

# Matrix Isolation Investigation of the Hydrogen Bihalide Anions

BRUCE S. AULT

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

Received September 14, 1981

Chemists have long realized the tremendous importance of the hydrogen bond in explaining physical and chemical phenomena in all areas of chemistry.<sup>1</sup> This type of interaction, which is intermediate in strength between normal chemical bonds and weak van der Waals interactions, accounts for effects as diverse as the expansion of water upon freezing and the structure of proteins. Since the first proposal<sup>2</sup> of a hydrogen-bonding interaction in 1903, and its subsequent clarification<sup>3</sup> in 1920, an immense amount of research has been devoted to this subject, employing all of the tools available to chemists. Perhaps one of the most sensitive and distinctive means of detection and characterization of a chemical bond is infrared spectroscopy.

The infrared spectrum of a species that is either intra- or intermolecularly hydrogen bonded provides a definitive criterion for the detection of a hydrogen bond as well as direct evidence of the role of the proton in the interaction. The most indicative vibrational mode is the hydrogen stretching frequency, which shifts to lower energies upon hydrogen-bond formation.<sup>4</sup> In addition, this mode is intensified dramatically and is broadened considerably, both aiding in the identification of this vibrational mode. Numerous studies<sup>5,6</sup> have also shown that the shift of this band in the hydrogen-bonded species from its position when not hydrogen bonded correlates well with important physical parameters, including hydrogen-bond enthalpy, interatomic distances, and chemical reactivity. Finally, it should be noted that while most commonly cited examples of hydrogen bonding are neutral species, such as H<sub>2</sub>O, ionic species are also well-known to demonstrate hydrogen-bonding interactions as well.

While the research on the nature of the hydrogen bond has been extensive, many unresolved questions remain about the nature of this interaction and how it might best be described. A model system for the hydrogen bond is the hydrogen bihalide anions, HX<sub>2</sub><sup>-</sup>, for these anions exhibit a very strong interaction yet are triatomic species, which allows for detailed study. The first member of this series, HF<sub>2</sub><sup>-</sup>, was discovered<sup>7</sup> a number of years ago and is the most strongly bound hydrogen bihalide anion,<sup>8</sup> by roughly 188 kJ/mol relative to HF + F<sup>-</sup>. This anion has also been shown to be centrosymmetric in crystals with a variety of simple cations.<sup>9</sup> However, when Evans and Lo investigated<sup>10</sup> the HCl<sub>2</sub><sup>-</sup> anion in solution with a range of cations, they found two different forms of the anion under these

conditions. Type I, formed with certain cations, was postulated to be linear, but not centrosymmetric, and had a hydrogen stretching frequency near 1600 cm<sup>-1</sup>. Type II species were proposed to be linear and centrosymmetric, with a hydrogen stretching frequency between 700 and 800 cm<sup>-1</sup>. However, these studies did not provide an explanation for why two different species could be formed, nor did they indicate which would be the preferred structure of the anion in an environment free from solvent interactions.

Even less understood are the HBr<sub>2</sub><sup>-</sup> and HI<sub>2</sub><sup>-</sup> anions.<sup>11-13</sup> Do they prefer a type I or a type II structure, and what spectral characteristics do they display? Equally interesting questions arise concerning the mixed halogenated hydrogen bihalide anions, such as FHC1<sup>-</sup>. These species cannot have a center of symmetry, and it has not been determined whether these anions can have a spectrum and potential surface similar to that of a type II anion or whether they are constrained to the spectrum of a type I species. Lastly, the cyanide anion, CN<sup>-</sup>, has long been viewed by chemists as a "pseudohalogen", which suggests that hydrogen-bonded species such as FHCN<sup>-</sup> might be stable. A very small amount of work has been aimed in this direction in the gas phase,<sup>14</sup> and these studies suggest that the isolation of such species is feasible.

While many approaches have been applied to the spectroscopic study of hydrogen-bonded complexes, one of the most effective has been the matrix isolation technique.<sup>15</sup> In this technique, the species of interest are premixed with a large excess of an inert gas, often argon, and then frozen on a cold surface at between 4 and 20 K. Matrix isolation offers the advantages of an inert environment for the trapped species, band sharpening due to the cryogenic temperatures and minimal interactions, and no rotational substructure which characterize vibrational band contours in the gas phase. This technique can be, and has been, applied to species that are relatively stable and nonreactive as well as to highly reactive transitory species.<sup>16,17</sup>

Neutral hydrogen-bonded complexes are readily iso-

(1) Pimentel, G. C.; McClellan, A. "The Hydrogen Bond"; W. H. Freeman and Co.: San Francisco, 1960.

(2) Werner, A. *Ber.* 1903, 36, 147.

(3) Latimer, W. M.; Rodebush, W. H. *J. Am. Chem. Soc.* 1920, 42, 1419.

(4) Badger, R. M.; Bauer, S. H. *J. Chem. Phys.* 1937, 5, 839.

(5) Pimentel, G. C.; Sederholm, C. H. *J. Chem. Phys.* 1956, 24, 639.

(6) Gordy, W.; Nielsen, A. H. *J. Chem. Phys.* 1940, 8, 170.

(7) Pitzer, K. S.; Westrum, E. F., Jr. *J. Chem. Phys.* 1947, 15, 526.

(8) Peterson, S. W.; Levy, H. A. *J. Chem. Phys.* 1953, 20, 704.

(9) Foster, M. S.; Beauchamp, J. L. *Chem. Phys. Lett.* 1975, 31, 479.

(10) Evans, J. C.; Lo, Y.-S. *J. Phys. Chem.* 1966, 70, 11.

(11) Evans, J. C.; Lo, Y.-S. *J. Phys. Chem.* 1967, 71, 3942.

