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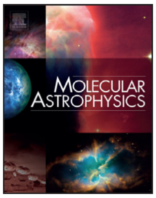

Research Paper

Providing theoretical data for detection of four formamidic acid isomers in astrophysical media

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ABSTRACT

We present a theoretical study, so that molecular data (geometrical parameters, vibrational frequencies, infrared intensities, electronic energies, enthalpies, and Gibbs energies) of four formamidic acid (FA) isomers (labeled here as FA1, FA2, FA3, and FA4) and formamide ($HCONH_2$) are obtained from CCSD/cc-pVTZ, CCSD/aug-cc-pVTZ, CCSD/cc-pVQZ, and CCSD(T)/cc-pVTZ calculations. Furthermore, on the basis of insufficient or even lacking theoretical and experimental results in the literature, we employed the aforementioned theory levels to determine benchmark values of dipole moments and rotational constants for these four FA isomers in order to contribute for their detection in astrophysical environments. Besides, we provide for the first time data about forward and reverse rate constants (200–4000 K) and Arrhenius' parameters for each interconversion reaction between pairs of FA isomers as well as for the tautomeric process involving FA4 and formamide, which were calculated from a Complete Basis Set (CBS) extrapolation equation obtained at CCSD/cc-pVTZ optimized geometries. Our kinetic analysis indicated a faster interconversion between the FA structures in comparison with the FA4 $\leftrightarrow$ $HCONH_2$ process, suggesting that these isomers could co-exist in astrophysical media. Finally, we estimated that these isomers may be detected with relative abundances, $[FA_x]/[HCONH_2]$ ($x = 1$, 2, 3, and 4), between ~0.01 and ~0.1% in astrophysical sources at chemical equilibrium conditions and temperatures around 1000 K. However, these ratios can become as high as ~1, ~3, and ~5%, respectively, in hotter regions with temperatures around 2000, 3000, and 4000 K (expected, for example, in massive star-forming regions).

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1. Introduction

Formamide, $HCONH_2$, is a molecule widely studied, what is mainly explained because this compound is considered a precursor for more complex molecular structures of biological interest, such as amino acids and proteins (Coutens et al., 2016; Nguyen et al., 2013). In regarding to astrophysical media, $HCONH_2$ has been observed in surveys of SgrB2(OH), SgrB2(N), Orion-KL, NGC 7538, W3(H_2O), W3(OH), W51M, M17 SW, G34.3, and DR21(OH), as well as on the Hale–Bopp comet (Adande et al., 2013). These last authors have observed formamide in new regions of massive star formation and, due to that finding, they stated that those environments presenting high-pressure and large-temperature conditions seem to be more favorable for the detection of $HCONH_2$.

Several routes are proposed in the literature to explain the origin of formamide in space, which include gas phase mechanisms (such as $H_2CO + NH_4{}^+$ or $H_2CO + NH_2$) and reactions on ice mantles (hydrogenation of HNCO or OCN as well as interactions between $CO + NH_3$, $HCO + NH_2$, and $HCOOH + NH_3$) (Barone et al., 2015; Redondo et al., 2014). In this context, Coutens et al. (2016) reinforce that experiments performed for the aforementioned hydrogenation of HNCO onto grains evidenced a low efficiency for this mechanism in cold environments, not explaining the correlation observed for HNCO and formamide abundances in several astrophysical sources. Anyway, there is still a lack of reliable estimates for rate constants of several of the aforementioned processes (Adande et al., 2013), so that these and other proposals for mechanisms that can elucidate the $HCONH_2$ formation remain still in debate (Coutens et al., 2016).

On the other hand, the main processes for thermal decomposition of formamide seem to be known. Nguyen et al. (2011) performed an extensive theoretical study about some possible channels for $HCONH_2$ decomposition. They considered single-step processes as well as multiple-step ones, where some formamide isomers (such as nitromethane, nitrone, formaldoxime, aminohydroxycarbenes, and formamidic acids) are intermediate compounds. Thus, these authors concluded that nitromethanes, nitrones, and formaldoximes are ~50 kcal mol^{-1} less stable than $HCONH_2$ and thereby these compounds are probably not involved in the prin-

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cipal pathway for formamide decomposition. Moreover, the dehydrogenation pathway is suggested as being mainly processed by a one-step mechanism, whereas the conversions of formamide into $CO + NH_3$ and $H_2O + HNC$ are multiple-step reactions. However, some of the main conclusions of Nguyen et al. (2011) regard the decomposition into H_2O and HCN, which is demonstrated to be the most favorable channel for thermal decomposition of formamide, requiring necessarily some formamidic acid isomers (FAs) as intermediates. Experimentally, Duvernay et al. (2005) also observed H_2O–HCN and H_2O–HNC complexes as primary products during the photolysis of $HCONH_2$.

Based on the classical Strecker reaction (Lazcano and Bada, 2003), Saitta and Saija (2014) also argue that, once produced, formamide can give origin to more complex compounds or it might be converted into formamidic acid, which follows by decomposition into water and hydrogen cyanide, as commented before. Nevertheless, the formamide decomposition should not be a major difficulty for prebiotic molecule formation, once amino acids (such as alanine, aspartic acid, and α-aminobutyric acid) can also be obtained from oligomerization of HCN (Harada, 1967). In turn, Orgel (2004) reinforces this appointment reporting the possibility for the synthesis of adenine, guanine, beyond other molecules, from HCN polymerization. This hypothesis also includes the ribonucleic acid (RNA) formation, since one of the possible routes that explain its origin considers the condensation of HCN and H_2O. Thus, taking into account that H_2O and HCN are abundant compounds in the interstellar medium (Nguyen et al., 2013), it would be better not to disregard the relevance of HCN oligomerization/polymerization along further studies concerned with the investigation of alternative production routes for prebiotic molecules in those environments enriched with this compound. Accordingly, $HCONH_2$ is considered a potential nonvolatile source of HCN (Adande et al., 2013; Barks et al., 2010).

