Molecular structure and infrared spectra of (HXeCN)$_n$ (n = 2, 3 or 4)

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ABSTRACT

The structure, energetics, and vibrational spectra of the (HXeCN)$_2$ dimer were investigated at the CCSD(T), MP2 and B3LYP levels. Such properties of the (HXeCN)$_3$ trimer and (HXeCN)$_4$ tetramer were investigated at the B3LYP level. The dimer, trimer, and tetramer were predicted to have a C_{2h}, C_{2v}, and D_{2d} structure, respectively. In all of these oligomers, the N···Xe intermonomeric interaction is the most important one for holding the monomers together. Included with the ZPVE and BSSE, the stabilization energy of the dimer is 12.36 kcal/mol at the CCSD(T) level, while those of the dimer, trimer, and tetramer are 10.42, 18.23, and 31.34 kcal/mol, respectively, at the B3LYP level. At the B3LYP level, with respect to those of the isolated monomer, the C−Xe and Xe−H asymmetric stretching frequencies are shifted by −11.2 and +128.0 cm^{-1} for the dimer, −51.6, +220.7 and −11.5, +96.6 cm^{-1} for the trimer, and −14.1 and +201.8 cm^{-1} for the tetramer.

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1. Introduction

Noble gas chemistry has developed rapidly since the xenon compounds XePtF$_6$ [1], XeF$_4$ [2], and XeF$_2$ [3] were synthesized. The first HNgY (where Ng is a noble gas atom and Y is an electronegative atom or fragment) species, HXeCl, HXeBr, HXeI, and HKrCl, were prepared and characterized by Pettersson et al. [4]. Shortly, HXeCN and HXeNC were also synthesized [5]. To our knowledge, 25 HNgY species have been synthesized so far [6,7].

One of the interesting and active research fields of the HNgY species is to explore, either theoretically and experimentally together or theoretically alone, the interaction of an HNgY molecule with another small molecule. The example complexes are as follows: HXeH···H$_2$O [8], ClKrH···N$_2$ [9,10], FArH···N$_2$ [10–12], FKrH···N$_2$ [10], FArH···CO [12], FArH···P$_2$ [11], FHeH···N$_2$ [13], FHeH···OC [13], FHeH···He [13], FArH···Ng (Ng = He, Ne, Ar, Kr) [14], FNgH···Y (Ng = He, Ar, and Kr; Y = OC, CO, N$_2$, P$_2$, H$_2$O, NH$_3$) [15], HXeCCH···Ng (Ng = Ar, Kr, and Xe) [16], HXeY···HX (X, Y = Cl, Br) [17], HKrCl···HCl [18], FCCArH···C$_2$H$_2$ [19].

Compared to the wealth documentation of the heterogeneous HNgY dimers, reports on the homogeneous HNgY dimers or oligomers are fairly limited. Cohen and Gerber have explored the dynamics of (HArF)$_2$ dimer on an ab initio potential energy surface and found that the dimer is chemically unstable and decomposes spontaneously into two HF molecules and two Ar atoms [20]. Lundell et al. [21] have investigated the structure, energetics, and vibrational spectra of the (HXeH)$_n$ (n = 2, 3 or 4) oligomers at the MP2/LJ18/6-311++G(2d,2p) level and found that, (i) the HXeH monomers are parallel, rather than bifurcated, to each other in all of the three oligomers, (ii) the intermonomeric interaction is of electrostatic nature, and (iii) for the dimer, the BSSE-corrected interaction energies are −0.97 and −0.58 kcal/mol, respectively, at the MP2 and CCSD(T) levels. Sheng and Gerber [22] have investigated the (HXeCCH)$_2$ dimer at the MP2(full)/LJ18/6-311++G(2d,2p) level, the (HXeCCH)$_4$ tetramer at the MP2(full)/LJ18/6-31G(d,p) level, and the crystal structure of HXeCCH at the BLYP/LJ18/6-31G(d,p) level with periodic boundary conditions and found that, (i) the dimer has a C_i symmetry, the tetramer has a D_{2d} symmetry, and the structure of unit cell of the crystal is similar to that of the tetramer, (ii) the HXeCCH monomers of the dimer and tetramer become bent, as compared to the linear isolated monomer, and (iii) at the MP2 level, the interaction energies of the dimer and tetramer are −6.66 and −19.40 kcal/mol, respectively.

