

SCIENTIFIC REPORT

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STSM Topic: R-matrix calculations for the dissociation mechanism of Feshbach resonances in ethers and alcohols

Host: Jimena Gorfinkiel, Open University, Department of Physics and Astronomy, Milton Keynes (GB),

J.Gorfinkiel@open.ac.uk

Purpose of the visit

The visit represents the collaboration between the Department of Chemistry, Fribourg University and Physics and Astronomy Department of The Open University.

In my research, I observed dramatic differences in the electron-induced fragmentations of alcohols and ethers. The purpose of my research stay was to gain the theoretical understanding of my experimental observations by calculating the properties of the resonances mediating the fragmentation.

Jimena Díaz Gorfinkiel, lecturer at the Physics and Astronomy Department of The Open University, has a great expertise in calculating the properties of resonances in electron-molecule collisions using the R-matrix method and was ideally suited to guide me in this effort.

Description of the work carried out during the visit

The hydroxyl group is ubiquitous in living organisms. For this reason, in our earlier work we have studied compounds containing hydroxyl and amino groups which can be considered to be models for biomolecules. We extended our work to the study of the fragmentation of the ether bond, found in ribose and tetrahydrofuran (THF).

Our recent results showed an important difference between alcohols and ethers. The alcohols are characterized by three Feshbach resonances whereas only a higher Feshbach resonance appears for ethers.

A similar observation has been made concerning the parent state of the Feshbach resonances, the Rydberg state by Melvin Robin. He concluded that the Rydberg states are strongly perturbed in alcohols but this perturbation is not present in ethers.

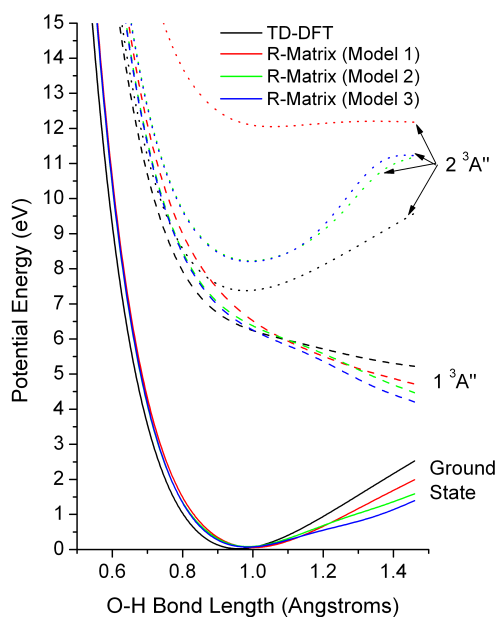
We tried to understand the mechanism of dissociation for Feshbach resonances for one model compound - methanol. As such a number of calculations are required on several points on the O-C stretch and O-H stretch using the R-matrix code. The work carried at Open University was aimed at calculating the potential energy curves of the Feshbach resonances for the model compound and aimed to determine if the observation made by Melvin Robin for Rydberg states is also valid for Feshbach resonances.

Description of the main results obtained

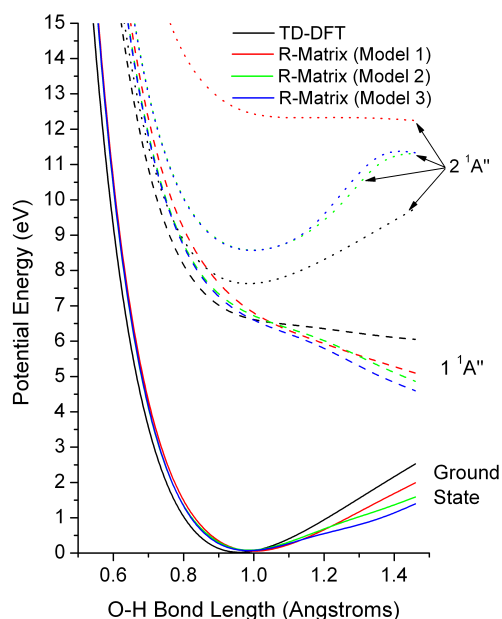
Before starting running any calculation a training period was necessary to learn how to run the R-Matrix code and how to interpret the output of the code since it lacks a user-friendly interface.

Running any calculation with the R-matrix code requires the completion of several steps. The first step was to determine a correct model for describing the target molecule. Since the purpose of these

calculations was to stretch the O–C and O–H bond, the main concern was that the chosen model should give accurate results for all bondlengths studied.