(12) Schroder, L. W. *J. Chem. Phys.* 1970, 52, 1972.

(13) McDaniel, D. H.; Vallee, R. E. *Inorg. Chem.* 1963, 2, 996.

(14) Sullivan, S. A.; Beauchamp, J. L. *Int. J. Mass Spectrom. Ion Phys.* 1978, 28, 69.

(15) Van Thiel, M.; Pimentel, G. C. *J. Chem. Phys.* 1960, 32, 133.

(16) Craddock, S.; Hinchcliffe, A. J. "Matrix Isolation"; Cambridge University Press: New York, 1975.

(17) Andrews, L. *Annu. Rev. Phys. Chem.* 1971, 22, 109.

Bruce Ault was born on Oct 3, 1948 in Altadena, CA, and received his bachelors degree from Caltech in 1970. He obtained his Ph.D. from the University of California, Berkeley, in 1973, working with Professor George Pimentel, after which he spent 3 years at the University of Virginia as an Instructor/Postdoctoral Fellow. Dr. Ault joined the faculty of the Chemistry Department of the University of Cincinnati as an Assistant Professor in 1976 and was promoted to Associate Professor in 1980. He has also been selected as a Dreyfus Teacher-Scholar for 1980-1985. His research interests lie in the area of the low-temperature spectroscopy of intermediate chemical species, both neutral and charged.

lated in inert matrices, and often assume a gas-phase like structure, rather than the known crystal structure. For example, the codeposition of a sample of  $\text{NH}_3$  diluted in argon with a sample of  $\text{HCl}$  diluted in argon allows for the formation and isolation<sup>18</sup> of the strongly hydrogen-bonded complex  $\text{NH}_3\cdot\text{HCl}$ , with a structure quite different from the known  $\text{NH}_4^+\text{Cl}^-$  crystal. In recent years, matrix isolation techniques have been extended to the study of ionic species in matrices, in many cases providing the first spectra of free or nearly free ions.<sup>19</sup> These ions are often formed through the input of high amounts of energy, utilizing either microwave discharge techniques or vacuum ultraviolet photolysis, to fragment and/or ionize a stable precursor molecule. In addition, the salt/molecule technique was developed in 1975 to allow for the formation of ions in matrices at thermal energies.<sup>20</sup> In this approach, an alkali halide salt molecule is vaporized from a high-temperature oven and codeposited with a suitable acid diluted in argon. The reaction mixture is then condensed on a cryogenic surface, and the reaction products are trapped. An alkali halide salt molecule is a rather good halide ion donor, so that transfer of the halide anion from the salt to the acid might occur to form a matrix-isolated ion. However, the electrostatic attraction between the newly formed anion and the remaining alkali metal cation is sufficiently strong that ion separation cannot occur, and the anion of interest is trapped in an ion pair with the alkali metal cation. It appeared likely that the reaction of an alkali chloride salt, such as  $\text{CsCl}$ , with a mixture of  $\text{HCl}$  in argon would lead to formation of the  $\text{HCl}_2^-$  anion paired with the  $\text{Cs}^+$  cation. With the interest in these anions as models for hydrogen bonding, the questions underlying the type I vs. type II structures, and the spectroscopic advantages inherent in the matrix isolation technique, this system seemed to be a natural choice for a study using the salt/molecule reaction technique.

Two related sets of observations have increased interest in the hydrogen bihalides. In 1968, Noble and Pimentel passed a gas phase mixture of  $\text{HCl}$ ,  $\text{Cl}_2$ , and argon through a microwave discharge apparatus and condensed the products into an argon matrix.<sup>21</sup> They assigned an extremely intense band and two less intense bands to the neutral hydrogen-bonded species  $\text{HCl}_2$  and determined that this radical had a linear, centrosymmetric geometry. A year later, Milligan and Jacox extended these studies and on the basis of their work argued that the isolated product was, in fact, the  $\text{HCl}_2^-$  anion.<sup>22</sup> Noble, Pimentel and co-workers extended these studies to the analogous bromide<sup>23</sup> and iodide<sup>24</sup> systems, assigning the products in each case to the neutral species. Milligan and Jacox meanwhile provided more evidence that the anion had been formed in each case.<sup>25</sup> Compelling arguments were put forward on both sides of this controversy, and no clear-cut verdict had been reached at the time of the inception of the salt/molecule technique. If this technique could

provide the infrared spectrum of the  $\text{HCl}_2^-$  anion in an argon matrix, comparison could be made to the spectra obtained by both research groups and a resolution to this question might be made. This, of course, would require that the alkali metal cation provide little, if any, distortion on the anion, a point which would certainly have to be addressed during any such investigation. A possible resolution to this question, coupled with the inherent interest in the hydrogen bihalide anions, provided the motivation for this investigation.

### The $\text{HF}_2^-$ Anion

The hydrogen bifluoride anion,  $\text{HF}_2^-$ , was chosen to test the idea that the reaction of an alkali halide salt molecule with a hydrohalic acid would lead to hydrogen bihalide anion formation. A great deal is known about  $\text{HF}_2^-$ ; its vibrational spectrum is established in a variety of crystals, and its geometry is known from X-ray crystal structures. When  $\text{CsF}$  was vaporized at 500 °C and codeposited with a sample of  $\text{Ar}/\text{HF}$  at a concentration of 1000/1, a number of product bands were observed, indicating immediately that a reaction had occurred.<sup>26,27</sup> However, the  $\text{HF}_2^-$  anion could not account for all of the observed bands, suggesting that more than one species was present. When more dilute samples of  $\text{HF}$  in argon (up to 5000/1) were employed, many of these bands disappeared, and only a very intense, broad band at 1364  $\text{cm}^{-1}$  and a sharp band at 1217  $\text{cm}^{-1}$  remained. These results suggested that the bands observed at higher concentrations were due to aggregates, which is consistent with the fact that species such as  $\text{H}_2\text{F}_3^-$  and  $\text{H}_3\text{F}_4^-$  are known.<sup>28</sup> The two remaining bands which were dominant at high dilution agree very well with the antisymmetric hydrogen stretching mode and the bending mode of the  $\text{HF}_2^-$  anion.<sup>29</sup> The band at 1364  $\text{cm}^{-1}$  is particularly characteristic, with its considerable intensity and breadth, of a hydrogen stretching vibration in a strongly hydrogen-bonded complex. As anticipated, the bending mode at 1217  $\text{cm}^{-1}$  was sharp and much less intense.

