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A QUANTUM MECHANICAL STUDY ON CH_2NS^+ FAMILY OF CATIONS, POSSIBLE INTERSTELLAR SPECIES

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Abstract. It is demonstrated on quantum mechanical grounds that the dissociative recombination of $HSCNH^+$ with an electron, a reaction of interest to the chemistry of molecular interstellar clouds, leads either to HSCN or to HNCS. The $HSCNH^+$ cation, thus far undiscovered in space, is therefore proposed as a precursor for both neutral interstellar species, while H_2NCS^+ (32 kJ/mol more stable than $HSCNH^+$, according to our quantum-chemical calculations) can yield only HNCS. Calculations of potential energy surfaces were carried out for both cationic precursors.

1 Introduction

HNCS and HSCN were predicted as the lowest energy structures among the molecules sharing the same stoichiometry, with HSCN being 26 kJ/mol less stable than HNCS (Wierzejewska & Moc 2003). The importance of HSCN would therefore be negligible if thermodynamic equilibrium between the two species existed. Both molecules are nevertheless detected in the interstellar medium (Frerking *et al.* 1979; Halfen *et al.* 2009), and the HSCN abundance in the prominent molecular cloud Sgr B2 is only three times lower than that of HNCS (Adande *et al.* 2010; Halfen *et al.* 2009). Adande *et al.* (2010) proposed cationic precursors for the following reactions:

$NCS^+ + H_2 \rightarrow HNCS^+ + H$

$HNCS^+ + H_2 \rightarrow H_2NCS^+ \ / \ HNCSH^+ + H$

$HNCSH^+ + e^- \rightarrow HNCS/NCSH + H$

$H_2NCS^+ + e^- \rightarrow HNCS + H.$

The identification of H_2NCS^+ or its isomers is crucial for uncovering the HNCS/HSCN astrochemistry.

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Here we report the first results of a theoretical study on relevant dissociative recombination processes for H_2NCS^+ isomers.

2 Theoretical methods

The Gaussian 03 (Frisch *et al.* 2004) software package was used throughout this study. Preliminary structures of H_2NCS^+ isomers were indicated by the density functional theory, B3LYP/aug-cc-pVTZ (Becke 1993; Kendall *et al.* 1992; Lee *et al.* 1988). The coupled cluster theory level (Kendall *et al.* 1992; Pople *et al.* 1987) with single and double (CCSD/cc-pVTZ) excitations was employed to perform the final geometry optimizations and the potential energy surface (PES) scans.

3 Results and discussion

Structures corresponding to the deepest minima on the singlet potential energy surface of $CH_2NS^+$are presented in Figure 1. Vibrational frequency calculations allowed for the distinction between true minima and saddle points. The radio astronomical detection of the most stable singlet isomers **1** and **2** seems to be feasible, given their predicted electric dipole moments of 3 D.

Within a quiescent interstellar cloud, dissociative recombination consists of the collision of a cation M^+ with a slow electron, which creates M in one of many highly excited electronic states, near the ionisation limit. Neutral M is then subjected to a range of different unimolecular transformations governed by potential energy surfaces of its ground or excited states. The simplification applied here, as well as in similar studies (Kołos *et al.* 2009; Osamura *et al.* 1999), consists in reducing the problem to the ground PES. While the neglect of rearrangements taking place in excited electronic states removes severe computational difficulties, it has to be regarded as a preliminary approach, showing the fate of only those M species which would rapidly pass to the ground state. The coupling between excited and ground states is in fact not expected to be strong for a 5-atom molecule. We have analysed, along these lines, the dissociation of the radical species H_2NCS and HNCSH (denoted **R1** and **R2** in Fig. 2).

