer configuration. This same structure is also predicted, by the way, by application of a simple HOMO-LUMO interaction model.¹ In the present work we further explore, through electric deflection studies of halogen and interhalogen complexes, the extent of structural similarity between free dimers and crystal nearest neighbors.

EXPERIMENTAL

The experimental methods used in this work are similar to those described previously by Novick *et al.*³ The complexes were in every case formed by an adiabatic nozzle expansion with argon used as a carrier gas for the sample in order to promote cluster formation. The specific source conditions used to prepare each cluster are shown in Table I. Once formed, the complexes passed through a differential pumping chamber and into

an experimental chamber where they encountered an inhomogeneous quadrupolar electrostatic field. This focusing field was 60 cm long with an entrance aperture of 0.261 cm in diameter. The operating pressure in this region was typically $\sim 3 \times 10^{-7}$ Torr. This quadrupolar field focused polar beam species around a beam obstacle and onto the detector slits. Nonpolar species were thrown off the beam axis and thus missed the detector. The detector is a large 60° sector magnetic mass analyzer with a Weiss-type electron bombardment ionizer. The ionization current is approximately 130 mA at 200 V. The mass resolution used in the present work is $\sim 1/200$. In every case, the cluster's parent mass peak was monitored as indicated in Table I. With the exception of the ICl species, individual isotopic species are seen for each of the clusters. Because of the characteristic isotopic ratios which were observed, there is no possibility of confusion as to the chemical identity of the ion. In general, for asymmetric tops with second-order moments the limit of our detection sensitivity is ~ 0.2 D, while for symmetric tops with first-order moments, it is somewhat better.

The experimental results are straightforward for all species except fluorine dimer. Because of the weak focusing observed in this case, special attention was paid to the integrity of this particular polarity determination. The $(\text{F}_2)_2$ parent peak, F_4^+ , exhibited a strong temperature dependence characteristic of a weakly bound complex. While neither F_5^+ nor F_6^+ were observed in the mass spectrum, nonfocusing F_2^+ was seen. A small amount of F_3^+ was observed under a much larger background feature. It was not possible to see it focus, however, owing to the relative sizes of the background and the F_3^+ fragment. While weakly polar ArF_2^+ was observed, we saw no evidence of higher clusters containing argon and fluorine. Thus, it seems improbable that the weak focusing observed at F_4^+ is due to the fragmentation of higher polymers; e.g., $(\text{F}_2)_n + e^- \rightarrow \text{F}_4^+ + (\text{F}_2)_{n-2} + 2e^-$. Reproducibility of results was assured not only by repeating experiments on a given apparatus, but also by running the experiment on a separate but similar apparatus. This, of course, tended to discriminate against apparatus misalignments and other artifacts. As an instrumental check, argon dimer was examined carefully for signs of focusing and found to show none.

RESULTS AND DISCUSSION

The molecular crystal structures of Cl_2 , Br_2 , I_2 , and IBr are isomorphous.⁴ Thus, our determination that

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TABLE I. Experimental conditions and results.

Species	Ion detected	Nozzle diameter (μm) and nozzle material	Nozzle temp. ($^{\circ}\text{K}$)	% Sample gas in argon	Total gas pressure (Torr) behind nozzle	% Focusing ^c at a given quadr. field voltage (kV)	Polarity
$(\text{Cl}_2)_2^{\text{a}}$	Cl_4^+	25, Monel	240	5	800	10%, 25	Polar
$(\text{Cl}_2)_3^{\text{a}}$	Cl_6^+	25, Monel	240	5	800	0%, 25	Nonpolar
$(\text{Br}_2)_2$	Br_4^+	60, Glass	325	60 ^b	760	2%, 40	Polar
$(\text{ClF})_2$	Cl_2F_2^+	25, Monel	300	10	760	30%, 30	Polar
$(\text{ClF})_3^{\text{a}}$	Cl_3F_3^+	25, Monel	230	5	760	0%, 25	Nonpolar
$(\text{ICl})_2$	I_2Cl_2^+	60, Glass	325	20 ^b	760	50%, 25	Polar
$(\text{ICl})_3$	I_3Cl_3^+	60, Glass	325	20 ^b	760	8%, 35	Polar
$(\text{F}_2)_2$	F_4^+	25, Monel	90	40	1400	0.5%, 20	Very slightly polar

^aResults from Ref. 1. Percent focusing for $(\text{Cl}_2)_2$ is given for the A field only to facilitate comparisons with our apparatus.

