Ab Initio Calculations of the Structure and Harmonic Frequencies of the Fluoro(hydrocyano)krypton(II) Cation [HC≡N–Kr–F]$^+$

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The structure and harmonic frequencies of the [HC≡N–Kr–F]$^+$ cation have been calculated with the inclusion of correlation effects; excellent agreement with the limited experimental vibrational data is found and the calculations clearly suggest a stronger Kr–F bond compared to that in KrF_2.

The first example of krypton bonded to an element other than fluorine has recently been reported.[1] The [HC≡N–Kr–F]$^+$ cation has been synthesised and characterized by low-temperature Raman and n.m.r. spectroscopy. However, no direct information on the bond lengths of this species is available, and only two vibrational frequencies have been associated with this cation.

In order to provide accurate theoretical structural characteristics of this molecule, we here describe calculations of both the geometry and vibrational frequencies of [HC≡N–Kr–F]$^+$, carried out at a level that includes correlation effects. A double zeta basis of contracted Gaussian functions, augmented by polarization functions was used. For fluorine, carbon, and nitrogen a (9s5p) basis contracted to (4s2p)[2] and augmented by d polarization functions[3,4] was used. For hydrogen a (4s) basis, contracted to (2s)[2] and augmented by a p polarization function[3] was employed. The krypton basis was (13s9p5d)[5] contracted to (8s6p2d). A krypton f polarization function with exponent of 0.65 was used. This value of the exponent was found to be optimal in a calculation of KrF^+ at the restricted Hartree–Fock level. Correlation effects were included by the use of Moller–Plesset perturbation theory (MP2)[6] and the calculations were carried out using the program CADPAC[7] on the CRAY-XMP48 of the Rutherford Appleton Laboratory.

A linear configuration was found to be a minimum on the potential energy surface, with the optimal bond lengths as shown in Figure 1. The bond lengths of the HC≡N moiety are close to those in free HC≡N,[8] whilst the predicted Kr–F bond length (1.831 Å) is considerably shorter than the value measured in KrF_2 (1.889 Å).[9] The predicted harmonic

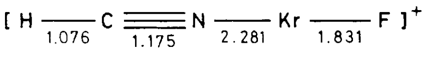

Figure 1. Calculated bond lengths (Å) of [HC≡N–Kr–F]$^+$.

Table 1. Calculated[a] harmonic frequencies of [HC≡N–Kr–F]$^+$.

Frequency/cm^{-1}	Symmetry	Mode
117.1	π	δ(F–Kr–N–C)
243.7	π	δ(F–Kr–N–C)
267.1	Σ	ν(Kr–N)
562.3 (560)	Σ	ν(Kr–F)
751.8	π	δ(N–C–H)
2100.3 (2158)	Σ	ν(N–C)
3446.0	Σ	ν(C–H)

[a] The two measured experimental frequencies are shown in parentheses.

frequencies are shown in Table 1, and clearly support the association of the bands observed[1] at 560 cm^{-1} and 2158 cm^{-1} with the $[HC{\equiv}N{-}Kr{-}F]^+$ species and their assignment to ν(Kr–F) and ν(C–N) respectively. The accuracy with which we have reproduced these observed frequencies suggests that our values predicted for the other five modes will be of value in interpreting future experimental vibrational data on this molecule.

A comparison of the measured vibrational frequencies of $HC{\equiv}N$[10] with those of $[HC{\equiv}N{-}Kr{-}F]^+$ shows a small (61 cm^{-1}) increase in ν(C–N) for the cation. Comparison of a calculation we have carried out of the harmonic frequencies of $HC{\equiv}N$ with our calculation of $[HC{\equiv}N{-}Kr{-}F]^+$ also reveals a corresponding small increase (103 cm^{-1}) in ν(C–N). It is of interest that our calculations also predict a small decrease (0.01 Å) in the C–N bond length on formation of the cation. More significant however, is the considerable shortening of the Kr–F bond (0.06 Å) and corresponding increase in ν(Kr–F) (97 cm^{-1}) when our calculated values for $[HC{\equiv}N{-}Kr{-}F]^+$ are compared with the experimental values for the difluoride.[1,9] These changes clearly suggest a more covalent Kr–F bond in the cation.

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