A computational study of novel MF₃H₂ and MF₃H₂···Y clusters (M = Li; Y = OH$_2$, OH(CH$_3$), O(CH$_3$)$_2$, NCH and NH$_3$) or (M = Na, K; Y = NCH)

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ABSTRACT

Energetically stable clusters MF$_3$H$_2$ (M = Li, Na, K) were predicted at the MP2/6-311++G(d,p) level of theory, with the stability increasing with the size of the metal atom M. These species are dominated by strong electrostatic interactions resulting from a combination of H-bonding and M–F bonding. These clusters are further stabilized by complexation to bases like OH$_2$, OH(CH$_3$), O(CH$_3$)$_2$, NCH and NH$_3$. The atomic charge distributions, electron density and negative Laplacian of the electron density were found to be useful parameters in rationalizing the structural, spectroscopic and bonding characteristics of these novel species.

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1. Introduction

Quantum chemistry is now routinely used to provide valuable physical insight into chemical problems dealing with structure and reactivity due mainly to the widespread availability of powerful computers and the development of more efficient and accurate theoretical methods. Quantum chemical approaches are not only interpretive but they also allow for the prediction of new compounds which may be amenable to experimental synthesis. Two interesting articles that provide an overview of what is possible with regards to the quantum mechanical prediction of novel inorganic species are in Refs. [1,2].

In this paper we explore the computationally predicted stability and properties of a number of novel alkali metal clusters, which may be represented by the chemical formula MF$_3$H$_2$ (M = Li, Na, K), and complexes formed by these clusters with some electron-donating compounds such as OH$_2$, OH(CH$_3$), O(CH$_3$)$_2$, NCH and NH$_3$. The LiF$_3$H$_2$ cluster was considered as the prototypical metal cluster and the full range of properties of interest, as well as properties for its complexes with all five electron-donating bonding partners, were computed. These metal clusters were found to be cyclic and may be considered as being comprised of MF and HF molecular subunits bound together mainly by strong electrostatic forces which arise from a combination of the large partial charges on the atomic centers.

Within this framework, the cyclic LiF$_3$H$_2$ cluster can be denoted as HF···LiF···HF, with the terminal H and F atoms closing the ring (see Fig. 1 for the cyclic geometry). Consequently, the structure, bonding and spectroscopic characteristics of this cluster (and the other clusters and complexes) are considered in this work as resulting from a combination of H- and Li-bonding to the F atoms interspersed within the molecule. The other MF$_3$H$_2$ species are treated in a similar fashion.

Hydrogen bonding is a well-known and extensively studied non-covalent interaction involving the interaction between a proton donor (X–H) and a proton acceptor Y, denoted as X–H···Y, where Y contains an electron rich site [3,4]. X and Y in most complexes is usually an electronegative atom like O or F (as is the case in the present work). Hydrogen bonding is usually dominated by an electrostatic interaction between the proton donor, which is attracted to the region of high electron density on the proton acceptor [3,4]. However, intermolecular charge transfer delocalization or the extent of covalency can be significant and becomes increasingly important depending on the nature of the interacting molecules and the strength of the H-bonded interaction [5–7].

Hydrogen-bond formation usually has well-defined characteristics, including a drop in the X–H vibrational stretching frequency (a red shift) and an increase in its infrared intensity, as well as an extension of the X–H bond from its equilibrium disposition [3,4]. There are also many known instances of H-bonding where the opposite of these features are observed; i.e. an increase in the X–H vibrational stretching frequency (a blue shift) and a decrease of its infrared intensity, accompanied by contraction of the X–H bond [8–10]. This non-conventional H-bonding has been called
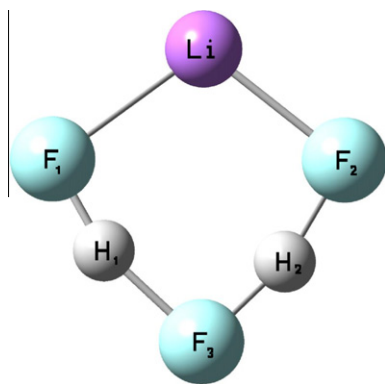
Fig. 1. Optimized structure of LiF_3H_2.

"blue-shifting", in contrast to the normal red-shifting H-bonding, by some authors [8].

Lithium bonding, denoted as X–Li···Y, is a much less well-studied non-covalent interaction that bears many similarities with hydrogen bonding, including the red-shifting and blue-shifting characteristics noted above, in relation to the influence of the Y molecule on the X–Li bond. It was theoretically predicted by Kollman et al. [11] and confirmed by Ault and Pimentel [12]. The Li-bond, due to its highly polar nature and large dipole moment, would be expected to be a relatively strong non-covalent interaction, as well as the other X–M···Y interactions. As we shall see later, this is consistent with the large binding energies computed for the optimized structures of the MF_3H_2 clusters and their complexes.

We note a previous study of H-bonding in $LiHF_2$, $NaHF_2$ and KHF_2 molecules [13], where similar cyclic geometries were predicted from CCSD/6-311++G(d,p) calculations and in which the authors state that the H-bonding in these complexes is covalent in character. The present work predicts larger and substantially more stable cyclic clusters and as far as we are aware no previous theoretical studies have been reported in the literature.

2. Computational methodology

The calculations were performed using the Gaussian 03 suite of programs, at the MP2/6-311++G(d,p) level of theory [14]. The MF_3H_2 clusters and their complexes were optimized to minima on their respective potential energy surfaces, which was confirmed through inspection of the harmonic vibrational frequencies which showed that there were no imaginary frequencies.

