Journal of Molecular Spectroscopy 310 (2015) 8–15

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

On the FCNS ⇆ FC(NS) reaction: A matrix isolation and theoretical study

Attila Tajti [b], Leonie Anna Mück [a], Ádám László Farkas [b,c], Melinda Krebsz [b], Tibor Pasinszki [b], György Tarczay [b,*], Péter G. Szalay [b,*]

[a] Institut für Physikalische Chemie, Johannes Gutenberg-Universität, Duesbergweg 10-14, 55099 Mainz, Germany
[b] Institute of Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest 112, Hungary
[c] Bolyai College, Eötvös University, Nándorfejérvári út 13, H-1117 Budapest, Hungary

ARTICLE INFO

Article history:
Received 15 October 2014
In revised form 24 November 2014
Available online 9 December 2014

Keywords:
Photochemistry
Matrix isolation spectroscopy
Conical intersections
Molecular dynamics simulations
Ab initio computations of excited states
Molecular switches

ABSTRACT

The FCNS ⇆ FC(NS) photoisomerization process is a simple model system for molecular switches. Here, we examined the switching processes by experimental and theoretical methods. Prior matrix-isolation IR spectroscopic studies were complemented by matrix-isolation UV spectroscopic measurements to assist the interpretation of the mechanism of the ring closure and opening processes and to verify the accuracy of the computations on the vertical excitation energies. Vertical excitation energies were computed by the EOMEE-CCSD, MCSCF, and MR-CISD methods. Conical intersections were also searched for and three conical intersections along the reaction path FCNS → FC(NS) were located, one conical intersection between the 2A′ and 1A″ state, one between the 1A″ and 1A′ state and one where all three states intersect. The ring opening and closing processes were simulated by non-adiabatic dynamics propagation with the trajectory surface hopping method. The combined computational and experimental results suggest that upon 365 nm irradiation the ring closure FCNS → FC(NS) occurs under participation of all three conical intersections, while 254 nm irradiation causes ring opening FC(NS) → FCNS. Both processes, especially the ring opening, are accompanied by fragmentation into FCN+S.

1. Introduction

Covalent pseudohalides exhibit very rich and varied chemistry due to their diverse structure, reactivity, and stability. Considering the sulfur containing derivatives bearing the CNS functional group, four low-energy open-chain isomer pseudohalide families can be deduced. Thiocyanates (-SCN) and isothiocyanates (-NCS), in general, are stable and isolable compounds widely used and studied in various fields of chemistry [1,2]. Nitrile sulfides (-CNS), although unstable, have become important transient species in cycloaddition reactions in organic chemistry [3–5]. Since they cannot be isolated in the pure state due to bimolecular reactions, they are hardly investigated, and only six derivatives, namely H-, F-, Cl-, NC-, CH_3-, and C_6H_5-CNS, have been spectroscopically identified to date, all of them in low-temperature noble gas matrices at cryogenic temperatures [6–11]. Very little is known experimentally about thiofulminates (-SNC); only HSNC was identified at low temperature by IR spectroscopy [12]. In addition, two high-energy open-chain (-NSC and -CSN) and three cyclic non-pseudohalide isomers (-C(NS), -N(CS), and -S(CN)) can be deduced from the CNS group [13], and these isomers are expected to play a role in isomerization processes of pseudohalides. Only one molecule of these latter five derivatives, FC(NS), the subject of the present paper, has been experimentally identified to date by IR spectroscopy [7].

Some of the present authors have recently generated FCNS in solid argon matrix at low temperature and studied its photoisomerization by IR spectroscopy [7]. It was observed that FCNS isomerized upon 365 nm UV irradiation into the ring thiazirine isomer FC(NS), and the thiazirine partially isomerized back to FCNS upon 254 nm irradiation. Although the FCNS ⇆ FC(NS) isomerization reactions were not quantitative (there is a loss due to dissociation), this system is one of the simplest among molecular switch models. Most importantly, the size of this system allows modeling with high-level theoretical methods both in electronic structure calculation and in molecular dynamics simulations.

The FCNS ⇆ FC(NS) isomerization process is of crucial importance in finding a synthetic route to thiazirines, thus the aim of the present study is to shed light on the FCNS ⇆ FC(NS) photoisomerization process. In order to do this, high-level multireference configuration interaction singles and doubles (MR-CISD) calculations are applied to describe the potential energy surfaces along the reaction path, and non-adiabatic dynamics propagation with the trajectory surface hopping method has been performed. Since our previous experimental work aimed to identify FCNS and FC(NS)

---

[*] Corresponding authors at: Pázmány Péter stny. 1/A, H-1117 Budapest, Hungary.
E-mail addresses: tarczay@chem.elte.hu (G. Tarczay), szalay@chem.elte.hu (P.G. Szalay).

http://dx.doi.org/10.1016/j.jms.2014.12.004

by IR spectroscopy, UV spectra of these molecules have not been recorded and we augment the present theoretical work with matrix-isolation UV (MI-UV) spectroscopic experiments.

2. Methods

2.1. Experimental methods

The matrix isolation IR spectroscopic experiments, which prove the ring closure of FCNS upon 365 nm UV irradiation and the ring opening of FC(NS) upon 254 nm UV irradiation, were published before [7]. Here we present the details of the matrix isolation UV spectroscopic measurements of the two species only.

The 3,4-difluoro-1,2,5-thiadiazole precursor was synthesized from the dichloro-derivative with potassium fluoride in sulfolane, according to a known literature method [14]. Starting materials were commercial products (Aldrich). The purity of the synthesis product was checked by gas-chromatography, and found to be >98%. The contaminants are less volatile than the precursor, which means that the premix contained less impurity.