Geometries of flat **R1** and **R2** radicals are significantly different from those of their respective cations **1** and **2**, yet the energetic separations **R1-R2** and **1-2** are very similar. The CCSD/cc-pVTZ energy of **R2** (ZPE-corrected) is 40 kJ/mol higher than that of **R1**. The ionisation energy of both radicals is approx. 645 kJ/mol. Radicals **R1** and **R2** may yield several species, namely:

$H_2NCS(\mathbf{R1}) \rightarrow HNCS + H$ ($E_a = 182$ kJ/mol)
$H_2NCS(\mathbf{R1}) \rightarrow H_2NC + S$ ($E_a = 353$ kJ/mol)
$H_2NCS(\mathbf{R1}) \rightarrow H_2N + CS$ ($E_a = 382$ kJ/mol)

$HNCSH(\mathbf{R2}) \rightarrow HNC + SH$ ($E_a = 57$ kJ/mol)
$HNCSH(\mathbf{R2}) \rightarrow HNCS + H$ ($E_a = 120$ kJ/mol)

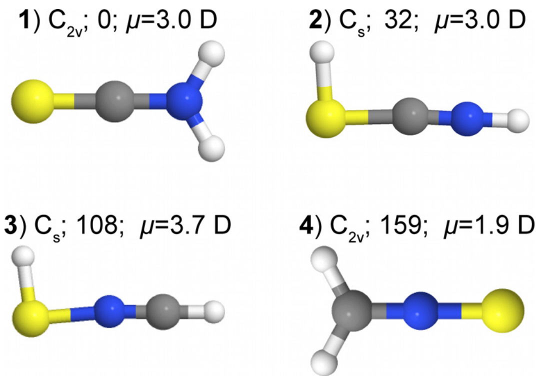

Fig. 1. CH_2NS^+ cationic structures corresponding to the lowest energy minima of the singlet PES. Isomer labels and symmetry designations are followed by CCSD/cc-pVTZ relative energies (kJ/mol; corrected for the zero-point vibrational energy, calculated with respect to the most stable species; 1 eV $\approx$ 96 kJ/mol), and by electric dipole moment values.

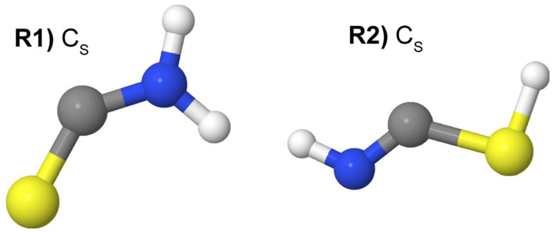

Fig. 2. Geometries of H_2NCS and HNCSH radicals (Å, degrees) calculated by CCSD/cc-pVTZ.

HNCSH(**R2**) $\rightarrow$ H + NCSH (E_a = 158 kJ/mol).

The activation energy E_a is predicted to be the lowest for the dissociation of radical **R2** into HNC and SH. This reaction, while important as an **R2** destruction route, cannot significantly increase the amount of abundant interstellar HNC or SH molecules. Of note, **R2** may yield HNCS and HSCN. It can also, formally, dissociate into HN and CSH, but this latter reaction is not likely, with its predicted E_A value of 684 kJ/mol, *i.e.* higher than the excess energy with which the neutral radical is produced.

In the case of **R1**, the lowest activation energy is predicted from the dissociation of **R1** into HNCS and H. The E_a values are significantly higher for other processes. The calculated heights of energetic barriers indicate that HNCS should be produced more efficiently than HSCN, in accordance with interstellar abundance measurements.

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4 Summary

HNCS and NCSH can be formed in the interstellar medium from the two cationic precursors: $HNCSH^+$ and H_2NCS^+. The calculated heights of the energy barriers indicate that HNCS should be produced more efficiently than HSCN, in qualitative consistence with interstellar abundance measurements. Molecules HNC, HS, H_2NC, CS and NH_2 can arise in associated dissociative recombinations. Y-shaped H_2NCS^+ and L-shaped $HNCSH^+$ species are the most stable isomers of this stoichiometry, and, with their predicted electric dipole moments of 3 D, are likely to be discovered with microwave spectroscopy.

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