INVESTIGATION OF BIOMOLECULES AND REACTIVE SPECIES BY MATRIX ISOLATION AND LASER SPECTROSCOPIC METHODS

(FINAL REPORT)

In the research statement we have proposed to extend our former (mostly matrix isolation) spectroscopic studies to more complicated systems (i.e., larger biomolecules and reactive species more difficult to prepare). We also proposed to investigate molecular physics phenomena (e.g., H-tunneling, intermolecular vibrational energy redistribution, light induced reactions) at low-temperatures. We intended to carry out instrumental developments, including both the improvement our matrix isolation experimental techniques and construction of modern gas phase spectroscopic setups.

The results of the different topics are summarized in the sections A– E. In the research proposal we predicted that "We expect that at least 70–80% of the proposed investigations and developments can be fully completed, but at the same time the new results can open new directions which are not planned." We believe that the 70–80% is fulfilled, but because some subprojects could not be completed and some other subprojects, that were not included in the proposal, were triggered by some unexpected experimental results or by collaborations, the structure of the report slightly differs from that of the proposal.

A) Instrumental developments

Due to the shutdown of the mechanical workshop at our Institute and unforeseen technical difficulties we could complete somewhat less construction works as we planned. Nevertheless, a couple of important improvements were carried out, which open new possibilities in the spectroscopic investigations.

We have completed our jet-cooled laser induced fluorescence (LIF) and disperse fluorescence (DF) setup. This setup is capable to acquire spectroscopic information on the electronic excited state at a resolution of 0.06 cm^{-1} (LIF detection) and on the electronic ground state at few cm^{-1} resolution (DF detection). A heatable sample inlet was designed for non-volatile samples, and an optical arrangement was set up to prepare radicals and reactive species by UV laser photolysis in the molecular beam. (See results in Section E.)

A new head was designed for one of our matrix isolation setup to make it capable for matrix-isolation Raman optical activity (MI-ROA) investigation of chiral species. This setup is under test.

We have planned to construct a cavity ringdown spectroscopy setup for studying radicals. The basic version of this setup (including the sample cell, Raman shifter to produce NIR laser radiation, optics, and the controlling software) is ready, but more work will be needed to make it feasible for spectroscopic detection of short-lived radicals.

B) Conformational distribution of small biomolecules and structure of biomolecule·water complexes

We have analyzed the conformational space of several amino acids, including cysteine, serine and proline [1–3]. In each case the spectral analysis was based on matrix isolation IR spectroscopy combined by NIR infrared laser irradiation. In the more complicated cases special 2D correlation analysis was also used. Besides stable conformers we could identify short-lived conformers that convert to lower-energy forms by H-atom tunneling. The tunneling life times were also determined.

We have also investigated the structure of glycine·H_2O complexes. We have shown that the selective narrow-band laser irradiation can induce the structural change of the complex, which – similarly to the case of amino acid monomers – can be used for unambiguous structural identification. Applying this method, we could identify formerly experimentally unobserved structural forms of the glycine·H_2O complex [4]. We have carried out numerous experiments applying the same method for cytosine·H_2O complex, but these experiments failed, which is most likely due to IVR (intramolecular vibrational redistribution) channels that do not induce structural changes.

In a cooperation with Stephan Coussan at Aix Marseille University, we have investigated the differences of the effects of selective IR and NIR irradiation on matrix isolated glycine and glycine·H_2O complex. The results on these two model systems could be generalized for other applications: The comparison of MIR and NIR induced conformational changes can facilitate the conformational analysis in complicated cases. While the simpler difference spectra obtained by MIR irradiations can be good starting points of the spectral analysis, the NIR irradiations are important to obtain spectra with better signal-to-noise level and also to access the conversion paths with larger barriers, and therefore, to observe more conformers in the spectra [5].

We have carried out a systematic structural investigation on the Ac-(Ala)$_n$-OMe (n=1–4) model peptides. The IR and VCD spectra were recorded both in solutions and in an Ar matrix [6]. The analysis of the spectra was supported by ab initio computations. We have identified the structural motifs in different media, a somewhat unexpected helical motif was observed in DMSO. The most important message of this work was that the matrix isolation method can support the structural investigation not only the biomolecular building blocks, but also that of small peptides with 3–4 amino acid residues. In a former theoretical work, we have investigated the VCD robustness of the amide-I and amide-II vibrational modes of small peptide models [7]. This experimental work on Ac-(Ala)$_n$-OMe peptides was in correspondence with one of the conclusions of the theoretical study: with increasing number of amino acid residues, not only the VCD rotational strength, but also the VCD robustness is increasing.