Deuterium isotopic substitution, an effective tool of vibrational spectroscopists, demonstrated that these bands were due to hydrogenic vibrations, showing shifts to 969 and 880  $\text{cm}^{-1}$ , respectively. The ratio of frequencies of the hydrogen- and deuterium-containing species is also an informative parameter. Here, a value of 1364/969 = 1.41 indicates that the vibration is relatively harmonic with some quartic contribution (harmonic value is 1.396) and supports a linear geometry. Since the  $\text{HF}_2^-$  anion is well-known to be linear and centrosymmetric<sup>9</sup> ( $D_{\infty h}$  point group) and the vibrational frequencies here match very closely, it can be safely concluded that the anion formed in a matrix-isolated ion pair with the  $\text{Cs}^+$  cation is also effectively centrosymmetric. Of course, in a contact ion pair with the  $\text{Cs}^+$  cation the  $\text{HF}_2^-$  anion cannot be literally centrosymmetric, but the spectra indicate that the effective potential function for the observed vibration is centrosymmetric.

The  $\text{HF}_2^-$  anion was recently investigated in argon matrices, after formation through the photoionization method.<sup>30</sup> This approach, which will be discussed in

(18) Ault, B. S.; Pimentel, G. C. *J. Phys. Chem.* **1973**, *77*, 1649.

(19) Andrews, L. *Annu. Rev. Phys. Chem.* **1979**, *30*, 79.

(20) Ault, B. S.; Andrews, L. *J. Am. Chem. Soc.* **1975**, *97*, 3824.

(21) Noble, P. N.; Pimentel, G. C. *J. Chem. Phys.* **1968**, *49*, 3165.

(22) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1970**, *53*, 2034.

(23) Bondybevy, V.; Pimentel, G. C.; Noble, P. N. *J. Chem. Phys.* **1971**, *55*, 540.

(24) Noble, P. N. *J. Chem. Phys.* **1972**, *56*, 2088.

(25) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1971**, *55*, 2550.

(26) Ault, B. S. *J. Phys. Chem.* **1978**, *82*, 844.

(27) Ault, B. S. *J. Phys. Chem.* **1979**, *83*, 837.

(28) Tuck, D. G. *Prog. Inorg. Chem.* **1968**, *9*, 161.

(29) Jones, L. H.; Penneman, R. A. *J. Chem. Phys.* **1954**, *22*, 781.

Table I  
Infrared Band Positions for the Hydrogen Stretching  
Vibration  $\nu_3$  of the Hydrogen Bihalide Anions

anion	method	$\nu_3$ , $\text{cm}^{-1}$	ref
$\text{HF}_2^-$	salt/molecule <sup>a</sup>	1364	27
$\text{HF}_2^-$	photoionization	1377	39
$\text{HCl}_2^-$	salt/molecule <sup>a</sup>	723	33
$\text{HCl}_2^-$	photoionization	696	22
$\text{HBr}_2^-$	salt/molecule <sup>a</sup>	727	34
$\text{HBr}_2^-$	photoionization	728	23
$\text{HI}_2^-$	salt/molecule <sup>a</sup>	673	35
$\text{HI}_2^-$	photoionization	682	24

<sup>a</sup> Cesium cation.

more detail later in this Account, allows for the formation of isolated anions, and hence can provide a comparison of the ion-paired anion and the isolated anion. As can be seen in Table I, the results are quite similar; the isolated anion absorbs at  $1377\text{ cm}^{-1}$ , which compares to the  $1364\text{ cm}^{-1}$  value observed here with the cesium cation. Perhaps more importantly, the hydrogen/deuterium frequency ratio of 1.426 observed for the isolated anion is quite close to the 1.410 value obtained here. This agreement is particularly significant in that the same characteristic quartic contribution to the potential function is observed. These results confirm the value of the salt/molecule reaction technique for the formation of such anions, particularly under conditions where the photoionization method is not effective.

For further tests on the role of the cation in anion formation, similar studies were carried out with KF and NaF. The results here, which have been confirmed by numerous other salt/molecule studies, indicate that the smaller the cation the lower the yield of product anion<sup>31,32</sup> and the greater the distortion of the anion. The  $\text{K}^+\text{HF}_2^-$  ion pair showed a split hydrogen stretching motion, with components near  $1314$  and  $1372\text{ cm}^{-1}$ , while the  $\text{Na}^+\text{HF}_2^-$  ion pair showed the hydrogen stretching motion shifted to  $1284\text{ cm}^{-1}$ . These data, and the data taken from other studies, suggest that the salt/molecule technique is most effective when large, diffuse cations are employed, and under these conditions the anion formed most closely resembles the isolated anion. Consequently, most of the remaining work to be discussed deal with the cesium cation, except where significant cation effects are noted.

