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Anharmonic calculation of structural and vibrational properties of the isolated complexes $[F(HF)_2]^-$, $[F(DF)_2]^-$, and $[F(TF)_2]^-$

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ABSTRACT

The electronic structure of the isolated $[F(HF)_2]^-$ complex is calculated at the MP2/6-311++G(3df,3pd) level with the correction for the basis set superposition error taken into account. The equilibrium geometry of the complex is determined. Based on the four-dimensional (4D) potential energy and dipole moment surfaces calculated at this level of theory in the space of four variables describing the changes in the hydrogen bond lengths and the bond lengths of molecular subunits, the 4D anharmonic vibrational problem is solved by the variational method for the $[F(LF)_2]^-$ (L = H, D, T) complexes. The vibrational energy levels, the transition frequencies and absolute intensities are determined for the three isotopomers. The conventional assignment of infrared absorption bands associated with the intramolecular stretches is improved. The isotope effect on the geometrical parameters of the $[F(HF)_2]^-$ anion is studied by calculating the vibrationally averaged values of internuclear separations, their rms deviations, and the standard deviation of the H-bond asymmetry parameter for a number of vibrational states of the isotopomers. The vibrationally averaged values of the dipole moment are also computed.

1. Introduction

The difluorohydrogenate anion $[F(HF)_2]^-$ belongs to the strongest hydrogen bonded systems. Along with other related anions $[F(HF)_n]^-$, the $[F(HF)_2]^-$ anion was the object of extensive experimental and theoretical studies motivated, in particular, by strongly pronounced manifestations of hydrogen bonding in this compound. These studies are considerably hampered by the fact that this complex is observed not in the gas phase, but in crystalline compounds or multicomponent solutions. The geometric structure of the $[F(HF)_2]^-$ anion was studied by the X-ray and neutron diffraction methods. It was found [1,2] that the anion has C_{2v} symmetry with the FFF angle of about 135° and the F...F bond length of 2.33 Å. This complex was studied by the methods of infrared absorption and Raman spectroscopy; however, the studies are not numerous, mostly performed at low resolution, and the assignment is frequently tentative or controversial. The infrared spectra of $[F(HF)_2]^-$ and $[F(DF)_2]^-$ in the region of 450–2500 cm^{-1} were recorded in solid KH_2F_3 and KD_2F_3 [3], and the spectra of $[F(HF)_2]^-$ in the region of 350–2700 cm^{-1} at temperatures of 12 and 300 K were recorded in crystals and solutions containing potassium cations [4] and a number of complicated amines [5,6]. The bands at 455–480 cm^{-1} were assigned to the F...F stretching modes, the bands at 1020–1150 cm^{-1} were attributed to F–H–F bending modes. The strongest featureless band at 1800 cm^{-1} was assigned to both F–H stretches in [4,5] and to the symmetric H–F stretch in [6]. FTIR spectra of the isolated $[F(HF)_2]^-$, $[FHFDF]^-$, and $[F(DF)_2]^-$ anions were recorded in solid argon and neon matrices at 12 K [7]. Bands at 1815 cm^{-1} in Ar and at 1836 cm^{-1} in Ne were attributed to the antisymmetric H–F stretch. The authors inferred that the weak symmetric H–F stretching band should lie at 1600 cm^{-1}.

Properties of the hydrogen fluoride anions $[F(HF)_n]^-$ were also studied by the methods of NMR spectroscopy. The comprehensive review [8] presents a detailed discussion of many aspects of using the NMR technique to study the isotope effects in hydrogen bonded systems. Liquid state NMR experiments at $T = 110–150$ K were carried out on mixtures of tetrabutylammonium fluoride with HF dissolved in freons [9]. In this study the high resolution NMR spectra of hydrogen bonded species in slow proton and hydrogen bond exchange regime were recorded. All hydrogen and fluorine chemical shifts were determined for $[F(HF)_n]^-$ with $n = 1–4$, as well as the one-bond and two-bond spin–spin coupling constants. The H/D isotope effects on the NMR parameters were studied in analogous experiments on partially and fully deuterated anions [10]. The use of model equations relating the valence bond orders, internuclear distances, and the two-bond coupling constants allowed the authors to improve the effective values of internuclear separations and to examine the correlation between geometrical and NMR parameters. Many correlations between the experimentally observed changes in the NMR parameters and the internuclear distances have been reproduced theoretically.

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However, there are some discrepancies. Possible inaccuracies introduced by the assumptions underlying the model equations are discussed by the authors.

A number of papers was devoted to the quantum-mechanical calculation of the electronic structure, vibrational properties and NMR characteristics of the $[F(HF)_n]^-$ anions. Of these systems the triatomic $[FHF]^-$ anion has been most thoroughly studied by the theoretical methods. Detailed list of references may be found in the recent paper [11] devoted to solution of the anharmonic two-dimensional (2D) vibrational problem in the space of internuclear separations. This calculation based on the high-precision potential energy surface yielded reliable information on the energy levels, transition frequencies and relative intensities, and the changes in the bond lengths on isotopic substitution. Calculations of the larger complexes are not numerous. They were performed at lower levels of theory, and the vibrational properties were studied, as a rule, in the harmonic approximation. Some studies aimed to reveal the general trends across the sequence of related compounds, they considered the $[F(HF)_2]^-$ anion among other more complicated systems [12]. In [13] thermodynamic calculations on the $[F(HF)_n]^-$ anions and other cationic and neutral species were carried out by the semiempirical methods and by ab initio methods at moderate levels of theory. The 3D anharmonic vibrational problem for the $[F(HF)_2]^-$ complex was solved by the variational method with the FFF angle and two H-bond distances considered explicitly [14]. This study predicted the frequencies of H-bond stretching and bending vibrations in agreement with the experimental findings. The Car–Parinello molecular dynamics study [15] of the structure and dynamical behaviour of a mixture of solvated potassium cations and polyfluoride anions suggested that the vibrational band of $[F(HF)_2]^-$ observed near 1800 cm^{-1} in experiments [3–6] should be attributed to the antisymmetric H–F stretch and a band near 2400 cm^{-1} to the symmetric H–F stretch. This conclusion was made on the basis of analysis of the average cross correlation of the velocity of the hydrogen atoms.