We have contributed to the investigation of H-bonded networks in uracil derivatives by recording the MI-IR spectra of the monomers in Ar matrix [8].

C) Photochemistry of biomolecular building blocks

The photochemical decomposition of glycine and alanine were investigated both in the gas phase and in Ar matrix. In the first case the photolysis was investigated at the astrophysically relevant wavelength of H Lyman α radiation, the experiments were carried out at the Swiss Light Source, using mass spectrometric and PEPICO analysis. In Ar matrix broad-band soft UV radiation was used, and the analysis was based on IR spectroscopy. According to the original plan we intended to publish these results in a single article, qualitatively characterizing the decomposition channels and we also wanted to determine absolute decomposition cross sections. It has turned out that the absolute cross sections strongly depend on the quality of the matrix, which makes their determination in the matrix unreproducible. Therefore, we will publish the gas phase MS and PEPICO studies separately [9]. The Ar-matrix photolysis results of glycine of alanine might be published in a combination with photolysis experiments carried out on several amino acids, these reports will focus only on the decomposition products.

D) Tunneling and IVR processes

As it is mentioned in Section A, we have observed some short-lived conformers of several amino acids that are prepared by NIR irradiation in matrices and that convert to lower-energy forms at 10 K. In the preparation the IVR processes play a crucial rule, while it was proven that the back conversion in the 10 K dark matrix taking place by tunneling. We have investigated both phenomena (i.e., IVR and tunneling) on simple model molecules.

We have prepared the high-energy conformer of trifluoro- [10] and tribromo-acetic acid [11]. In the latter case we have observed an interesting, new phenomenon: “matrix-site changing mediated by conformational conversion”. Briefly, the vibrational excitation of cis-TBAA converts predominantly the cis-TBAA molecules located in a specific matrix site into trans-TBAA; then, subsequent relaxation (by tunneling) of the generated higher-energy trans conformer back to the cis form populates almost exclusively another, possibly more stable matrix site.

We have also studied the so-called “remote switching” effect in an asymmetrically substituted dicarboxylic acid, E-glutaconic acid [12]. It was shown that the selective excitation of the O−H stretching overtone of one of the carboxylic groups can induce the conformational change (trans to cis) of the other carboxylic group, located at the other end of the E-glutaconic acid molecule. According to our interpretation, in this case the IVR process acts through eight covalent bonds in this flexible molecule before the excess energy completely dissipates into the matrix. Since the scientific discussion with the reviewers of this paper indicated that further experimental and theoretical proofs would be necessary to completely convince the scientific community that in this “remote switching” process really the IVR is the driving force, and not a simple statistic heat distribution, we have started the investigation of other similar systems. We have partially analyzed our experiments on the NIR laser induced “remote switching” effects in hydroxy benzoic acids [13].

E) Preparation and investigation of reactive species and their complexes

Applying both gas-solid phase reactions (by immediate trapping of the products in low temperature Ar) and photolysis in the matrix we have prepared and spectroscopically characterized many astrochemically relevant pseudohalogen molecules. We have completed the analysis of the MI-IR spectra of NCSeCN and NCSCN [14]. Among the photolysis products we have identified three formerly unknown species: NCSeNC, NCSNC, NCNCSe, as well as NCNCS. We have also studied the photoisomerization of NCSeSeCN to the newly observed NCSeSeNC isomer [15]. Among the photolysis products of amino oxadiazoles and amino thiadiazoles, we have identified the novel H_2NCNX, H_2NNCX, $H_2NC(NX)$, and HNNC(H)O (X=O,S) species [16,17,18]. In an analogous reaction CF_3CNS was prepared and spectroscopically characterized in an Ar matrix [19].

One of our former matrix-isolation IR spectroscopic experiments, which proved the ring closure of FCNS upon 365 nm UV irradiation and the ring opening of FC(NS) upon 254 nm UV irradiation, was extended by matrix-isolation UV measurements, and these experimental findings were simulated by non-adiabatic dynamics propagation with the trajectory surface hopping method [20], which shed in light of the mechanism of these processes.