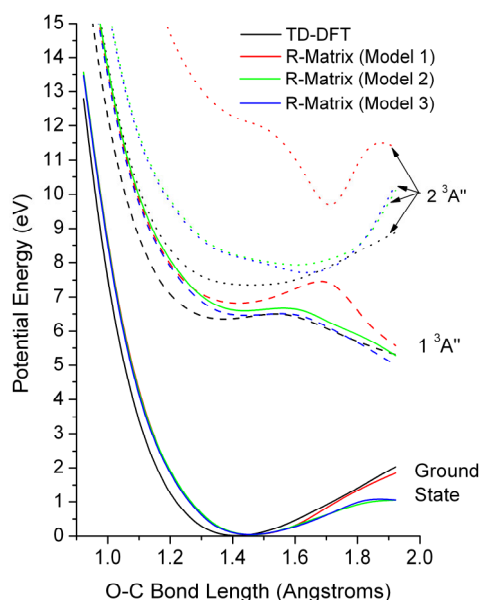
(a) The first two triplet excited states



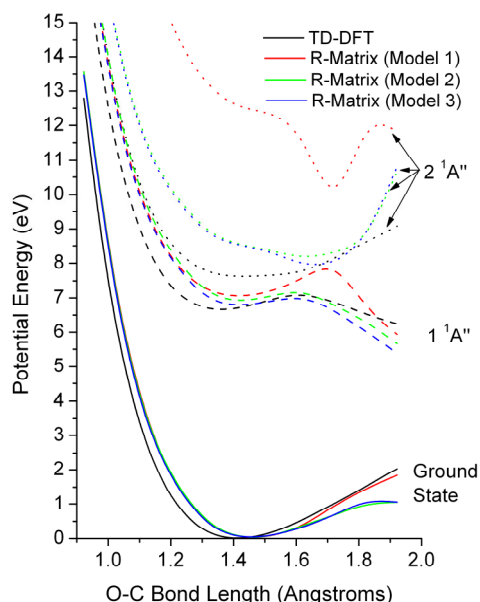
(b) The first two singlet excited states

Fig. 1. The first excited states of methanol as calculated with TD-DFT (black line) and with the R-Matrix suite using three different models for the target molecule in the case of O–H stretch.

Several models have been tested (10 in total). Some of the results are presented in fig. 1 and 2. These figures show a comparison between the first two triplet and singlet A'' excited states calculated with different models. The previous calculations¹, performed with TD-DFT method, were used as a reference. The first model tested in R-matrix theory was the one used Bouchiha *et al.*². The results obtained with this model did not agree very well with the reference calculations. A new model needed to be found.



(a) The first two triplet excited states



(b) The first two singlet excited states

Fig. 2. The first excited states of methanol as calculated with TD-DFT (black line) and with R-Matrix theory using three different models for the target molecule in the case of O–C stretch.

¹ B. C. Ibanescu and M. Allan, *Phys. Chem. Chem. Phys.*, **2008**, DOI: 10.1039/b806578k.

² D. Bouchiha, J. D. Gorfinkiel, L. G. Caron, and L. Sanche, *J.Phys. B*, **2006**, 39, 975.

Three possibilities to improve the results were investigated. The first possibility was to change the basis-set used to describe the molecule. This option was found too complex to implement at the present stage of the calculations. Another possibility was to modify the complete active space (CAS) model used to calculate the electronic structure of the molecule. Test calculations performed with different CAS models showed that for the chosen molecule this is not a feasible option due to computational limitations. The third possibility was to change the averaging procedure used to calculate the natural orbitals. This was the option chosen. The model 2 presented in fig. 1 and 2 is a model with different averaging parameters for the natural orbitals while model 3 is model that describes the electronic structure of the molecule most accurately under the given conditions. There were other parameters, such as the dipole moment, used to test the accuracy of the calculations. Scattering calculations to determine the resonance positions and widths are under way.

A second goal of the mission was to transfer the know-how to Fribourg University and be able to run the calculations independently, either on the same molecule or on a different one. The R-matrix suite was compiled on the Fribourg cluster and some of the calculations are now being run here.

Projected publications/articles resulting or to result from the STSM (if applicable)

The preliminary data obtained during the stay at Open University are analyzed at present time and will be presented in near future at scientific conferences. Moreover a short paper will be prepared for publication after completing the data with further calculations.