



COMPUTATIONAL STUDY OF H-A-X (A = GROUP TWO ATOMS, X = F, Cl, Br) MOLECULES

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ABSTRACT

Theoretical calculations at the HF and DFT levels of theory were performed on the H-A-X (A = group two atoms, X = F, Cl, Br) molecules. The vibrational wavenumbers, bond lengths, infrared intensities and Raman activities are reported. The study predicts that H-Be-X and H-Mg-X are stable while H-Ca-X is unstable.

Key words: HF, DFT calculations, Halides.

INTRODUCTION

Quantum chemical calculations and spectroscopic characterization of organic compounds, free radicals, radical anions etc. have found considerable amount of interest in recent years.¹⁻⁴ Accurate and efficient calculation of spectroscopic constants for a wide range molecular systems employs readily available methods and basis sets.^{5,6} Experimental evidence seems to indicate that reactions of group 2 atoms with hydrogen halides may proceed via the formation of a stable complex. For example trajectory calculations on the Ca + HF reaction showed that a deep H-Ca-F potential energy well dominates the collision dynamics of the reaction.⁷ Subsequent work of Ca + DF also supports this mechanism.⁸ The simple atom exchange reaction $\text{Be} + \text{HF} \rightarrow \text{BeF} + \text{H}$ involving the lightest group 2 element, beryllium has also been studied⁹⁻¹³ and these studies indicate that the reaction proceeds via a very deep potential well corresponding to stable, linear structure H-Be-F. The transition state is much bent and apparently facilitates the insertion of Be into HF in order to form the complex more easily. The infrared vibrational intensities and polar tensors of HFCO and DFCO are reported by Martins *et al.*¹⁴ using computational method. Kurita *et al.*¹⁵ reported the relationship between force constants and bond lengths for CX (X = C, Si, Ge, N, P, As,

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O, S, Se, F, Cl and Br) single and multiple bonds. The C-S barrier and vibrational analyses of (halocarbonyl) sulfenyl halides XCO-SX (X = F, Cl and Br) was reported by Badawi.¹⁶ The vibrational spectra of group IIB elements halides MX₂ and their dimers M₂X₄ (M = Zn (II), Cd (II) and Hg (II); X = F, Cl, Br and I) have been systematically investigated theoretically and the optimized geometries, calculated vibrational frequencies are evaluated via comparison with experimental data.¹⁷ A scaled quantum mechanical force field for the sulfuryl halides SO₂X₂ (X = F, Cl, Br) was reported by Fernandez *et al.*¹⁸ Durig *et al.*¹⁹ reported the theoretical calculations on the structural parameters and vibrational spectra of some XNCS and XSCN (X = H, F, Cl, Br) molecules. Theoretical study of XPO (X = H, F, Cl, Br) molecules, structural and molecular properties are reported by Puzzarini.²⁰ *Ab initio* study of the ground and low lying excited electronic states of NiX₂ and FeX₂ (X = F, Cl, Br, I) molecules was reported by Sliznev *et al.*²¹ A scaled quantum mechanical force field for the sulfuryl halide, SO₂XF (X = Cl, Br) halides was reported by Fernandez and Varette.²² NMR, infrared, solvation and theoretical investigation of the conformational isomerism in 1-haloacetones (X = Cl, Br and I) was also reported.²³ In the present work, we perform *ab initio* calculations at the HF and B3LYP levels of theory to determine the optimized structure and harmonic vibrational frequencies of H-A-X molecules (A = group 2 atoms, X = halogens).

COMPUTATIONAL DETAILS

Calculations were carried out for the H-A-X molecules (A = group 2 atoms, X = halogens) using Gaussian03 program²⁴ on a personal computer at the HF and B3LYP levels of theory using the standard 6-311G(2df, 2pd) basis set, except for the bromine atom, where a 6-311G(df,pd) basis set was employed. Geometry optimizations followed by calculations of vibrational wave numbers were performed. The bond lengths and vibrational wave numbers (scaled) are given in Tables 1 and 2.

RESULTS AND DISCUSSION

The bond lengths calculated for H-Be-X (Table 1) indicate that the H-Be bond lengths are close in value. But Be-X bond length is in the increasing order Be-Br > Be-Cl > Be-F. The change in the H-Be bond length is almost negligible, where as the Be-X bond length increases with increasing size of the halide atom. Consequently, the high wave number, Be-H stretching value is relatively unaltered from molecule to molecule and the H-Be-X bending mode is also not much affected by the X atom. But the Be-X stretching wavenumber varies significantly, ranging from a value of 671, 787 and 1164 cm⁻¹ for X = Br, Cl, F at the DFT level. H-Ca-X and For H-Mg-X molecules show similar variations. For H-

Ca-X molecule, there is one imaginary frequency, which shows the unstable structure of this system. The studies predict that H-Be-X and H-Mg-X are very stable linear triatomic molecules where as H-Ca-X is unstable. The thermodynamic parameters, thermal energy E, specific heat capacity Cv and entropy S are given in Table 3.

