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COST Office

149 avenue Louise • P.O. Box 12 • 1050 Brussels • Belgium
Tel: +32 (0)2 533 38 00 • Fax: +32 (0)2 533 38 90
E-mail enquiries: office@cost.esf.org • Website: <http://cost.cordis.lu>
R.P.M.861.794.916 – Tribunal de Commerce de Bruxelles



SHORT-TERM SCIENTIFIC MISSION

SCIENTIFIC REPORT

COST Action Number: P9

Applicant's Name and Institution: **Perun Serhiy, Institute of Physics, Polish Academy of Sciences**

Host's Name and Institution: **Domcke Wolfgang, Chair of Theoretical Chemistry, Department of Chemistry, Technical University of Munich**

Period: from 1/11/2004 to 28/11/2004

Place: Garching (D)

Reference code: **COST-STSM-P9-00639**

PURPOSE OF THE VISIT

The main task of my short-term scientific mission (STSM) at the Technical University of Munich was to get acquainted with the software for ab initio quantum-chemical calculations implemented at the computer network in Munich (Turbomole and Molpro program packages). This software is planned to be used for the completion of my study on the mechanisms of photostability of the DNA bases.

DESCRIPTION OF THE WORK

Among the variety of available ab initio electronic-structure methods, only few are suitable for the study of excited states of larger molecules. The efficiency of the CASSCF (Complete-Active-Space Self-Consistent-Field), TDDFT (Time-Dependent Density Functional Theory) and CC2 (Second-Order Approximate Coupled-Cluster) methods has recently been proven in excited-state explorations of several medium-size molecules. The implementation of these methods in the Molpro and Turbomole ab initio quantum chemistry packages provides unique and powerful tools for studies of photophysical processes in molecules of biological interest.

My main efforts during my STSM were concentrated at improving my knowledge and experience in the application of the methods mentioned above to investigations of molecules of biological importance. The 2-aminopurine (2AP) isomer of adenine and the adenine-thymine (AT) base pair were selected as subjects of my explorations.

It is believed that a proton-transfer reaction in the AT base pair can provide an additional mechanism of photostability of this system. The energetic stabilisation of the $^1\pi\pi^*$ charge transfer (CT) excited state along the proton-transfer reaction path leads to a S_1 - S_0 conical intersection. The efficiency of the relaxation via this mechanism is determined by the barrier on the adiabatic potential-energy surface of the S_1 state, which separates the Franck-Condon region from the conical intersection. To estimate the height of this barrier, the LIIC (Linearly Interpolated Intrinsic Coordinate) reaction path was constructed from the optimised ground-state geometry and the minimum geometry of the CT state. Single-point energy calculations with the CC2 method were performed with the Turbomole package. The reliability of the TDDFT method for the calculation of excited-state potential-energy functions was also checked.

The results of the CC2 calculations on the AT Watson-Crick base pair predict the existence of a barrier of about 1 eV between the minimum of the lowest excited state ($^1n\pi^*$) and the $^1n\pi^*$ -CT crossing point (Fig 1). However, a careful analysis of these results and further optimisations of the geometry of the lowest excited singlet state indicate deficiencies of the LIIC computational strategy which can lead to a significant



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1 quai Lezay-Marnésia, B.P. 90015, 67080 Strasbourg cedex, France

overestimation of the barrier. The presence of only two hydrogen bonds between adenine and thymine, in contrast to the three hydrogen bonds in the guanine-cytosine Watson-Crick dimer, does not provide the AT dimer with the necessary rigidity. A significant geometry change is expected during the proton transfer, which is not accounted for in the LIIC procedure. For this reason, the construction of the coordinate-driven minimum-energy path, obtained by the optimisation of the energy of the lowest excited state, seems to be necessary for the correct description of the proposed photochemical stabilization mechanism. Exploratory studies with the TDDFT method have shown the inapplicability of this relatively inexpensive method, as a consequence of the pronounced CT character of the S_1 state. The use of the computationally more expensive CASSCF method appears necessary for the solution of this problem.