### The $\text{HCl}_2^-$ Anion

The above studies of the  $\text{HF}_2^-$  anion serve to establish the credibility of the salt/molecule reaction technique and to suggest that further reactions might occur in argon matrices. Much less is known about the  $\text{HCl}_2^-$  anion; the solution studies of Evans and Lo have provided the bulk of the spectroscopic information about this anion.<sup>10</sup> Ambiguity, however, results from their determination that two types of  $\text{HCl}_2^-$  anions exist in solution, one an asymmetric type I anion and the other a centrosymmetric type II anion. The salt/molecule technique might well indicate the preferred form of the anion, as well as definitive spectra. When CsCl was vaporized and codeposited<sup>33</sup> with a sample of Ar/HCl at a dilution of 400/1, a single intense absorption was observed, at  $723\text{ cm}^{-1}$ , with a half-width of roughly  $15$

$\text{cm}^{-1}$ . Similar results were obtained with all of the remaining alkali metal cations, but with lower yield and some shifting of band positions. The band at  $723\text{ cm}^{-1}$  falls squarely in the region that Evans and Lo established for the hydrogen stretching mode of the type II  $\text{HCl}_2^-$  anion, between  $700$  and  $800\text{ cm}^{-1}$ , immediately suggesting that the isolated, ion-paired  $\text{HCl}_2^-$  anion is a type II anion.

When CsCl was reacted with DCl in argon and the products were trapped at  $15\text{ K}$ , the major absorption feature was observed at  $507\text{ cm}^{-1}$ , supporting the assignment to the hydrogen (deuterium) stretching motion. The hydrogen/deuterium frequency ratio, 1.42, is very unusual in that it is larger than the harmonic value of 1.40 (ratios as high as 1.50 were observed with other alkali metal cations). This deviation from the harmonic value is a consequence of the anharmonic character of the vibration. However, the leading term in the anharmonic portion of any potential function is cubic,  $-ax^3$ , which must shift the observed ratio below the harmonic value, i.e., below 1.40. The observation of a shift above the harmonic value indicates that the cubic term is not present and that the quartic term, which can be either positive or negative, dominates the anharmonic potential. This can only occur when the absorbing species has a center of symmetry, so that terms involving odd powers in  $x$  in the potential function must go to zero. This argument provides strong support for a structure for the  $\text{HCl}_2^-$  anion which is centrosymmetric, in agreement with the prediction of Evans and Lo for a type II anion. Again, the cation is certainly present in these ion pairs, so the symmetry designation for the anion must be an effective spectroscopic symmetry. Within this limitation, it is apparent that the preferred form of the  $\text{HCl}_2^-$  anion is a linear, centrosymmetric species with a hydrogen stretching frequency near  $720\text{ cm}^{-1}$ .

### The $\text{HBr}_2^-$ and $\text{HI}_2^-$ Anions

Less is known about the  $\text{HBr}_2^-$  and  $\text{HI}_2^-$  anions than their lighter counterparts. Two studies<sup>11,12</sup> of the  $\text{HBr}_2^-$  anion have been carried out; they indicate the presence of both type I and type II anions, while the one available spectrum<sup>13</sup> of the  $\text{HI}_2^-$  anion indicated a type I structure. The codeposition<sup>34</sup> of CsBr with HBr diluted in argon gave rise to a broad, intense band at  $727\text{ cm}^{-1}$ , along with a weaker counterpart at  $904\text{ cm}^{-1}$ . Over a number of experiments at different concentrations, these two bands maintained a constant intensity ratio, suggesting that a single species was responsible for the two absorptions. The very intense band was located only  $4\text{ cm}^{-1}$  away from the hydrogen stretching vibration of the  $\text{HCl}_2^-$  anion, showed a deuterium shift to  $504\text{ cm}^{-1}$ , and is easily assigned to the hydrogen stretching mode of the  $\text{HBr}_2^-$  anion. In this particular vibration, the hydrogen atom is experiencing a very broad potential minimum which should be not severely affected by a change in terminal atoms from Cl to Br. The position of this band also suggests a type II anion, as does the hydrogen/deuterium shift ratio of 1.44, by use of the arguments presented above for the  $\text{HCl}_2^-$  anion. The weaker band, at  $904\text{ cm}^{-1}$ , might be assigned either to the bending mode of the anion or to a combination mode of the  $727\text{-cm}^{-1}$  band with a low frequency mode.

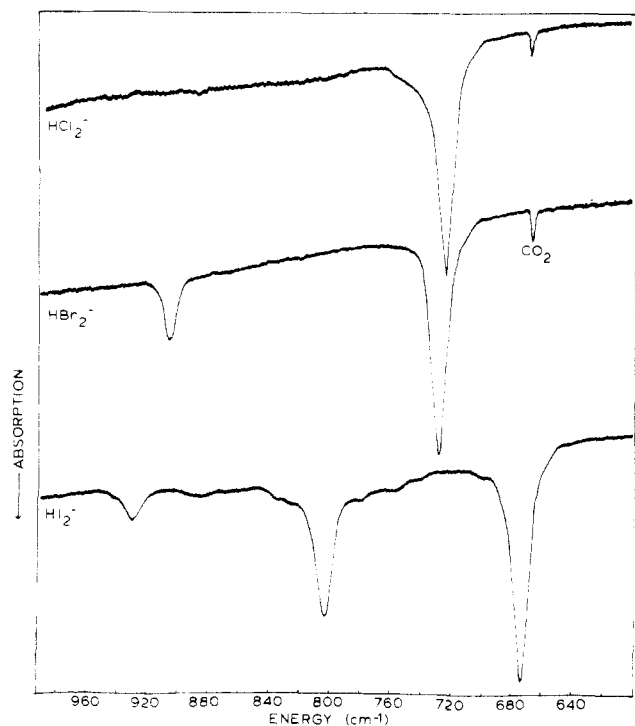
(30) McDonald, S. A.; Andrews, L. *J. Chem. Phys.* 1979, 70, 3134.

(31) Ault, B. S. *Inorg. Chem.* 1979, 18, 3339.