In this paper, we will explore the stability, molecular structure, and infrared spectra of the homogeneous dimer, trimer, and tetramer of the HXeCN molecule.

2. Computational details

Quantum chemical calculations were performed with the Gaussian 03 programs [23]. The HXeCN dimer was investigated at the CCSD(T), MP2(FC), and B3LYP levels of theory while the trimer and tetramer were investigated at the B3LYP level. The CCSD(T) method requests a coupled cluster calculations using single, double, and perturbative triple excitations from the Hartree–Fock determinant [24–26]. MP2(FC) requests a Hartree–Fock calculation followed by

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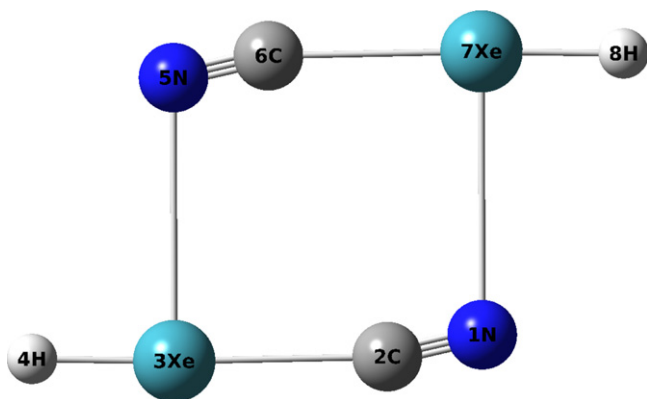E-mail address: flyskyliugq@126.com (G. Liu).

Fig. 1. Structure of the $(HXeCN)_2$ dimer optimized at the B3LYP level.

Møller–Plesset correlation energy correction truncated at second order [27–29] and requests the inner shells excluded from the correlation calculation. The B3LYP method is Becke's three parameter hybrid functional [30] in conjunction with Lee, Yang, and Parr's correlation functional [31]. For the CCSD(T) calculations, the 6-311++G(2d,2p) basis set [32] was used for N, C, and H atoms. For the MP2(FC) and B3LYP calculations, the 6-311++G(3df,3pd) [32] basis set was used for these three atoms. For all of the calculations, the Stuttgart/Dresden ECP MWB46 and the GTO valence basis set (6s6p3d1f)/[4s4p3d1f] [33] were always applied to Xe atom. This ECP and basis set has been applied to Xe atom for the theoretical investigations of the compounds CH_3NgF [34] and RXeXeR′ [35]. The Natural Bond Orbital (NBO) theory [36] was used to analyze the charge distributions of the HXeCN dimer, trimer, and tetramer. The optimized stationary points were confirmed to be true minima rather than transition states or higher-order saddle points by followed harmonic frequency calculations. The interaction energies of the three oligomers were corrected for the basis set superposition error (BSSE) with the counterpoise method [37,38].

3. Results and discussions

As shown in Fig. 1, at the B3LYP level of theory, the $(HXeCN)_2$ dimer was optimized to an energy minimum with planar C_{2h} symmetry. Such C_{2h} structure was confirmed stable at the MP2 and CCSD(T) levels. Note that the CCSD(T)-optimized planar C_s geometry deviates only very slightly from the C_{2h} symmetry. For the B3LYP-, MP2, and CCSD(T)-optimized structures of the dimer, the T1 diagnostics of Lee and coworkers [39] were computed as 0.0178, 0.0174, and 0.0186, respectively, which are less than 0.02 and assure the validity of single-determinant wave functions.

For comparisons with $(HXeCN)_2$, the $(HXeNC)_2$ dimer was also optimized at the MP2 level of theory with the 6-311++G(2d,2p) basis set for the H, C, and N atoms. During the optimization processes, the $(HXeNC)_2$ dimer decomposes gradually into two HCN molecules and two Xe atoms. Note that the HXeCN monomer is lower in energy than the HXeNC monomer by 7.34 and 6.86 kcal/mol, respectively, at the MP2/LJ18 and MP2/R18 levels [5].