It is obvious that the anharmonicity effects should be taken into account in calculations of polyatomic compounds to obtain correct values of vibrational absorption characteristics and the NMR parameters. This problem was addressed in many publications. We will mention here only a few papers dealing with the anharmonicity and isotope effects in hydrogen bonded systems. Various aspects of the vibrational isotope effects in hydrogen bonds were thoroughly analyzed in the review [16]. In particular, the effects caused by anharmonicity of potential curves, the presence of large-amplitude bending vibrations, and the tunneling through the potential barrier were considered. The importance of inclusion of the anharmonic coupling between the proton stretching vibration and the H-bond stretch was investigated in [17] for the systems with traditional and proton-shared hydrogen bonds for the example of the complexes $FH:NH_3$, $ClH:NH_3$, and $BrH:NH_3$. The anharmonic calculations of the stretching modes of the bihalide anions XHX^- (X = F, Cl, Br) were performed on 2D potential surfaces computed at different ab initio levels of theory [18]. The anharmonic frequency values thus obtained are close to the experimental results with the antisymmetric modes being most sensitive to the level of theory. The correlation between the vibrational spectroscopic and NMR properties of hydrogen bonded systems was considered for the example of $ClH:NH_3$ complex [19]. The relationships between the X...Y distance in an X...H–Y hydrogen bond, the anharmonic proton stretching frequency, the hydrogen NMR chemical shift, and the X...Y spin–spin coupling constant were investigated. The relative values of different contributions to the $^2J_{ClN}$ coupling constant were analyzed. The vibrational effects on $^2J_{FF}$ were considered at the high level of theory for the FHF^- and FDF^- anions [20]. The strong decrease in the coupling constant due to averaging over the ground vibrational state was found from solution of 2D anharmonic problem with a high-precision potential energy surface. Among other interesting results the considerable cancellation of the changes in different contributions to the spin–spin coupling constant with variation in the internuclear separations was obtained. This cancellation effect explains the small change in the total coupling constant upon excitation of the symmetric mode. The results of these and other studies were summarized in the review [21].

The above calculations of anharmonic vibrational problems were carried out, as a rule, in the 2D approximation. Solution of such problems in more than two dimensions encounters significant computational difficulties. At present such studies are infrequent. As an example, we may note two state-of-the-art calculations of this type, namely, the 4D calculation of the O...H...O fragment of $H_5O_2^+$ by the ab initio molecular dynamics technique [22] and the rigorous full-dimensional quantum dynamics calculation of the vibrational energies of $H_3O_2^-$ [23]. As far as we know, multidimensional quantum-mechanical calculations on the $[F(HF)_2]^-$ anion have not yet been reported.

The purpose of this paper is to study the structure of the isolated $[F(LF)_2]^-$ (L = H, D, T) anions at a sufficiently high level of theory, to calculate the frequencies and absolute intensities of transitions between the vibrational states in an anharmonic approximation, and to analyze the isotope effects on the spectroscopic and geometrical parameters. Analysis of these effects requires the simultaneous consideration of two low-frequency H-bond stretching vibrations and two high-frequency stretches of hydrogen fluoride molecules in a complex. Thus, it is necessary to solve at least a 4D anharmonic vibrational problem for each of the isotopomers. To our knowledge, there are no experimental data on the $[F(TF)_2]^-$ anion; nonetheless, we consider this system as well to study the internal dynamics of the complexes in question in more detail.

2. Method of electronic structure calculations

The electronic structure calculations of the $[F(HF)_2]^-$ complex were carried out using the GAUSSIAN 03 package of codes [24]. The equilibrium geometry and the potential energy and dipole moment surfaces were calculated at the MP2/6-311++G(3df,3pd) level of theory. The basis set comprises 153 atomic functions constructed from 216 primitive Gaussians. This approximation was chosen as a compromise between the desirable accuracy and the amount of computer time required to perform calculations for a large number of points in the space of vibrational coordinates. The equilibrium nuclear configuration of the complex is characterized by the following calculated values: $r(H–F) = 0.9955$ Å, $R(F...H) = 1.3704$ Å, $R(F...F) = 2.3659$ Å, and the FFF angle $\vartheta = 130.0^o$. These values are in good agreement with the most accurate results obtained in previous calculations: $r(H–F) = 0.997$ Å, $R(F...H) = 1.350$ Å, and $\vartheta = 134.2^o$ in the MP2/6-311+G** calculation [13], and $r(H–F) = 1.0037$ Å, $R(F...H) = 1.3705$ Å, and $\vartheta = 128.8^o$ in the CCSD(T)/aug-cc-pVDZ calculation [25]. The minimum electronic energy of the complex is −300.510161 au. With values of −100.332820 and −99.732134 au calculated, respectively, for the energies of a free HF molecule and an F^- anion in the same approximation, we obtain a value of 295.1 kJ/mol for the binding energy per hydrogen bond, which is in agreement with a value of 284.4 kJ/mol found in the ab initio molecular dynamics simulation [26]. For the equilibrium geometry of $[F(HF)_2]^-$, the Mulliken atomic charges are 0.6743 (H atom), −0.9358 (central F), and −0.7064 (terminal F).

To examine the influence of the limited size of the basis set on the predicted properties of interest to us, we also solved the 2D problem of H–F stretching vibrations with fixed lengths of the