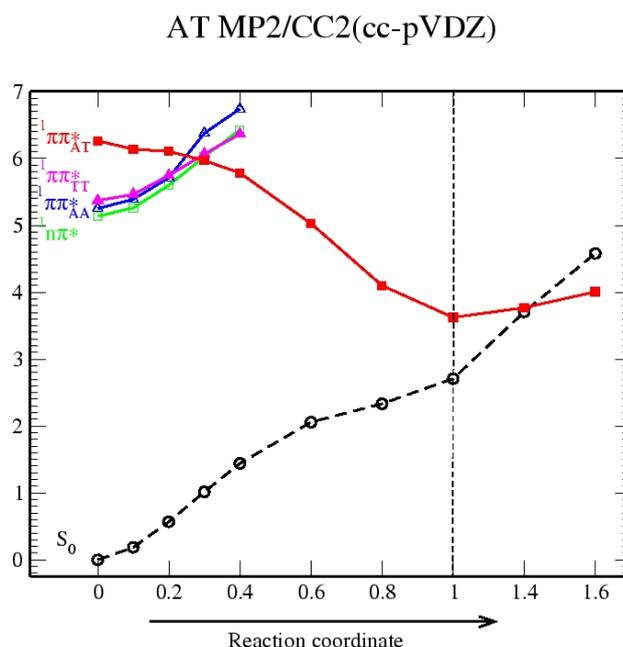


Fig.1 CC2 potential-energy profiles of the ground state and four lowest excited states of AT the base pair along the LIIC reaction path for proton-transfer from adenine to thymine.

2AP, which is a highly fluorescent isomer of adenine, was the second system studied during my short-term visit. In adenine, an out-of-plane deformation of the six-membered purine ring probably governs the photophysics of the lowest excited states. Using a similar methodology as in the previous studies on adenine, CASSCF calculations for 2AP were performed with the Molpro package. The results predict the existence of two S_1 - S_0 conical intersections, which, in contrast to adenine, lie higher in energy than the minimum of the lowest excited state. This fact and the presence of two barriers, which separate the Franck-Condon region from the S_1 - S_0 conical intersections, can be the reason for the unusually high quantum yield of fluorescence of 2AP.

MAIN RESULTS

During my short-term visit at the Chair of Theoretical Chemistry of the Technical University of Munich, extensive calculations with the Turbomole and Molpro packages have been performed on the AT base pair and on the 2AP molecule.

The exploration of the proton-transfer reaction in the AT base pair along the LIIC reaction path with the CC2 method predicts a barrier of 1 eV, which separates the Franck-Condon region from the S_0 - S_1 conical

intersection. The results reveal the necessity of further calculations, which will include the geometry optimisation of the lowest excited state with CIS and CASSCF methods to obtain a better estimate of the barrier height.

The calculations on 2AP have revealed the existence of two S_1 - S_0 conical intersections, which, however, are higher in energy than the minimum of the potential-energy surface of the lowest excited state. These findings explain the unusually high quantum yield of fluorescence of 2AP.

FUTURE COLLABORATION WITH HOST INSTITUTION

Contacts between the research groups in Warsaw and in Munich were established the mid 1980s. Since this time, the joint research resulted in several dozens of joint publications. My STSM within the framework of the COST P9 action served the continuation of this scientific activity. The numerous personal contacts that were established during my visit and the results which were obtained indicate very promising prospects for the further collaboration between the two research groups in the area of the photophysics of biomolecules.

PROJECTED PUBLICATIONS

A publication on the photophysics of 2AP, based on the results obtained during the STSM, is in preparation.

A seminar presentation with the title "Ab initio search for radiationless decay paths in adenine", summarising the work done in Warsaw and in Garching, was given in the Theoretical Chemistry seminar of the TUM on 23.11.2004.

Date: 30.11.2004

Signature:

CONFIRMATION BY THE HOST INSTITUTE OF THE SUCCESSFUL EXECUTION OF THE MISSION

Serhiy Perun has been visiting here for four weeks in November 2004. During his stay, he performed extensive calculations of excited-state reaction paths and potential-energy functions of 2-aminopurine and the adenine-thymine Watson-Crick dimer. We had many fruitful discussions and Serhiy interacted strongly with several group members. Through this STSM, the collaboration of the two research groups in Warsaw and Garching has been considerably strengthened. The results obtained are of high relevance for the goals of the P9 COST project.

(Prof. Dr. W. Domcke)
Director of the Institute of Theoretical Chemistry

Date: 4. 12. 2004

Signature: