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Equilibrium structure and energetics of CHNO isomers: Steps towards ab initio rovibrational spectra of quasi-linear molecules

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Abstract

We report large-scale electronic structure calculations for fulminic acid, HCNO, isocyanic acid, HNCO, and cyanic acid, HOCN, in their ground electronic states. The coupled cluster CCSD(T) method including all single and double excitations and a perturbative term for connected triple substitutions is used in conjunction with large correlation consistent polarized valence basis sets of the form cc-pVXZ ($X = 2$–6) and cc-pCVXZ ($X = 2$–5). Our results show the importance of including all electrons in the correlation treatment to obtain a converged molecular structure for the extremely floppy HCNO molecule and the correct energetics of the three isomers. All-electron correlation calculations and frozen core calculations with very large basis sets clearly converge towards a linear electronic minimum for HCNO surrounded by a very large flat region of the potential energy surface for hydrogen bending motions. For each of the three isomers we have computed the barrier to linearity along the respective minimum energy path and several spectroscopic parameters and equilibrium rotational constants.

Keywords: Ab initio calculation; CHNO; Equilibrium structure; Quasi-linear molecules; Potential energy surface

1. Introduction

Molecules with a nonlinear electronic minimum but a low barrier to linearity allowing a large amplitude bending motion may exhibit rovibrational spectra with level patterns reminiscent of molecules with a rigid linear skeleton and are usually referred to as quasi-linear molecules [1–3]. The large amplitude bend contributes a vibrational angular momentum which couples with the overall rotational angular momentum. Furthermore, the bending motion is frequently coupled with the high-frequency stretch modes. The combination of these features leads to particularly complicated rovibrational spectra, exhibiting many fascinating features, such as Fermi and *l*-type resonances, Coriolis coupling, and large centrifugal distortion.

Fulminic acid, HCNO, is one of the most important representatives of this class of molecules and has been subjected to extensive previous experimental [2,4–9] and theoretical [10–16] analyses. Winnewisser et al. [4] were the first to propose in 1971 a quasi-linear molecular model for the fulminic acid molecule. An unreasonably short r_s(HC) distance of 1.0266 Å was initially derived from the microwave data within a linear molecule model for HCNO [4]. A deviation from Bernstein's rule [17] for CH stretching fundamentals motivated Winnewisser et al. to suggest a nonlinear equilibrium structure, possessing an HCN angle of ca. 162°. The classification of quasi-linear molecules proposed in Ref. [6] places HCNO rather close to the linear molecule limit. A semirigid bender study of Bunker et al. [10] led to the conclusion that HCNO has a linear equilibrium structure and bent vibrationally averaged structures. A small barrier to linearity of 11.5 cm^{-1} was determined

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for the effective ground-state potential energy profile along the HCN angle. Such a structure was actually called quasi-bent in Ref. [10].

The electronic structure problem of HCNO has turned out to be particularly hard, leading to strongly basis set and correlation method dependent results, such that the equilibrium geometry and the size of the barrier to linearity, if there is any, are still unclear. Whereas MP2, MP4, and MCSCF calculations favour a nonlinear structure, a linear equilibrium was found at the SCF, MP3, CISD, and CCSD levels of theory [11,14], and also with CCSD(T)/TZ2P [12]. Koput et al. [14] deduced a small barrier to linearity of 7 cm^{-1} by means of CCSD(T)/cc-pVQZ. Several ab initio studies have additionally reported harmonic vibrational frequencies and/or energetics for the system [H,C,N,O] [13,15,16,18]. So far, there is, however, only a single study providing variational results for rovibrational states of HCNO. In that study, Pinnavaia et al. [13] developed and employed a six-dimensional MP2/DZP potential enery surface, on which the optimized bent HCNO configuration is ca. 330 cm^{-1} more stable than the optimized linear configuration.