The degassed precursor was mixed with argon (from Messer, purity 99.9997%) in a 1:1000 mole ratio in a glass vacuum line. The gas mixture was deposited onto a 12–14 K CsI window mounted on a Janis CCS-350R cold head cooled by a CTI Cryogenics 22 closed-cycle refrigerator unit. The flow rate was regulated by an MKS flow controller system. The flow rate was ca. 0.3 sccm ($\sim$0.75 mmol h^{-1}). The temperature of the copper cold head was set by a Lake Shore 321 thermostat equipped with a silicon diode thermometer. After the matrix deposition, the CsI window was cooled down to 8–10 K and kept there for all other experiments.

In the photolysis experiments the matrix was irradiated by a Cathodeon HPK 125 W high-pressure mercury lamp through a quartz window and an interference filter (254 or 365 nm, FWHH 10 nm).

Absorption UV spectra were recorded by a Varian Cary3E spectrometer, using 5 nm min^{-1} scan rate, 0.333 nm step size, and 1 nm spectral band width. The data were collected in the 190–400 nm spectral region.

2.2. Computational methods

Initial calculations of the potential surfaces of the excited states have been performed at the EOMEE-CCSD [15] level. It was, however, recognized that a conical intersection involving the ground state is important for the studied reaction, therefore the use of a multireference method is unavoidable. The Multiconfiguration Self-Consistent-Field (MCSCF) and Multireference Configuration Interaction with single and double excitations (MR-CISD) methods were used. (For a recent review of these methods see Ref. [16].) After appropriate tests, a Complete Active Space (CAS) reference space including four electrons and six orbitals (4×6 CAS) was selected since it gave a qualitatively correct description of the states of interest. Excitation energies were calculated at (state averaged) MCSCF(4,6)/cc-pVDZ [17] and MR-CISD(4,6)/cc-pVDZ levels of theory. The size-consistency error was corrected using the Pople version of Davidson-correction [18]; these results will be denoted by MRCI+Q_P in what follows. Transition moments and oscillator strengths were also calculated at MR-CISD(4,6)/cc-pVDZ level of theory. Geometry optimizations on the crossing seam were conducted at MCSCF(4,6)/cc-pVDZ level of theory using the algorithm described in Ref. [19] considering also non-adiabatic coupling vectors [20]. All these calculations were performed by the COLUMBUS quantum chemical program package, version 7.0 [21]. Non-adiabatic dynamic propagation with the trajectory surface hopping method [22] was carried out using the program package Newton-X, version 1.2 [23]. The necessary data for this direct dynamics (energy, gradients, non-adiabatic coupling vectors, transition moments) were also calculated at MCSCF(4,6)/cc-pVDZ level of theory using again the COLUMBUS program package. The vibrational frequencies of the ground state necessary to generate the initial conditions for the simulation were calculated at B3LYP [24]/def2-TZVPP [25] level of theory using the aoforce module of the TURBOMOLE quantum chemical program package, version 6.1 [26]. For the reaction pathway from FCNS to FC(NS) 200 trajectories were considered in the final statistical analysis, while for the reverse reaction pathway from FC(NS) to FCNS 100 trajectories were calculated.

3. Results

3.1. Experimental results

Our previous matrix isolation IR spectroscopic investigations proved that 365 nm irradiation of FCNS leads to the formation of FC(NS). IR observations also proved that FC(NS) can be converted back to FCNS by 254 nm irradiation, but this conversion is at least an order of magnitude slower than the FCNS → FC(NS) conversion. The IR spectroscopic results also revealed that the FCNS → FC(NS) conversion takes place without N–S bond rupture, since in separate experiments in which the matrix contained only FCN and S the 365 nm irradiation did not lead to FC(NS).

In order to help understanding of these photochemical processes and check the accuracy of the computed excitation energies of FCNS and FC(NS), the same matrix isolation experiments were repeated but now using UV spectroscopic detection. Results of each step of these experiments are shown in Fig. 1. In details, first the 3,4-difluoro-1,2,5-thiadiazole precursor in a 8 K Ar matrix was irradiated by 254 nm UV light. As can be seen in the Figure this wavelength is located in the middle of the first UV band of the precursor. According to the IR spectroscopic results, the products of this photolysis are FCN and FCNS. Since FCN does not have absorption at wavelengths longer than 200 nm, the two new bands with maximum absorbance at 206 and 349 nm can unambiguously be assigned to FCNS. Note that the latter band has substantial absorption intensity at 365 nm. A very broad band is observed in this spectrum between ca. 260 and 300 nm. Since the intensity of this band does not decrease upon subsequent 365 nm photolysis (see middle panel of Fig. 1), it does not belong to FCNS, but might belong to a minor side product of the 254 nm photolysis of the precursor.

After generating FCNS and completely photobleaching the precursor, the matrix was irradiated with 365 nm UV light. The difference of the spectra recorded before and after the 365 nm photolysis (middle panel of Fig. 1) also shows that a low-intensity band between ca. 245 and 290 nm appears upon this photolysis. (Note that due to the slightly different scattering of the two spectra the baseline is not zero.) Based on the former IR spectroscopic observation this band can be assigned to FC(NS). In correspondence with the former IR spectroscopic results, this band very slowly decreases (see bottom panel of Fig. 1) upon subsequent 254 nm photolysis, while the 206 and 349 nm bands of FCNS reappear.

It can be seen that the absorbance intensities of the bands of FCNS compared to the band of FC(NS) in the two difference spectra (middle and bottom panels in Fig. 1) are different, the bands of FCNS are less intensive in difference spectrum corresponding to the 365 nm photolysis. This indicates that the FCNS ↔ FC(NS) photoisomerization reaction in one or both directions is not quantitative. One of the possible side channels can be the dissociation to FCN and S atom, which are the products of broad band UV photolysis. (Note that if the precursor had not been completely