As a part of a Fulbright visit the PI spent 5 months at the Keck Astrochemistry Laboratory at University of Hawaii, USA and established a collaboration with Prof. Ralf Kaiser. Although the visit of the PI was primarily supported by the Hungarian Fulbright Association, the travel was also supported by OTKA. The necessary data analyses, including quantum chemical computations, were performed at Budapest. On this visit the PI has learnt the instrumental requirements on working reactive matrices, including electron irradiations of astrophysically relevant ices. This project is closely related to our (OTKA supported) experimental projects in Budapest on the preparation of reactive astrochemical species. This visit was also important for current instrumental developments in our laboratory, because the PI is currently constructing a new novel astrochemical ice setup under a ‘Lendület’ project. As a part of this collaboration we have investigated the products formed when pure SiH_4, or binary SiH_4:CO, or binary SiH_4:CO_2 ices were irradiated by electrons. In the case of pure SiH_4 ices we have identified higher-silanes (Si_nH_{2n+2}) up to $Si_{19}H_{40}$[21]. These very large silanes were not observed before; these materials can be important precursors for Si CVD processes, and they are potential fuels of rockets. Among the products of e-irradiated SiH_4:CO ice, we have identified a novel molecule, silyl ketene [22]. By computational studies, we have also contributed to the experimental identification of the elusive $Si(H)_2Ge$ molecule [23].

Using our jet-cooled LIF/DF setup, we have studied the structure and spectroscopically characterized some atmospherically relevant fluorinated alkoxy radicals, including the $F_nH_{3-n}CH_2O$ series [24]. These species are atmospheric decomposition products of hydrofluorocarbons (HFCs), which are pollutants with very high global warming potentials (GWP) and long lifetime.

References*

[1] E. E. Najbauer, G. Bazsó, S. Góbi, G. Magyarfalvi, G. Tarczay, Exploring the Conformational Space of Cysteine by Matrix Isolation Spectroscopy Combined with Near-Infrared Laser Induced Conformational Change, J. Phys. Chem. B 118, 2093 (2014)

[2] E. E. Najbauer, G. Bazsó, R. Apóstolo, R. Fausto, M. Biczysko, V. Barone, G. Tarczay, Identification of Serine Conformers by Matrix Isolation IR Spectroscopy Aided by Near Infrared Laser Induced Conformational Change, 2D Correlation Analysis, and Quantum Mechanical Anharmonic Computations, J. Phys. Chem. B 119, 10496 (2015)

[3] A. Schneiker, G. Bazsó, M. Biczysko, Tarczay, Identification of Proline Conformers by Matrix Isolation Spectroscopy Combined with Near-Infrared Laser Induced Conformational Change, manuscript in preparation; [A. Schneiker BSc diploma work, Eötvös University, 2018.]

[4] L. Kócs, E. E. Najbauer, G. Bazsó, G. Magyarfalvi, G. Tarczay, Near-Infrared Laser Induced Structural Changes of Glycine·Water Complexes in Ar Matrix, J. Phys. Chem. A 119, 2429 (2015)

[5] S. Coussan, G. Tarczay, Infrared laser induced conformational and structural changes of glycine and glycine·water complex in low-temperature matrices, Chem. Phys. Lett. 644, 189 (2016)

[6] B. Légrady, E. Vass, G. Tarczay. Matrix-isolation vibrational circular dichroism spectroscopy in structural studies of peptides: Conformational landscape of the Ac(-Ala)$_{1–4}$-OMe depsipeptide series, J. Mol. Spectrosc. 351, 29 (2018)

[7] S. Góbi, G. Magyarfalvi, G. Tarczay, VCD Robustness of the Amide-I and Amide-II Vibrational Modes of Small Peptide Models, Chirality 27, 625 (2015)

[8] Z. Szekrényes, P. R. Nagy, G. Tarczay, L. Maggini, D. Bonifazi, K. Kamarás, Direction-dependent secondary bonds and their stepwise melting in a uracil-based molecular crystal studied by infrared spectroscopy and theoretical modeling, Chem. Phys. Lett. 691, 163 (2018)