High-quality rovibrational calculations are the ultimate means to clarify the characteristic rovibrational spectral patterns by theoretical means. The starting point for such calculations is an accurate potential energy surface (PES), which samples large portions of the available configuration space, covering at least those degrees of freedom which are essential for understanding the internal molecular dynamics. The quasi-linear species HXYZ with a hydrogen atom attached to a (nearly linear) chain of heavy atoms pose a very demanding computational task from both the electronic structure and rovibrational point of view because of the strongly anharmonic large amplitude HXY bending vibration.

With the ultimate goal to develop a full-dimensional potential energy surface for the fulminic acid molecule in its electronic ground state, our initial purpose was to study the equilibrium structure with a high level of accuracy and to identify the best trade-off between accuracy and expense of computer time. However, our calculations beyond the frozen-core approximation showed a prominent contribution of core correlation at the equilibrium internuclear geometry of HCNO. Since this quantity is relevant for the calculation of energetics of the [H,C,N,O] system, we have extended our work to include HNCO and HOCN, too.

Isocyanic acid, HNCO, is the most stable among all CHNO isomers [19]. It is energetically followed by cyanic acid, HOCN, and fulminic acid, HCNO. From the historical point of view, the isomers are important because of the first experimental evidence of isomerism in 1826, when Liebig and Wöhler agreed that HNCO and HCNO possess the same chemical composition, but are structurally distinct [20]. The CHNO isomers (most prominently HNCO) are expected to participate in interstellar chemistry and to play a major role in the RAPRENO$_x$ process for NO reduction in combustion [18,21–23]. HNCO is considered also to be quasi-linear, exhibiting a barrier to linearity of 1899 cm^{-1} according to a semirigid bender analysis of Niedenhoff et al. [24] Whereas both HCNO and HNCO possess very rich rovibrational spectra in the gas phase [2,4–9], HOCN could be studied solely under matrix conditions [20,25] For HNCO and HOCN, Pinnavaia et al. reported only perturbational results [13]. We refer to Refs. [13,14,16] for an overview of the previous experimental and theoretical work on the CHNO isomers.

Energy levels associated with a large amplitude bending vibration may develop a pattern typical for linear molecules, even for a bent equilibrium structure [1,26]. This was found in our recent study [27] on cyanocarbene, HCCN. In spite of a nonlinear equilibrium structure, characterized by $\angle(\mathrm{HCC})_e$ of 147° and $\angle(\mathrm{CCN})_e$ of 175° for a MR-ACPF PES, the rovibrational energy levels of the radical were easily assigned following the conventional linear molecule notation. This phenomenon hinges on the barrier to linearity, determined to be 287 cm^{-1} for HCCN. Numerically exact rovibrational states of HCCN were calculated for $J = 0$–4, using the method described in Ref. [28]. This type of treatment is the next logical step of our HCNO project.

In the present work, extensive ab initio calculations of the electronic ground state with coupled cluster techniques and large basis sets have been performed for each of the three isomers studied. Two families of basis sets were employed to approach the one-particle basis-set limit, including valence and all-electron correlation (Section 2). The geometries of the minima have been optimized via numerical gradient techniques (Section 3.1). The barriers to linearity and isomerization energies have been derived (Section 3.2). The harmonic vibrational frequencies have been computed in order to characterize the stationary points (Section 3.3). The minimum energy paths along the bending angle HXY have been obtained for planar HCNO, HNCO, and HOCN by relaxing the other coordinates (Section 3.3).

2. Electronic structure calculations

The ab initio calculations presented below have been carried out by means of the coupled-cluster method, which explicitly includes all single and double excitations, as well as a noniterative perturbative treatment of connected triple substitutions. Dunning's correlation consistent double ($X = 2$), triple ($X = 3$), quadruple ($X = \mathrm{Q}$), quintuple ($X = 5$), and sextuple ($X = 6$) polarized valence basis sets, commonly termed cc-pVXZ, have been used [29].

Initially only valence electrons were correlated (the frozen-core approximation). Our test calculations for all-electron correlation, however, quickly showed that inclusion of the three 1s-like core orbitals located on carbon, nitrogen, and oxygen into the active space has an important influence on the geometrical parameters of HCNO. We have, thus, decided to study in detail also the correlation consistent