

Structure, Stability, and Vibrational Spectrum of HCNKrF⁺

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Non-relativistic quantum chemical *ab initio* calculations including electron correlation effects have been carried out for the electronic ground state of HCNKrF⁺, the first experimentally observed stable compound with a nitrogen–krypton bond; the geometrical structure, the stability towards dissociation into HCN and KrF⁺, and the harmonic vibrational spectrum have been determined computationally and are compared with the experimental results.

While many neutral and ionic compounds containing a noble gas element (He–Rn) are known in the gas phase, the situation is completely different when stable salts are considered. No salt or stable solution containing a noble gas lighter than krypton has ever been prepared.¹ And for Kr, the variety of known stable compounds is very limited: until recently, no example was known in which Kr was bonded to an element other than fluorine. However, Schrobilgen² recently reported the successful synthesis of the first compound in which Kr chemistry has been extended to molecules where the noble gas element is bound also to a non-fluorine element, *i.e.* the HCNKrF⁺ cation. HCNKrF⁺ was prepared from HCNH⁺AsF₆[−] and KrF₂ in HF at −60°C and is stable below −50°C. Schrobilgen characterized the cation by low-temperature Raman and n.m.r. spectroscopy. However, in Schrobilgen's experiment no structural data or energetic details about the stability of HCNKrF⁺ could be obtained. We now report our theoretical results for the geometry of ground state HCNKrF⁺, its stability towards the most favourable dissociation reaction, *i.e.* HCNKrF⁺ → HCN + KrF⁺, and also the theoretically predicted harmonic vibrational frequencies along with the corresponding *i.r.* intensities and Raman activities. The main objective of our paper is to complement the experimental investigation of Schrobilgen² to get a more detailed picture of this unusual new compound.

The equilibrium geometry, harmonic frequencies, *i.r.* intensities, and Raman activities have been calculated at the HF-SCF level using a standard 6-31G** GTO basis set for H,C,N,F and a 13s 10p 6d 1f primitive set contracted to 5s 4p 3d 1f for Kr.³ This basis set has been taken from Huzinaga's compilation⁴ with an additional f-function with exponent = 0.06. Using the same basis set, the results have been refined by including electron correlation effects using Moller–Plesset perturbation theory, terminated at second order.⁵ However, the program used⁶ did not allow the determination of Raman activities at the correlated level; they are reported at the SCF level only. Improved relative energies were finally obtained by single point energy calculations at the MP2 optimized geometries, using full fourth order Moller–Plesset perturbation theory. Relativistic effects have not been included. However, since they only effect the inner electrons, this neglect is not expected to have a severe impact on the bonding in HCNKrF⁺. Although this level of theory is probably not well suited to give very accurate quantitative

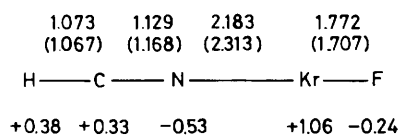


Figure 1. Equilibrium geometry (Å) and atomic charges for HCNKrF⁺. MP2 with HF values in parantheses.

results, it will certainly provide qualitatively correct answers. If not otherwise noted, data in the discussion refer to the MP2 energies and the MP2 geometries and frequencies.

In Table 1 the relative, total, and zero-point-vibrational energies are collected, while Figure 1 shows the optimized geometries and the Mulliken charge distribution⁷ computed from the SCF wavefunction. Table 2 contains the harmonic vibrational frequencies, along with their *i.r.* intensities and Raman activities.

As expected, HCNKrF⁺ assumes a linear equilibrium geometry and has a ¹Σ⁺ electronic ground state. The N–Kr bond is relatively long (2.18 Å), whereas the C–N bond shows a shortening of 0.01 Å and the Kr–F bond an increase of 0.05 Å compared to free HCN and KrF⁺, respectively. The effects of electron correlation on the geometry are most pronounced for the weak N–Kr bond, which is 0.13 Å shorter at MP2 than at Hartree–Fock and for the Kr–F bond which lengthens by 0.065 Å upon inclusion of electron correlation effects. Our predicted equilibrium bond distance for KrF⁺ (1.725 Å) compares reasonably well with the result of Liu and Schaefer (1.75 Å)⁸ who used a large STO basis set and a first order configuration interaction wavefunction. The N–Kr bond in HCNKrF⁺ is the result of a donor–acceptor interaction

Table 1. Total energy (Hartree), stabilization and zero-point energies, ZPE (kcal/mol), using the 6-31G**(H,C,N,F), 5s 4p 3d 1f (Kr) basis described in the text.