Equilibrium structures of the $(HXeCN)_3$ trimer and $(HXeCN)_4$ tetramer, optimized at the B3LYP level of theory, are presented in Figs. 2 and 3, respectively. As shown in Figs. 2 and 3, the trimer has a planar C_{2v} structure while the tetramer has a D_{2d} structure. The T1 diagnostics of these two B3LYP-optimized structures are 0.0176 and 0.0173, respectively, which are also less than 0.02. The geometrical parameters, more relevant vibrational frequencies and intensities, and NBO charges of the dimer, trimer, and tetramer, along with their variations with respect to those of the isolated
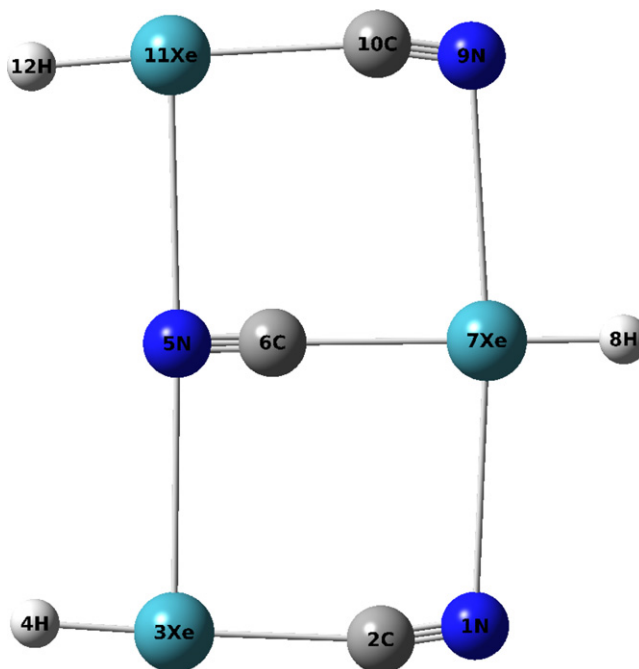

Fig. 2. Structure of the $(HXeCN)_3$ trimer optimized at the B3LYP level.

monomer, are presented in Table 1. These parameters of the HXeCN monomer are presented in Table 2.

As shown in Fig. 1, in the $(HXeCN)_2$ dimer, the two HXeC fragments are nearly parallel, which is similar to the arrangement of the $(HXeCCH)_2$ dimer [22]. However, the two terminal CH fragments are being distant from each other in the latter dimer (Fig. 1 of Ref. [22]) while the two terminal N atoms are approaching to each other in the former dimer (Fig. 1). On the other hand, in the latter dimer, the Xe-bonded C atom of one monomer has the shortest distance from the Xe atom of the other monomer [22]. In the former dimer, the N, rather than the Xe-bonded C, atom of one monomer has the shortest distance from the Xe atom of the other one.

Why do such structural differences appear? Lundell have pointed out that, for the $(HXeH)_2$ dimer, the interaction between molecular subunits is of electrostatic nature [21]. This should also be the case for the $(HXeCCH)_2$ and $(HXeCN)_2$ dimers. In the isolated HXeCCH monomer, the Xe atom carries the largest NBO positive charges (+0.77), the Xe-bonded C atom carries the largest NBO neg-
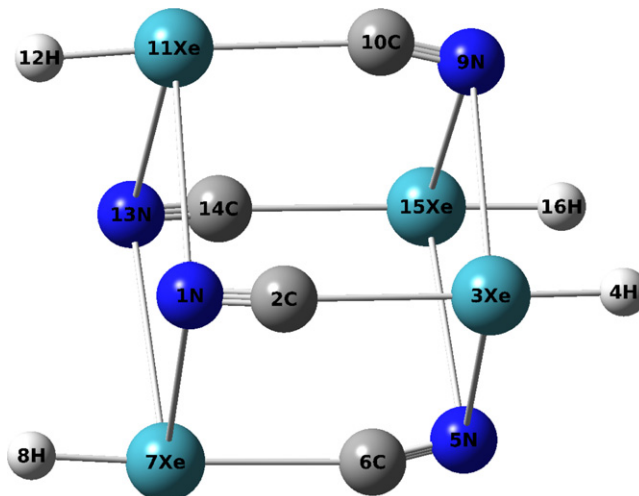

Fig. 3. Structure of the $(HXeCN)_4$ tetramer optimized at the B3LYP level.