(32) Hunt, R. L.; Ault, B. S. *Spectrochim. Acta, Part A* 1981, 37, 63.

(33) Ault, B. S.; Andrews, L. *J. Chem. Phys.* 1975, 63, 2466.

(34) Ault, B. S.; Andrews, L. *J. Chem. Phys.* 1976, 64, 1986.



**Figure 1.** Infrared spectra, over selected spectral regions, of the  $\text{HCl}_2^-$ ,  $\text{HBr}_2^-$ , and  $\text{HI}_2^-$  anions, each ion paired with  $\text{Cs}^+$ , in argon matrices.

However, the deuterium shift of this band was too small to be assigned to the bending mode. Rather, this band is assigned to the combination of the antisymmetric stretch,  $\nu_3$ , with symmetric heavy atom stretch,  $\nu_1$ . Since the symmetric stretch is independent of the hydrogen isotope, the deuterium shift of this combination should be less than 1.41, as was observed. This places the frequency of the symmetric stretch near  $177\text{ cm}^{-1}$ , which is quite close to the solution value from Raman spectra,  $170\text{ cm}^{-1}$ .

The codeposition<sup>35</sup> of  $\text{CsI}$  with  $\text{HI}$  diluted in argon gave rise to a similar, very intense band near  $673\text{ cm}^{-1}$ , with two weaker counterparts, at  $803$  and  $929\text{ cm}^{-1}$ . The band positions in the analogous deuterium experiment were  $468$  and  $587\text{ cm}^{-1}$  for the two most intense bands. The most intense band is easily assigned to the hydrogen stretching motion of the  $\text{HI}_2^-$  anion, as it is quite near the analogous bands for both  $\text{HCl}_2^-$  and  $\text{HBr}_2^-$ . The deuterium shift ratio for this band, 1.44, is suggestive of a center of symmetry, as is the location of this band, in the type II region. The weaker features at  $803$  and  $929\text{ cm}^{-1}$  are assigned, analogous to the  $\text{HBr}_2^-$  anion, to combination modes of  $\nu_1$  and  $\nu_3$ . In particular, the band at  $803\text{ cm}^{-1}$ , which shifts to  $587\text{ cm}^{-1}$  upon deuterium substitution, is assigned to the combination  $\nu_1 + \nu_3$ , while the band at  $929\text{ cm}^{-1}$ , which was much weaker, is assigned to the combination  $2\nu_1 + \nu_3$ . This places the fundamental  $0 \rightarrow 1$  transition of the symmetric stretch near  $130\text{ cm}^{-1}$ , and the  $1 \rightarrow 2$  transition near  $126\text{ cm}^{-1}$ . These values are well below those of  $\text{HCl}_2^-$  and  $\text{HBr}_2^-$ , which is anticipated on the basis of the increased mass of the halogen. Figure 1 shows representative spectra of the  $\text{HCl}_2^-$ ,  $\text{HBr}_2^-$ , and  $\text{HI}_2^-$  anions, ion paired in argon matrices.

The observation of a quartic contribution to the potential function, as indicated by the hydrogen/deuter-

ium frequency shift ratios, allows for further qualitative consideration of the shape of the potential energy surface. A one-dimensional oscillator with quadratic and quartic terms can be written in the form  $V = bx^2 + x^4$ , as has been discussed at length by Laane.<sup>36,37</sup> For large, positive values of  $b$ , the oscillator resembles a harmonic oscillator slightly perturbed by the quadratic contribution. On the other hand, negative values of  $b$  give rise to a double minimum potential surface, as are often postulated for hydrogen-bonded systems. For large negative values of  $b$ , the barrier height, which is given by  $b/4$ , is quite large. Since vibrational spectroscopy samples only the potential surface near the bottom of the well, it appears as an unsymmetrical harmonic oscillator. However, if  $b$  is small and negative, such that the height of the barrier roughly corresponds to the first vibrational spacing, then splitting of the degenerate levels of the two wells will occur. This will have spectroscopic consequences in the number of bands observed; the antisymmetric stretch should appear as a doublet, and the magnitude of splitting between the components of the doublet should change when deuterium is substituted. The spectra presented here are quite sharp and distinct, and no indication of level doubling and splitting is observed. This indicates that a double minimum potential surface with relatively low barrier is not likely. Nor is the potential surface with a high double minimum barrier likely. Rather, the spectra here for the  $\text{HX}_2^-$  anions in  $\text{M}^+\text{HX}_2^-$  ion pairs suggest a potential surface with a broad, symmetric single minimum. This observation is consistent with the very large shift of the hydrogen stretching frequency in the  $\text{HX}_2^-$  anions relative to the free  $\text{HX}$  molecule, indicating a very broad potential surface and low force constant.

The spectra obtained, and the conclusions reached, for all four of the hydrogen dihalide anions studied here are quite similar. All four showed an intense broad absorption with strong deuterium shift at relatively low energy, which can be assigned to the hydrogen stretching motion in a strongly hydrogen-bonded species. The position of this band and its shift upon deuteration indicate that these anions can be classified as type II, with a linear centrosymmetric geometry. One might readily conclude that the type I structures observed in solution must be due to perturbations caused by the large, bulky cations used in those studies. Certainly, the argon matrix spectra are more representative of the isolated  $\text{HX}_2^-$  anion, and the perturbation caused by the presence of the alkali metal cation is insufficient to lower the effective spectroscopic symmetry along the molecular axis.

#### Neutral vs. Anion

The microwave discharge matrix isolation studies of Pimentel and co-workers, in which they proposed formation of the analogous neutral radicals  $\text{HCl}_2$ ,  $\text{HBr}_2$ , and  $\text{HI}_2$ , can be reexamined at this point.<sup>21,23,24</sup> Milligan and Jacox argued that the species formed were the isolated anions, using vacuum ultraviolet radiation to generate the same absorptions.<sup>22,25</sup> It was hoped that formation of the anion in a matrix-isolated ion pair would provide clarification as to the charge on these

(35) Ellison, C. M.; Ault, B. S. *J. Phys. Chem.* 1979, 83, 832.

