Modeling of Metastable Atoms and Protonated Peptide Ions Interaction

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INTRODUCTION

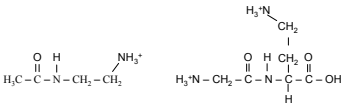
Electron capture dissociation (ECD) and electron transfer dissociation (ETD) have been in the focus of the study of peptide fragmentation mechanisms for quite a while now. Another recently introduced fragmentation method, which generates product ions similar to ECD, is based on the electron transfer from metastable, electronically excited atoms produced in a glow discharge. Understanding the mechanism of such process is important for further practical development of this new fragmentation technique.

METHODS

Ab initio quantum chemical calculations of the interaction of an electronically excited atom with a peptide ion are complicated. The relatively high excitation energy of an atom (11.6 eV in the case of metastable argon) leads to a substantial number of excited states of a peptide ion needed to be considered for the excited complex.

Calculations were performed using Gaussian 03W for Windows [1]. The Configuration Interaction with Single excitation (CIS) approach [1] was used. Mostly because of computational time restrictions we did not go beyond the 6-31+G(d) basis set of functions [1]. A total of 280 excited states were considered in CIS calculations. Transitions with the change of total spin were not considered in this work.

The structures, modeling peptide ions, are shown below:



We concentrated our attention on a singly charged peptide ion (Fig.6) and a doubly charged peptide ion (Fig.1).

Pseudo-crossing of the molecular potential surfaces were calculated and probabilities of transitions between the states of interest were estimated using Landau-Zener approximation [2].

Iso-density surfaces of certain molecular orbitals are presented in the figures below. The surface on the Ar atom represents one of the possible 3 p-orbitals from which the electron is excited (p-hole). An additional surface in each figure represents the orbital to which electron excitation occurs.

RESULTS

Figures 1 to 3 represent excited states that are relevant to the situation, when a peptide ion in ground state encounters a metastable Ar atom. The state illustrated by Figure 1 corresponds to the 96th excited state of the combined Ar – peptide ion system.

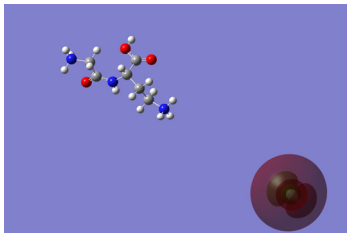


Figure.1. Molecular orbitals for the case **C**.

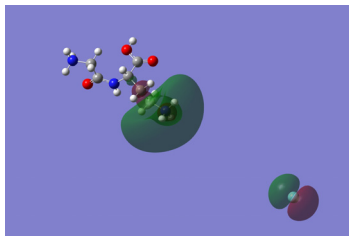


Figure.2. Molecular orbitals for the case **A**.

This is the initial state of the system, when a metastable atom of Ar is colliding with the peptide ion in the ground state. The transfer of an electron from this excited state of Ar to the peptide ion is the process of interest. We marked the group of states (with different p-holes) corresponding to this initial state by a letter **C**.

Groups of terms marked with letters **A**, **B**, and **D** correspond to ionic terms, when Ar+ is interacting with the peptide ion that acquired one electron from the Ar atom.

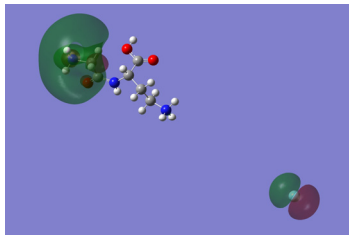


Figure.3. Molecular orbitals for the case **B**.

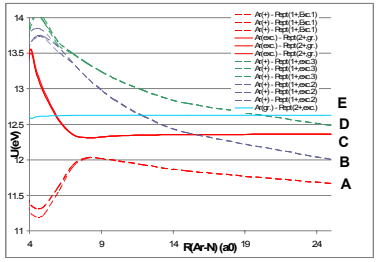


Figure.4. Selected potential energy curves of triplet states for the complex of Ar* and doubly charged peptide ion.

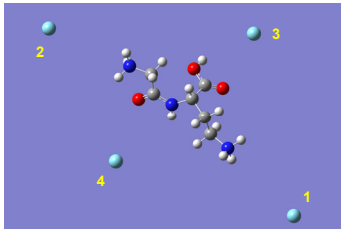


Figure.5. Four directions for the Ar atom to approach the peptide ion that were studied in this work.

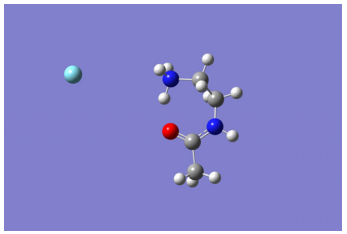


Figure.6. Singly charged model peptide.

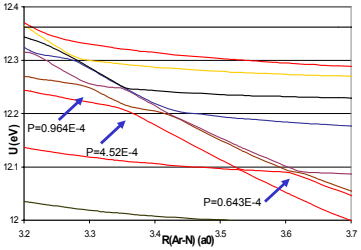


Figure.7. Details for the potential curves crossing for the peptide from figure 6.

Figure 4 illustrates potential energy curves for the system under consideration. The energy is presented as a function of the distance between the argon atom and the closest nitrogen atom of the peptide.

Ionic character of the **A, B,** and **D** states is obvious from the behavior of the corresponding potential curves.

The potential curve marked with the letter **E** in Fig.4 corresponds to Ar atom in ground state and excited peptide ion. Because of the inert nature of Ar in ground state it starts interacting with peptide ion only at a very close distance.

Similar potential curves were calculated for four directions of Ar* approaching the peptide ion. Those are shown in Figure 5 (one can see that the above discussion is related to the direction 1).

Probabilities for Ar* to leave its electron on the doubly charged peptide ion during collision (assuming thermal velocities) for trajectories 1 to 4 are 0.11, 0.50, $<10^{-5}$, $<10^{-4}$ accordingly.

Transfer of electron during collision of Ar* with the singly charged peptide ion moving at thermal velocities does not happen. Electron excitation energy of Ar* still can be transferred to peptide excitation due to non-adiabatic transitions with the probabilities indicated in Figure 7.

CONCLUSIONS

1. Transfer of electron from metastable Ar atom to doubly charged peptide ion happens with high probability.
2. In collision of Ar* with singly charged peptide ion there is no charge transfer, but electron excitation energy can be transferred with low ($\sim 10^{-4}$) probability.

REFERENCES

1. Foresman, J. B. , Frisch, A., *Exploring Chemistry With Electronic Structure Methods: A Guide to Using Gaussian (2nd edition)*. Gaussian, 1996
2. Nikitin, E.E., *Theory of fundamental atom-molecular processes in gases*.- Khimiya, Moscow, 1970