[9] G. Bazsó, A. Bődi, G. Tarczay, publication to be submitted

[10] R. F. G. Apóstolo, G. Bazsó, R. R. F. Bento, G. Tarczay, R. Fausto, The first experimental observation of the higher-energy trans conformer of trifluoroacetic acid, J. Mol. Struct. 1125, 288 (2016)

[11] Rui F. G. Apóstolo,G. Bazsó, G. Ogruc-Ildiz, G. Tarczay, R. Fausto, Near-infrared in situ generation of the higher-energy trans conformer of tribromoacetic acid: Observation of a large-scale matrix-site changing mediated by conformational conversion, J. Chem. Phys. 148, 044303 (2018)

[12] B. Kovács, N. Kus, G. Tarczay, R. Fausto, Experimental Evidence of Long-Range Intramolecular Vibrational Energy Redistribution through Eight Covalent Bonds: NIR Irradiation Induced Conformational Transformation of E-Glutaconic Acid, J. Phys. Chem. A 121, 3392 (2017)
[13] M. Balbisi, G. Tarczay, work in progress; [M. Balbisi, ÚNKP Conference oral presentation, 2018]
[14] T. Vörös, B. Pacsai, G. Magyarfalvi, G. Tarczay, Generation and spectroscopic identification of NCXNC and NCNCX (X=S, Se) in low-temperature inert matrices, J. Mol. Spectr. 316, 95 (2015)
[15] T. Vörös, PhD dissertation, Eötvös University, 2018.
[16] T. Vörös, G. H. Lajgút, G. Magyarfalvi, G. Tarczay, Photochemical generation of H_2NCNX, H_2NNCX, $H_2NC(NX)$ (X = O, S) in low-temperature matrices, J. Chem. Phys. 146, 024305 (2017)
[17] T. Vörös, G. H. Lajgút, G. Magyarfalvi, G. Tarczay, Photochemical Formation of Diazenecarbaldehyde (HNNCHO) and Diazenecarbothialdehyde (HNNCHS) in Low-Temperature Matrices, J. Phys. Chem. A 122, 1034 (2018)
[18] B. Keresztes, B. Solymosi, T. Vörös, G. H. Lajgút, G. Magyarfalvi, G. Tarczay, work in progress.
[19] T. Pasinszki, T. Vörös, G. Vass, G. Tarczay, I. Jalsovszky, Spectroscopy, Structure, Thermal and Photochemical Decomposition of 5-Chloro-3-trifluoromethyl-1,2,4-thiadiazole: Generation ofTrifluoroacetonitrile N-sulfide, manuscript is submitted for publication.
[20] A. Tajti, L. A. Mück, Á. L. Farkas, M. Krebsz, T. Pasinszki, G. Tarczay, P. G. Szalay, On the FCNS ↔ FC(NS) Reaction: A Matrix Isolation and Theoretical Study, J. Mol. Spectr. 310, 8 (2015)
[21] G. Tarczay, G. Förstel, P. Maksyutenko, R. I. Kaiser, Formation of Higher Silanes in Low-Temperature Silane (SiH_4) Ices, Inorg. Chem. 55, 8776 (2016)
[22] G. Tarczay, G. Förstel, S. Góbi, P. Maksyutenko, R. I. Kaiser, Synthesis of the Smallest Member of the Silylketene Family: $H_3SiC(H)=C=O$, ChemPhysChem 18, 882 (2017); Cover profile: ChemPhysChem 18, 867 (2017); Cover picture: ChemPhysChem 18, 865 (2017).
[23] A. M. Thomas, B. B. Dangi, T. Yang, G. Tarczay, R. I. Kaiser, A. H. H. Chang, T. L. Nguyen, J. F. Stanton, A M. Mebel, Synthesis of the Germaniumsilylene Butterfly Molecule ($Ge(\mu{-}H_2)Si$), submitted.
[24] G. Tarczay, G. Bazsó, B. Koncz, K. Hegedűs, Jet-cooled Laser Induced Fluorescence and Dispersed Fluorescence of $CH_xF_{3-x}CH_2O$ (x=1,2,3) radicals, manuscript in preparation; Poster presentations at the Chemistry and Physics at Low Temperatures 2018 (Laramie, USA) and at the European Congress on Molecular Spectroscopy 2018 (Coimbra, Portugália).

* Conference presentations and PhD or diploma theses are listed only if the publication is not yet submitted.

Budapest, September 24, 2018

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