(36) Laane, J. *Appl. Spectrosc.* 1970, 24, 73.

(37) Laane, J. Q. *Rev., Chem. Soc.* 1971, 25, 533.

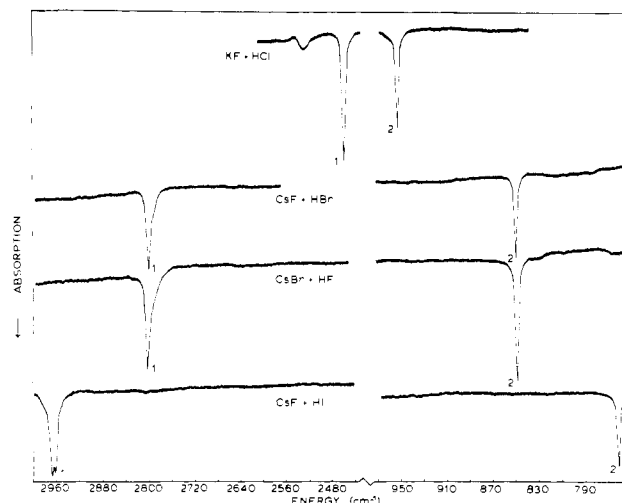
species. Both groups observed an intense band at  $696\text{ cm}^{-1}$  when chlorine was employed, and observed a quartic deuterium shift. When bromine was used, the intense band assigned to the hydrogen stretching motion was observed at  $728\text{ cm}^{-1}$ , while with iodine the band came at  $682\text{ cm}^{-1}$ . The band positions of the species in question match within a few wavenumbers in each case of the bands observed here, which are clearly due to the anion.

Table I lists the observed band positions for these anions, formed through both the salt/molecule technique and through microwave discharge techniques. In addition, the very distinctive anharmonic shifts, displaying quartic anharmonicity, agree very well with those observed here. Finally, the same set of combination bands,  $\nu_1 + \nu_3$  and  $2\nu_1 + \nu_3$ , were observed at nearly the same locations. In fact, the spectrum of the  $\text{Cs}^+\text{HI}_2^-$  ion pair could be nearly exactly superimposed on the spectrum reported for the " $\text{HI}_2$ " radical. The spectra data obtained here must certainly support the assertion of Milligan and Jacox that the species in question is the negative ion, not the neutral free radical. It must be noted, however, that these studies of Pimentel and co-workers provided the first evidence that ions could be formed and trapped in inert matrices by the application of microwave discharge techniques, and in doing so provided an entirely new avenue for matrix isolation. Since this pioneering work by Pimentel, several groups have conclusively demonstrated ion formation through microwave discharge techniques.<sup>38,39</sup> Their findings indicate that the mechanism of ion formation is photoionization by the high energy radiation emitted by the argon plasma during the discharge. Consequently, the term "photoionization" is probably more appropriate to describe this technique.

### Mixed Halogenated Anions $\text{XH}_2^-$

The hydrogen bihalide anions that incorporate two different halogen atoms have been subjected to considerably less study, and several interesting questions may be raised. First, what is the nature of the potential surface? The molecule may not have a center of symmetry, yet if the halogens are not too different, a broad, shallow potential function of a type II anion may still occur. Conversely, a type I structure may be preferential. Also, these anions may be formed in either of two ways; for example, the  $\text{ClHF}^-$  anion may be formed through either the reaction of  $\text{CsF}$  with  $\text{HCl}$  or the reaction of  $\text{CsCl}$  with  $\text{HF}$ . Will these two routes yield the same product? The answer to this question can provide information about the potential surface and activation energies.

All combinations of the four halogens were investigated, and both possible routes to each of the six mixed species were investigated.<sup>27,34,35</sup> The results were consistent throughout; a number of bands were observed in each spectrum. In fact, too many bands were observed to be assigned to a single triatomic absorber. Rather, the collective evidence suggests that the bands can be divided into two groups, implying the presence of two different reaction products. For example, the reaction of  $\text{CsCl}$  with  $\text{HBr}$  gave rise to a band at  $742\text{ cm}^{-1}$ , which could be assigned to one species, and band



**Figure 2.** Infrared spectra of the  $\text{ClHF}^-$ ,  $\text{BrHF}^-$ , and  $\text{IHF}^-$  anions in argon matrices with the indicated cation, over selected spectral regions. The number 1 and 2 by each band indicated which bands are assigned to type I and type II anions, respectively. Note that the synthesis of the  $\text{BrHF}^-$  anion by two different routes (second and third traces) leads to virtually identical spectra.

at  $1115$  and  $1365\text{ cm}^{-1}$ , which could be assigned to a second species. In each case, an intense band was observed in the spectral region associated with the hydrogen stretching motion of a type II anion, such as the  $742\text{-cm}^{-1}$  band in the reaction of  $\text{CsCl}$  with  $\text{HBr}$ . The deuterium shift in each case was nearly harmonic,  $1.40$ – $1.41$ , which is also reminiscent of a type II anion.

The second set of bands could be characterized by a single broad intense band with strong cubic anharmonicity between  $1000$  and  $3000\text{ cm}^{-1}$ , depending on the halogens employed, as well as a weaker, sharper band often at slightly lower energies. These two bands are characteristic of a type I anion, in terms of both band positions, shapes, and cubic anharmonicity in the potential function for the hydrogen stretching motion. It is also noteworthy that the same product bands in the same relative amounts were formed when the product species were approached from either direction, i.e.,  $\text{CsCl} + \text{HBr}$  or  $\text{CsBr} + \text{HCl}$ . This implies that the transition state is identical for either pathway. However, the relative amounts of the two product species were seen to change as the cation was altered. Bands due to the type I anion were relatively more intense with large, diffuse cations such as  $\text{Cs}^+$ , while the type II anion was more dominant with small cations such as  $\text{Na}^+$ .