In turn, once formamidic acids and aminohydroxycarbenes are intermediates in important reaction pathways regarding formamide, a better characterization of these isomers is important to improve the knowledge about formamide reactivity in gas phase (Luna et al., 1998). In this sense, we decided to focus our interest on determining better values for electronic, thermochemical, and chemical kinetic properties of FAs. Such molecules can also be addressed in the literature as formimidic acids (e.g. Duvernay et al., 2005) or even as methanimidic acids (e.g. Bünzli-Trepp, 2007). By far, we verified that the FA isomer labeled as FA4 in Fig. 1 is the most studied in the literature, once it is directly involved in the tautomerism with formamide, that is, the dynamical equilibrium between these two molecular structures driven by simple proton transfer (Fogarasi, 2010). Tautomerism can also occur for phenol-keto, imine-enamine, keto-enol, among other pairs of molecular families (Brown, 1994). Considering that HCN and HNC are molecules already observed in interstellar media, it is expected that the tautomeric process between these compounds will occur more easily in hotter regions of such environments (Vichietti and Haiduke, 2014).

Although the tautomeric process between $HCONH_2$ and FA4 presents a particular relevance for chemistry, biology, and pharmacy (Guzmán-Angel et al., 2016), there are not considerable experimental studies in the literature about properties of FAs, especially for the other three stable isomers of FA4, which are represented as FA1, FA2, and FA3 in Fig. 1. In this sense, we found just two experimental investigations, conducted by Maier and Endres (2000) and Duvernay et al. (2005), which are concerned with the vibrational spectra of FAs. Hence, the lack of experimental measurements turns quantum chemistry calculations into important tools to obtain valuable information about structures and properties in similar molecular systems (Kwiatkowsky and Leszczynski, 1992).

Fortunately, some thermochemical and electronic structure properties for FAs have been theoretically investigated by means of a large variety of quantum chemistry treatments, such as AM1 (Al-Omari, 2009), B3LYP (Duvernay et al., 2005), SCF (Kwiatkowsky and Leszczynski, 1992), G2MP2 (Kalia et al., 2007), MP2 (Liu et al., 2004), QCISD(T) (Piacenza and Grimme, 2004), and CCSDT//MP2 (Fogarasi, 2010). However, as mentioned before, we noticed that most of these theoretical studies are again concerned with providing data for FA4, whereas more detailed and accurate investigations about several electronic properties of FA1, FA2, and FA3 still need to be accomplished. In addition, specific details about the interconversion processes between these FA structures are still not well-known (Liu et al., 2004), so that reliable data from kinetic studies are also required.

The detection of new molecules in astronomical environments, beyond their obvious importance to the understanding of chemical processes for molecular formation and decomposition in such adverse conditions, is also relevant because it is possible to furnish substantial information about the physical conditions of the media where these compounds are inserted from the analysis of their vibrational and rotational spectra (Knez et al., 2003). Certainly, in the absence of experimental data, the identification of unknown molecules can be supported by means of spectra calculated via quantum chemistry treatments (Nguyen et al., 2011).

Thus, taking into consideration that FAs are important intermediates along the formamide decomposition routes, the present work is devoted to the determination of trustworthy data to guide the detection of these isomers in astrophysical environments. To the best of our knowledge, this study provides the most reliable estimates of bond lengths, bond angles, dihedral angles, vibrational frequencies, infrared intensities, and energetics performed up to now for FAs, which is accomplished by CCSD/cc-pVTZ, CCSD/aug-cc-pVTZ, CCSD/cc-pVQZ, and CCSD(T)/cc-pVTZ calculations. Moreover, we also furnish equilibrium estimates of dipole moments and rotational constants for the four FAs in study, which are properties that may contribute to drive astronomers in the detection of these isomers in interstellar media by means of rotational spectroscopy techniques. In addition, we also accomplish a chemical kinetic study, so that rate constants and Arrhenius' parameters for interconversion processes between pairs of FAs and for the tautomeric reaction between FA4 and formamide are determined along a large temperature range. Finally, we estimated FA abundances expected to be observed in regions where $HCONH_2$ is found.

2. Methodology

We performed electronic structure calculations with the Gaussian 09 computational package (Frisch et al., 2009) in order to provide several data for FAs and $HCONH_2$ in their ground electronic states. In this sense, equilibrium geometric parameters (bond lengths, bond angles, and dihedral angles), vibrational frequencies and infrared intensities of fundamental bands, dipole moments, rotational constants, and energetics (electronic energies, enthalpies, and Gibbs energies) of FAs and formamide were determined with Coupled Cluster Theory including single and double excitations (CCSD) along with cc-pVTZ, aug-cc-pVTZ, and cc-pVQZ basis sets. The appropriate electron densities from these calculations are used to property determinations. Beyond that, calculations using CCSD combined with a perturbative treatment for triple substitutions (CCSD(T)) and the cc-pVTZ basis set were also taken into account in this study. However, Gaussian 09 does not provide the correct electron densities for CCSD(T), avoiding the immediate obtaining of dipole moments and infrared intensities in this case. Alternatively, the CCSD(T) method can still be used along with applied dipolar electric fields of small magnitude (±0.0001 a.u.) to attain the respective dipole moment values as electronic energy

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