Table 1: Bond lengths

| H-Be –Halogen | | | | | |
|----------------------|------------|---------------|------------|----------------|------------|
| H-Be-Cl | | H-Be-F | | H-Be-Br | |
| HF | DFT | HF | DFT | HF | DFT |
| Be-H | Be-H | Be-H | Be-H | Be-H | Be-H |
| 1.3214 | 1.318 | 1.3269 | 1.3226 | 1.3216 | 1.3187 |
| Be-Cl | Be-Cl | Be-F | Be-F | Be-Br | Be-Br |
| 1.8061 | 1.7978 | 1.3553 | 1.3654 | 1.9657 | 1.9518 |
| H-Ca-Halogen | | | | | |
| H-Ca-Cl | | H-Ca-F | | H-Ca-Br | |
| HF | DFT | HF | DFT | HF | DFT |
| H-Ca | H-Ca | H-Ca | H-Ca | H-Ca | H-Ca |
| 2.0531 | 2.0182 | 2.0933 | 2.0674 | 2.0497 | 2.0196 |
| Ca-Cl | Ca-Cl | Ca-F | Ca-F | Ca-Br | Ca-Br |
| 2.5331 | 2.4964 | 1.9972 | 1.9683 | 2.6911 | 2.6473 |
| H-Mg-Halogen | | | | | |
| H-Mg-Cl | | H-Mg-F | | H-Mg-Br | |
| HF | DFT | HF | DFT | HF | DFT |
| H-Mg | H-Mg | H-Mg | H-Mg | H-Mg | H-Mg |
| 1.6872 | 1.681 | 1.6914 | 1.6834 | 1.6912 | 1.6856 |
| Mg-Cl | Mg-Cl | Mg-F | Mg-F | Mg-Br | Mg-Br |
| 2.1951 | 2.1972 | 1.7394 | 1.7577 | 2.3517 | 2.3498 |

Table 2: Calculated wave numbers

| H-Be-F | | | | | | |
|---------------|---------------------|-----------------------|-------------------------|---------------------|-----------------------|--------------------|
| HF | | | DFT | | | Assignments |
| Y | IR intensity | Raman activity | ν | IR intensity | Raman activity | |
| 509 | 289.98 | 0.57 | 524 | 228.13 | 0.64 | δ H-Be-F |
| 1120 | 90.54 | 4.06 | 1164 | 67.89 | 6.67 | ν Be-F |
| 2006 | 175.56 | 104.74 | 2113 | 129.86 | 101.84 | ν Be-H |

| H-Be-Cl | | | | | | |
|----------------|---------------------|-----------------------|------------|---------------------|-----------------------|--------------------|
| HF | | | DFT | | | Assignments |
| Y | IR intensity | Raman activity | Y | IR intensity | Raman activity | |
| 496 | 208.49 | 0.00 | 515 | 166.36 | 0.02 | δ H-Be-Cl |
| 739 | 103.68 | 7.96 | 787 | 87.10 | 12.88 | ν Be-Cl |
| 2007 | 203.60 | 117.78 | 2118 | 159.28 | 116.49 | ν Be-H |

| H-Be-Br | | | | | | |
|----------------|---------------------|-----------------------|------------|---------------------|-----------------------|--------------------|
| HF | | | DFT | | | Assignments |
| Y | IR intensity | Raman activity | Y | IR intensity | Raman activity | |
| 475 | 195.04 | 0.02 | 492 | 157.27 | 0.13 | δ H-Be-Br |
| 627 | 86.77 | 8.19 | 671 | 70.74 | 14.41 | ν Be-Br |
| 2005 | 216.82 | 123.19 | 2115 | 170.96 | 123.03 | ν Be-H |

Cont...