These data collectively have been taken to suggest that both a type I and a type II anion are formed when an alkali halide salt molecule reacts with a hydrohalic acid containing a different halogen. The first set of bands, with the intense product band near  $750\text{ cm}^{-1}$ , is assigned to the nearly centrosymmetric type II anion, while the second set of bands is assigned to the type I anion, with the broad, intense band assigned to the hydrogen stretching mode of this anion and the weaker band assigned to the bending mode. Figure 2 displays spectra of the  $\text{FH}_2^-$  anions over selected regions, while Table II lists band positions for the hydrogen stretching mode of each type I and type II anion. It is also interesting to note (see Table II) that the position of  $\nu_3$  for the type I anions correlates directly with the difference in proton affinity of the two terminal halide anions. The larger the difference, the smaller the shift

(38) Andrews, L.; Tevault, D. E.; Smardzewski, R. R. *Appl. Spectrosc.* 1978, 32, 157.

(39) Jacox, M. E., private discussions.

Table II  
Infrared Band Positions as a Function of Proton Affinities for the Matrix Isolated  $\text{XHX}^-$  Anions<sup>a</sup>

anion	$\nu_3$ , type I, $\text{cm}^{-1}$	$\nu_3$ , type II, $\text{cm}^{-1}$	$\Delta\text{PA}$ , <sup>b</sup> kcal	$\Delta\nu$ , <sup>c</sup> $\text{cm}^{-1}$	$\Delta\nu/\nu^d$
$\text{BrHCl}^-$	1110	742	10	1700	0.60
$\text{BrHI}^-$	920	666	10	1530	0.62
$\text{ClHI}^-$	1560	644	20	1250	0.44
$\text{ClHF}^-$	2491 <sup>e</sup>	933	37	1460	0.37
$\text{BrHF}^-$	2803	849	47	1157	0.29
$\text{IHF}^-$	2960	763	57	1000	0.26
$\text{FHCN}^-$	1800		4	2160	0.55

<sup>a</sup> Cesium cation. <sup>b</sup> Difference in proton affinities of the terminal halide anions. <sup>c</sup> Shift of type I  $\nu_3$  band from the free HX acid position. <sup>d</sup> Fractional shift of the  $\nu_3$  band from the free HX acid position. <sup>e</sup> Average of split band.

of  $\nu_3$  from that of the free acid. When the terminal halide anions have almost identical proton affinities, such as  $\text{ClHBr}^-$ , the shift is very large, and approaches the spectrum of a type II anion, which represents the limit of zero difference in proton affinity between the two halide anions.

An important question arises as to why two different species were formed, particularly when only one was formed in the  $\text{HX}_2^-$  studies. The change in relative intensities of the two species with a change in cation provides a hint as to the answer. There must be two trapping sites for the cation in an unsymmetrical anion  $\text{XHX}^-$ , either nearer the X or the X', whereas only one distinct trapping site exists for the symmetrical  $\text{XHX}^-$  anion. It is likely, then, that if the cation is trapped in one site a type I anion is formed, and if it is trapped in a second site, the type II anion is formed. The size of the cation would then affect the relative amounts of type I and type II anion formed, as is observed. That both species are formed and trapped under matrix isolation conditions suggests that the two sites are similar in energies, but does not indicate which form would be preferred for the isolated ion. The answer to this question must come from another technique, perhaps the photoionization approach. Nonetheless, the composite evidence suggests that the unsymmetrical hydrogen bihalide anions  $\text{XHX}^-$  can be formed in both type I and type II configurations and that the position of the alkali metal cation in the contact ion pair is an important factor in distinguishing the two forms.

While two coordination sites for the alkali metal cation are present, leading to two different product species, one might question whether the anion has a double minimum potential surface. As discussed above, this might manifest itself by a splitting of bands due to interaction with the top of the double minimum barrier. In several spectra, particularly those for the  $\text{ClHBr}^-$  anion, a distinct asymmetry was observed for the antisymmetric stretching mode of the type I anion, possibly indicating a slight level splitting. This symmetry disappeared for the deuterium analogue, as predicted for a double minimum potential. This provides at least some evidence for a distinct double minimum, but no firm conclusions can be drawn as to the details of the potential surface.

### The $\text{FHCN}^-$ Anion

An intriguing possibility which is presented by these results is the substitution of a pseudohalogen for a

halogen atom to form a novel "hydrogen bihalide" species. The cyanide anion,  $\text{CN}^-$ , has long been viewed as a pseudohalogen, with similar properties, and is a likely candidate. Beauchamp<sup>14</sup> has employed the ion cyclotron resonance technique (ICR) to observe the  $\text{FHCN}^-$  ion and was able to bracket the hydrogen-bond strength as being between that of  $\text{FHF}^-$  and  $\text{FHCl}^-$ . Waddington<sup>40</sup> has obtained some initial condensed phase indications of the  $\text{ClHCN}^-$  and  $\text{BrHCN}^-$  anions, but no firm conclusions were reached. These anions might also be approached from two different reactions, either  $\text{MX} + \text{HCN}$  or  $\text{MCN} + \text{HX}$ , much like the unsymmetrical bihalide anions.

