Journal of Fluorine Chemistry, 7 (1976) 453 - 455
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Received: August 19, 1975

PRELIMINARY NOTE

Matrix Isolation of Bromine Monofluoride

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Bromine monofluoride, BrF, was first reported by Ruff and Menzel as a component of Br_2-BrF_5 mixtures [1] and later observed as one of several products formed by low temperature fluorination of bromine [2]. These and subsequent studies have established that bromine monofluoride in such systems exists in equilibrium with bromine and higher bromine fluorides, but the lability of the monofluoride has precluded its isolation in the pure state [3]. A variety of spectral measurements, necessarily obtained from mixtures, have been reported for bromine monofluoride [3], but the precise location of the Br-F stretching frequency remains uncertain. The reported infrared spectrum, observed only at low resolution under less than ideal conditions, yielded a value of 669 cm^{-1} for the fundamental vibration [4], whereas values derived from the visible emission spectra of bromine-fluorine flames have been variously cited as 671 cm^{-1} [5], 672.6 cm^{-1} [6], or 673 cm^{-1} [7].

In view of the paucity of infrared data concerning this simple diatomic molecule, and in consideration of the manifest experimental difficulties associated with isolating pure BrF by conventional reaction techniques, we wish to report the results of recent matrix isolation experiments [8] in which we obtained a precise, well-resolved infrared spectrum of bromine monofluoride which was generated in a dilute argon matrix at 8°K in the absence of elemental bromine or higher bromine fluorides. The pertinent experimental methods for matrix isolation spectroscopy and photolysis are summarized elsewhere [9,10].

In the course of studies concerned with the vacuum-ultraviolet photolyses of SF_5X species in cryogenic matrices [8], we had discovered that photolytic decomposition involved both SF_5-X scission and molecular photoelimination of XF, with the latter process predominating in the case of SF_5Br. Thus the facile elimination process $SF_5Br + h\nu \rightarrow SF_4 + BrF$, where the SF_5Br was at a concentration of less than 0.3% in an argon matrix, provided an unexpectedly convenient means of generating BrF in a matrix at 8°K without formation of Br_2 or higher bromine fluorides. The infrared spectrum of BrF generated in this fashion showed a strong absorption at 650.5 cm^{-1}, a value which differs significantly from those previously reported. The Br-F force constant calculated from this frequency is 3.83 md/Å.

After taking into consideration the usual slight change of frequency on going from the gas phase to a cryogenic matrix, the major part of this downward shift from the reported gas phase values can be rationalized on the basis that, in all probability, the SF_4 + BrF photolysis products are contained in the same matrix cage. The proximity and subsequent interaction of a lone electron pair of an SF_4 molecule and a positively polarized bromine in BrF would therefore account for this decrease in the Br-F stretching frequency. Supportive evidence for this interpretation was provided in the analogous SF_5Cl argon matrix experiments where, in a similar manner, the stretching frequency of the ClF molecule (763.2 cm^{-1}) was shifted 7 cm^{-1} downward from that reported for the isolated molecule (770.2 cm^{-1}) in an argon matrix [11]. The appropriate gas phase and matrix frequencies are contained in Table 1.

The breadth of the 650.5 cm^{-1} absorption of BrF (HBW ~ 9 cm^{-1}) was a consequence of the nearly equivalent amounts of ^{79}Br and ^{81}Br isotopes present in natural abundance (50.54% ^{79}Br, 49.46% ^{81}Br). Unfortunately, the small calculated isotopic splitting (1.6 cm^{-1}) could not be resolved with sufficient accuracy.

TABLE 1

Fundamental Vibrations (cm^{-1}) of ClF and BrF molecules

Molecule	Gas phase	Matrix Ar/ClF	Matrix Ar/SF$_5$X
ClF[a]	786.3[b]	770.2[d]	763.2[e]
BrF	671 [c]	-	650.5[e]

[a] Chlorine-35 isotope.
[b] A. H. Nielsen and E. A. Jones, J. Chem. Phys. 19 (1951) 1117.
[c] Value obtained from emission band spectrum (Reference 5).
[d] Reference 11.
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