| H-Mg-F | | | | | | |
|---------------|---------------------|-----------------------|------------|---------------------|-----------------------|--------------------|
| HF | | | DFT | | | Assignments |
| Y | IR intensity | Raman activity | Y | IR intensity | Raman activity | |
| 302 | 404.81 | 2.40 | 303 | 305.51 | 5.05 | δ H-Mg-F |
| 686 | 66.27 | 1.87 | 707 | 50.23 | 4.54 | ν Mg-F |
| 1523 | 171.48 | 159.47 | 1604 | 120.14 | 192.76 | ν Mg-H |

| H-Mg-Cl | | | | | | |
|----------------|---------------------|-----------------------|-------------------------|---------------------|-----------------------|--------------------|
| HF | | | DFT | | | Assignments |
| Y | IR intensity | Raman activity | ν | IR intensity | Raman activity | |
| 292 | 332.97 | 1.83 | 300 | 251.52 | 3.97 | δ H-Mg-Cl |
| 433 | 61.91 | 5.98 | 453 | 53.80 | 11.77 | ν Mg-Cl |
| 1533 | 206.83 | 201.88 | 1610 | 156.11 | 256.20 | ν Mg-H |

| H-Mg-Br | | | | | | |
|----------------|---------------------|-----------------------|-------------------------|---------------------|-----------------------|--------------------|
| HF | | | DFT | | | Assignments |
| Y | IR intensity | Raman activity | ν | IR intensity | Raman activity | |
| 286 | 320.00 | 4.09 | 294 | 241.59 | 6.43 | δ H-Mg-Br |
| 350 | 47.59 | 5.95 | 366 | 40.22 | 12.12 | ν Mg-Br |
| 1520 | 231.35 | 195.86 | 1599 | 182.62 | 266.04 | ν Mg-H |

Cont...

| H-Ca-F | | | | | | |
|---------------|---------------------|-----------------------|-------------------------|---------------------|-----------------------|--------------------|
| HF | | | DFT | | | Assignments |
| Y | IR intensity | Raman activity | ν | IR intensity | Raman activity | |
| -74 | 621.36 | 3.23 | -179 | 550.22 | 7.84 | δ H-Ca-F |
| 525 | 142.83 | 0.83 | 568 | 136.38 | 4.24 | ν Ca-F |
| 1148 | 357.77 | 152.77 | 1206 | 284.71 | 303.28 | ν Ca-H |

| H-Ca-Cl | | | | | | |
|----------------|---------------------|-----------------------|-------------------------|---------------------|-----------------------|--------------------|
| HF | | | DFT | | | Assignments |
| Y | IR intensity | Raman activity | ν | IR intensity | Raman activity | |
| 120 | 550.79 | 4.59 | -81 | 490.87 | 8.07 | δ H-Ca-Cl |
| 307 | 81.29 | 0.97 | 330 | 89.17 | 3.25 | ν Ca-Cl |
| 1195 | 451.17 | 151.09 | 1265 | 448.75 | 256.57 | ν Ca-H |

| H-Ca-Br | | | | | | |
|-------------------------|---------------------|-----------------------|-------------------------|---------------------|-----------------------|--------------------|
| HF | | | DFT | | | Assignments |
| ν | IR intensity | Raman activity | ν | IR intensity | Raman activity | |
| 110 | 534.22 | 11.78 | -86 | 464.59 | 18.42 | δ H-Ca-Br |
| 243 | 50.37 | 1.61 | 263 | 53.89 | 4.51 | ν Ca-Br |
| 1214 | 481.33 | 170.10 | 1279 | 477.80 | 286.07 | ν Ca-H |

Cont...

Table 3: Thermodynamic parameters

| H-Be –Halogen | | | | | | |
|----------------------|----------------|------------|---------------|------------|----------------|------------|
| | H-Be-Cl | | H-Be-F | | H-Be-Br | |
| | HF | DFT | Hf | DFT | DFT | DFT |
| E | 7.745 | 7.629 | 8.347 | 8.165 | 7.539 | 7.428 |
| Cv | 7.835 | 7.935 | 7.336 | 7.473 | 8.156 | 8.256 |
| S | 52.379 | 52.449 | 49.570 | 49.702 | 55.179 | 55.252 |
| H-Ca-Halogen | | | | | | |
| | H-Ca-Cl | | H-Ca-F | | H-Ca-Br | |
| | HF | DFT | HF | DFT | HF | DFT |
| E | 5.348 | 4.091 | 4.272 | 4.232 | 5.325 | 4.065 |
| Cv | 10.525 | 6.698 | 6.180 | 6.191 | 10.673 | 6.825 |
| S | 62.536 | 56.710 | 53.762 | 53.704 | 65.516 | 59.362 |
| H-Mg-Halogen | | | | | | |
| | H-Mg-Cl | | H-Mg-F | | H-Mg-Br | |
| | HF | DFT | HF | DFT | HF | DFT |
| E | 6.199 | 6.105 | 6.510 | 6.388 | 6.088 | 6.004 |
| Cv | 9.529 | 9.624 | 8.909 | 9.060 | 9.759 | 9.846 |
| S | 57.061 | 57.255 | 54.158 | 54.450 | 59.826 | 60.021 |

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