Method	HCN	KrF ⁺	HCNKrF ⁺	<i>E</i> _{stab}
Hartree–Fock	−92.87668	−2848.47830	−2941.40706	31.1
MP2 (full)	−93.16646	−2848.96836	−2942.20191	42.1
MP2 (frozen)	−93.16183	−2848.93846	−2942.16697	41.8
MP3	−93.16167	−2848.94079	−2942.15910	35.5
MP4 (SDTQ)	−93.18391	−2848.96012	−2942.20852	40.4
ZPE (MP2)	9.4	1.0	11.7	
MP4 (SDTQ) + ZPE				39.1

Table 2. Vibrational spectrum of HCNKrF⁺. Frequencies^a (cm^{−1}), *i.r.* intensities (km/mol), Raman activities (Å⁴/amu).

Symmetry	Mode	Hartree–Fock			MP2	
		<i>v</i>	<i>i.r.</i> int.	Raman act.	<i>v</i>	<i>i.r.</i> int.
π	bend	107	14	1	108	10
π	bend	228	40	5	252	23
π	HCN bend	837	25	1	709	28
σ	KrN str.	198	73	0	267	68
σ	KrF str.	696	57	102	599	90
σ	NC str.	2190	256	99	1981	87
σ	HC str.	3193	136	34	3224	234

^a Hartree–Fock frequencies scaled by 0.89, MP2 frequencies scaled by 0.93.⁹

between the sp-lone pair on N of the Lewis base HCN and the empty σ^* (11σ) orbital on KrF⁺ as Lewis acid. This is also illustrated by the Mulliken charge distribution, which shows a charge transfer of 0.18e from the HCN to the KrF moiety compared to isolated HCN and KrF⁺. The association energy of HCN and KrF⁺ is, at the best theoretical level used and accounting for zero point energy differences, predicted to be 39.1 kcal/mol (1 cal = 4.1868 J). This is only marginally smaller than the D_0 value of 43.8 kcal/mol computed for KrF⁺ by Liu and Schaefer.⁸ The partial Raman spectrum observed experimentally by Schrobilgen² is in good agreement with the theoretically obtained harmonic frequencies (Table 2). In particular, the strong line observed at 560 cm⁻¹ and assigned to the KrF stretching mode has been calculated (after scaling with the standard factor of 0.93)⁹ as 599 cm⁻¹ with a large Raman activity (computed at HF only). The agreement for the CN stretch, experimentally observed at 2158 cm⁻¹, is less satisfactory. The scaled theoretical value of 1981 cm⁻¹ is significantly smaller, but it is known that a uniform scaling for MP2 frequencies overcorrects for multiple bond stretching modes.⁹ A case in point is N₂, where the unscaled MP2/6-31G* harmonic frequency is even smaller than the experimental harmonic frequency (2173 and 2360 cm⁻¹, respectively).⁹ The unscaled frequency of the CN stretching mode in HCNKrF⁺ is 2130 cm⁻¹. The low frequency bending modes, one of which is expected around 120 cm⁻¹ with high intensity,² occur in the theoretical spectrum at 108 and 252 cm⁻¹. However, the computed Hartree-Fock Raman activities are only small to modest for both degenerate modes.

In conclusion, our computational study has shown that (i) HCNKrF⁺ has a linear equilibrium geometry and a $^1\Sigma^+$ electronic ground state, (ii) the stability towards dissociation into HCN and KrF⁺ is predicted to be 39.1 kcal/mol, (iii) the

computed harmonic vibrational frequencies show good agreement with the experimentally obtained, partial Raman spectrum.

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