^bEstimated from vapor pressure data since condensed samples under argon were employed to prepare these species.

^c"% Focusing" is the percent of the straight-through beam recovered upon setting the quadrupole (A) field at a given voltage.

$(\text{Br}_2)_2$ is a polar complex is entirely analogous to the previous interpretation of $(\text{Cl}_2)_2$ results.

The crystal structure of ClF is not known. The observation that $(\text{ClF})_2$ is polar serves only to eliminate centrosymmetric configurations as possibilities for the structure of the dimer. The fact that $(\text{ClF})_3$ is nonpolar, even though it is composed of polar constituents, is, of course, suggestive of a symmetric cyclic structure.

The crystal structure of ICl, while not isomorphous to chlorine, displays a pattern of zigzag chains similar to that found in chlorine. Furthermore, in ICl, unlike in IBr, which is isomorphous to chlorine, there occur comparably short $\text{I}\cdots\text{I}$ and $\text{I}\cdots\text{Cl}$ intermolecular distances within the crystal.^{5,6} The observation that $(\text{ICl})_2$ is polar is consistent with the ICl crystal data and serves to eliminate the same dimer structures eliminated for $(\text{ClF})_2$. The gas phase trimer of ICl presents an interesting anomaly because unlike all other trimers studied to date, e.g., $(\text{Cl}_2)_3$,¹ $(\text{ClF})_3$,¹ $(\text{HF})_3$,⁷ $(\text{NO})_3$,³ it was found to be polar. This suggests to us that the free $(\text{ICl})_3$ mimics the ICl crystal by retaining the $\text{I}\cdots\text{I}$ intermolecular contacts found to be prevalent there.

The crystal structure of α -fluorine, while exhibiting a high degree of symmetry, does not display a unique pair of nearest neighbors as do chlorine and bromine. There are two configurations of fluorine pairs in the crystal which could be considered to be nearest neighbors.⁸⁻¹⁰ In both of them, the fluorine atoms form rhomboids, one of which is a near square. Clearly, either of these geometries in the free fluorine dimer would give rise to a nonpolar $(\text{F}_2)_2$ species. Computations by Koide and Kihara¹¹ and by Umeyama, Morokuma, and Yamabe¹² both predict nonpolar lowest energy $(\text{F}_2)_2$ configurations. A polar dimer is, of course, predicted for fluorine, as it was for chlorine, by application of HOMO-LUMO arguments.

As discussed earlier, the polarity of $(\text{F}_2)_2$ is weak but definite. It is to be expected that, given a polar con-

formation for $(\text{F}_2)_2$, the observed polarity will be small. The low boiling point of fluorine clearly establishes that the F_2 - F_2 interaction potential is weak and thus, that the charge distortion is likely to be small. Secondly, the angular dependence of the weak intermolecular potential in $(\text{F}_2)_2$ must be small. In a dimeric system at least two equienergetic configurations exist for a polar conformation. The rigidity of the system will determine to some extent the observed Stark effect. These two factors, small distortion and low angular rigidity, are the likely explanation for the weak polarity observed for $(\text{F}_2)_2$.

It appears that the closest comparison with fluorine is seen in the carbon monoxide system. The boiling points of F_2 and CO are within 2° of each other. The rotational energy level spacings of states which can be coupled by an anisotropic intermolecular potential are also quite similar since $B_{\text{F}_2} \approx \frac{1}{2} B_{\text{CO}}$. The $(\text{CO})_2$ system appears to exhibit nonrigidity, i.e., facile interconversion between isoenergetic configurations.¹³ These considerations indicate that the weak polarity of $(\text{F}_2)_2$ does not necessarily imply a rigid structure only slightly distorted from a nonpolar configuration. It is quite conceivable that the minimum energy conformation of $(\text{F}_2)_2$ is quite similar to $(\text{Cl}_2)_2$ and $(\text{Br}_2)_2$.

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