The reaction of  $\text{CsF}$  with  $\text{HCN}$  diluted in argon gave rise<sup>41</sup> to a dominant, broad feature at  $1800 \text{ cm}^{-1}$ , along with weaker, sharp features at  $2500$ ,  $1137$ , and  $1027 \text{ cm}^{-1}$ . Similar results were obtained with other alkali fluoride salts and  $\text{HCN}$ , as well as with  $\text{KCN}$  and  $\text{HF}$ . In addition, deuterium studies were conducted, and the three lower bands were observed to show a large deuterium shift, while the upper band showed only a small shift, although this band showed a large  $^{13}\text{C}$  shift. The dominant feature near  $1800 \text{ cm}^{-1}$ , with a deuterium shift to  $1420 \text{ cm}^{-1}$ , has all of the earmarks of a hydrogen stretching motion in a hydrogen-bonded anion, including intensity, breadth, and large cubic anharmonicity. Its location and cubic anharmonicity are both indicative of a type I anion, while no indication of a type II anion was detected. Falling at  $1800 \text{ cm}^{-1}$ , it lies at lower energy than the comparable mode in the type I anion  $\text{FHCl}^-$ , which is appropriate in view of the greater hydrogen-bond strength in  $\text{FHCN}^-$  relative to  $\text{FHCl}^-$ . The band at  $2500 \text{ cm}^{-1}$  was assigned to the C-N stretching mode in the anion, shifted up considerably from the value for free  $\text{HCN}$ , as is often observed for nitriles upon complexation.<sup>42</sup>

Finally, the two bands near  $1100 \text{ cm}^{-1}$  both showed strong deuterium shifts and slight  $^{13}\text{C}$  shifts and are assigned to the two components of the bending mode. This mode, which is doubly degenerate for a linear molecule, is apparently perturbed in such a fashion as to remove this degeneracy. From the results obtained with variation of the cation, it is most likely that the alkali metal cation is responsible for this perturbation and splitting of the two components of the bending mode. Nonetheless, the spectroscopic observation of the  $\text{FHCN}^-$  has been accomplished, and is supportive of a strongly hydrogen-bonded type I anion.

### Matrix Isolation Studies of Complexes

This Account describes one study of molecular complexes, formed through twin jet deposition, and leading to the formation of the hydrogen-bonded  $\text{HX}_2^-$  species. The matrix isolation technique is readily adaptable to the study of a wide range of complexes, most of which could be termed acid/base complexes. When the acid employed is a Brønsted acid, such as the hydrogen halides, the resulting complex may contain a hydrogen bond. These complexes may be either ionic, such as the work described here, or neutral, as in the work of Pimentel<sup>10</sup> and others. When the acid employed is a Lewis acid, then unusual molecular complexes *not* containing a hydrogen bond may be studied. For ex-

(40) Waddington, T. C., private communication.

(41) Ault, B. S. *J. Phys. Chem.* 1979, 83, 2634.

(42) Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* 1977, 23, 1.

ample,<sup>43</sup> the matrix codeposition of  $\text{SiF}_4$  with  $\text{NH}_3$  allowed for the isolation of the previously unreported intermediate 1:1 adduct  $\text{SiF}_4 \cdot \text{NH}_3$ .

The extension of this twin jet deposition technique, in principle, will permit the study of the full range of complexes from strongly hydrogen-bonded species to van der Waals molecules. The key factor for success of these studies is the relative acidities and basicities of the reactant species. This consideration arises from the fact that there is a finite mixing time during the deposition process, and reactions with small cross sections, such as for weak acids and bases, will give rise to small-to-undetectable amounts of product. The development of new deposition techniques that extend the mixing range and times will increase the applicability of matrix isolation to the study of weak molecular complexes.<sup>44</sup>

### Conclusions

The studies discussed in the Account serve to demonstrate that the salt/molecule technique does provide a unique route to the synthesis and characterization of the hydrogen bihalide anions, which then serve as a model system for hydrogen-bonding interactions. The spectra show quite clearly that the preferred geometry for all four of the  $\text{HX}_2^-$  anions is a linear, centrosymmetric  $D_{\infty h}$  configuration, a type II structure in the notation of Evans and Lo. All of the  $\text{HX}_2^-$  anions were spectroscopically characterized by an intense, broad absorption at relatively low energies which has been assigned to the hydrogen stretching vibration, indicating a very broad potential function for the hydrogen atom.

(43) Ault, B. S., *Inorg. Chem.* 1981, 20, 2817.

(44) Ault, B. S., to be published.

This is indicative of a quite strongly hydrogen-bonded species, in agreement with many thermochemical measurements. The salt/molecule technique also allowed for the synthesis of the unsymmetrical  $\text{XHX}'^-$  anions, with all combinations of halogens. Both forms of the anion, type I and type II, were observed, and the location of the cation in the ion pair apparently determines the structure of the anion. The preferred structure of these anions in the absence of any cation cannot be inferred from the data obtained here. These studies have also been extended to the synthesis and spectral characterization, for the first time, of the  $\text{FHCN}^-$  anion in agreement with the predictions of ICR.

As in any study, questions remain which might well be answered using other approaches. One such question deals with the nature of the potential surface and preferred configuration of the unsymmetrical  $\text{XHX}'^-$  anions. Also, the location of the cation in all of these ion pairs is not directly known, and determination of this may provide solution chemists with more information about the nature of contact ion pairs. Finally, what other "pseudohalogens" are capable of forming strong hydrogen bonds of this type, and can these provide additional models for the general phenomenon of hydrogen bonding? Certainly, only part of the picture is now clear, and many avenues are still open. Hopefully, chemists in all areas will be stimulated to continue investigations into the nature of the hydrogen bond.

*The author gratefully acknowledges support of this research by the National Science Foundation (Grant NSF CHE8100119) and the Dreyfus Foundation. The considerable assistance of Dr. Lester Andrews, particularly in the early phases of this research, is also gratefully acknowledged.*