Table 1 shows selected geometrical parameters (bondlengths and bond angles) for the LiF_3H_2 cluster and the LiF_3H_2···Y complexes (Y = OH_2, $OH(CH_3)$, $O(CH_3)_2$, NCH, NH_3). The interaction energy (ΔE), dipole moment (μ) and change in dipole moment on complexation ($\Delta \mu$), as well as the harmonic vibrational frequency and frequency shift of the FH stretching mode for the molecular subunit labeled F_1H_1 in the LiF_3H_2 cluster, are in Table 1; refer to Fig. 1 for the geometry and labeling of this cluster. The enhancement of the infrared intensity of the F_1H_1 stretch in the LiF_3H_2 clusters (relative to the isolated FH monomer) was computed as a ratio and is displayed in Table 1.

The partial atomic charges in these clusters were computed using the natural bond orbital (NBO) method [15] and is useful

Table 1

Selected properties of LiF_3H_2 and LiF_3H_2···Y (Y = OH_2, $OH(CH_3)$, $O(CH_3)_2$, NH_3, NCH) clusters computed at MP2/6-311++G(d,p), with the O or N atom of the Y subunit bonded directly to the Li atom. Refer to Fig. 1 for the structure of a typical cluster. The interaction energy ΔE refers to the energy of the LiF_3H_2···Y cluster with respect to the energy of the LiF + 2HF + Y fragments. The F_1H_1 harmonic stretching frequency (ω_1) in the LiF_3H_2 clusters, its frequency shift relative to the isolated FH molecule ($\Delta\omega_1$) and the ratio of the IR intensity of ω_1 in the complex and in the isolated monomer (I^{compl}/I^{mon}) are shown. Bond lengths (R) are in Angstrom, angles in degrees, interaction energies in kJ/mol, dipole moments (μ, $\Delta\mu$) in debye, and frequencies in cm^{-1}.

Property	LiF_3H_2	LiF_3H_2···OH_2	LiF_3H_2···$OH(CH_3)$	LiF_3H_2···$O(CH_3)_2$	LiF_3H_2···NCH	LiF_3H_2···NH_3
$R(Li–F_1)$	1.8203	1.8232	1.8390	1.8252	1.8149	1.8215
$R(Li–F_2)$	1.7501	1.8148	1.8020	1.8106	1.8147	1.8212
$R(F_1–H_1)$	1.0232	1.0436	1.0253	1.0420	1.0598	1.0619
$R(F_2–H_2)$	1.1467	1.0834	1.1098	1.0834	1.0603	1.0568
$R(H_1–F_3)$	1.3013	1.2568	1.2927	1.2596	1.2277	1.2241
$R(H_2–F_3)$	1.1245	1.1935	1.1601	1.1939	1.2271	1.2322
$R(Li–Y)$		1.9234	1.9070	1.8982	2.0549	2.0516
<Y–Li–F_1		151.2	144.6	139.2	128.6	125.8
<F_1–Li–F_2	105.8	103.9	103.6	104.2	102.7	102.9
ΔE	−189.9	−272.8	−280.2	−281.1	−258.5	−285.0
μ	4.909	7.654	7.712	7.821	9.623	8.029
$\Delta\mu$		0.558	0.872	1.414	1.713	1.385
ω_1	2384.2	2206.7	2357.1	2216.4	2168.4	2174.8
$\Delta\omega_1$	−1813	−1990	−1840	−1981	−2029	−2022
I^{compl}/I^{mon}	18.3	21.6	19.6	22.9	24.2	23.5

The $F_1–H_1–F_3$ and $F_2–H_2–F_3$ angles lie between 162° and 165°, and the $H_1–F_3–H_2$ angles lie between 92° and 93° for all complexes.

Table 2

NBO atomic charges (q) for LiF_3H_2 and LiF_3H_2···Y (Y = OH_2, $OH(CH_3)$, $O(CH_3)_2$, NH_3, NCH) clusters computed at MP2/6-311++G(d,p). Refer to Fig. 1 for the structure of a typical cluster. The electron density transfer (EDT in e) from Y to the LiF_3H_2 subunit is also shown. The changes in the atomic charges of LiF_3H_2 on complexation to Y are shown in brackets.

Property	LiF_3H_2	LiF_3H_2···OH_2	LiF_3H_2···$OH(CH_3)$	LiF_3H_2···$O(CH_3)_2$	LiF_3H_2···NCH	LiF_3H_2···NH_3
$q(Li)$	0.961	0.931 (−0.030)	0.926 (−0.035)	0.918 (−0.043)	0.921 (−0.040)	0.912 (−0.049)
$q(F_1)$	−0.674	−0.680 (−0.006)	−0.667 (0.007)	−0.678 (−0.004)	−0.691 (−0.017)	−0.691 (−0.017)
$q(F_2)$	−0.751	−0.709 (0.042)	−0.724 (0.027)	−0.706 (0.045)	−0.690 (0.061)	−0.687 (0.064)
$q(H_1)$	0.545	0.538 (−0.007)	0.542 (−0.003)	0.538 (−0.007)	0.535 (−0.010)	0.535 (−0.010)
$q(H_2)$	0.531	0.533 (0.002)	0.531 (0.000)	0.533 (0.002)	0.535 (0.004)	0.535 (0.004)
$q(F_3)$	−0.612	−0.631 (−0.019)	−0.629 (−0.017)	−0.632 (−0.020)	−0.634 (−0.022)	−0.635 (−0.023)
EDT		0.017	0.022	0.027	0.024	0.031