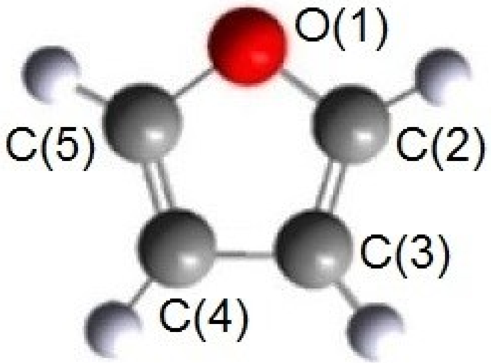
CATION-INDUCED ISOMERIZATION OF FURAN MOLECULE

TOMASZ J. WASOWICZ

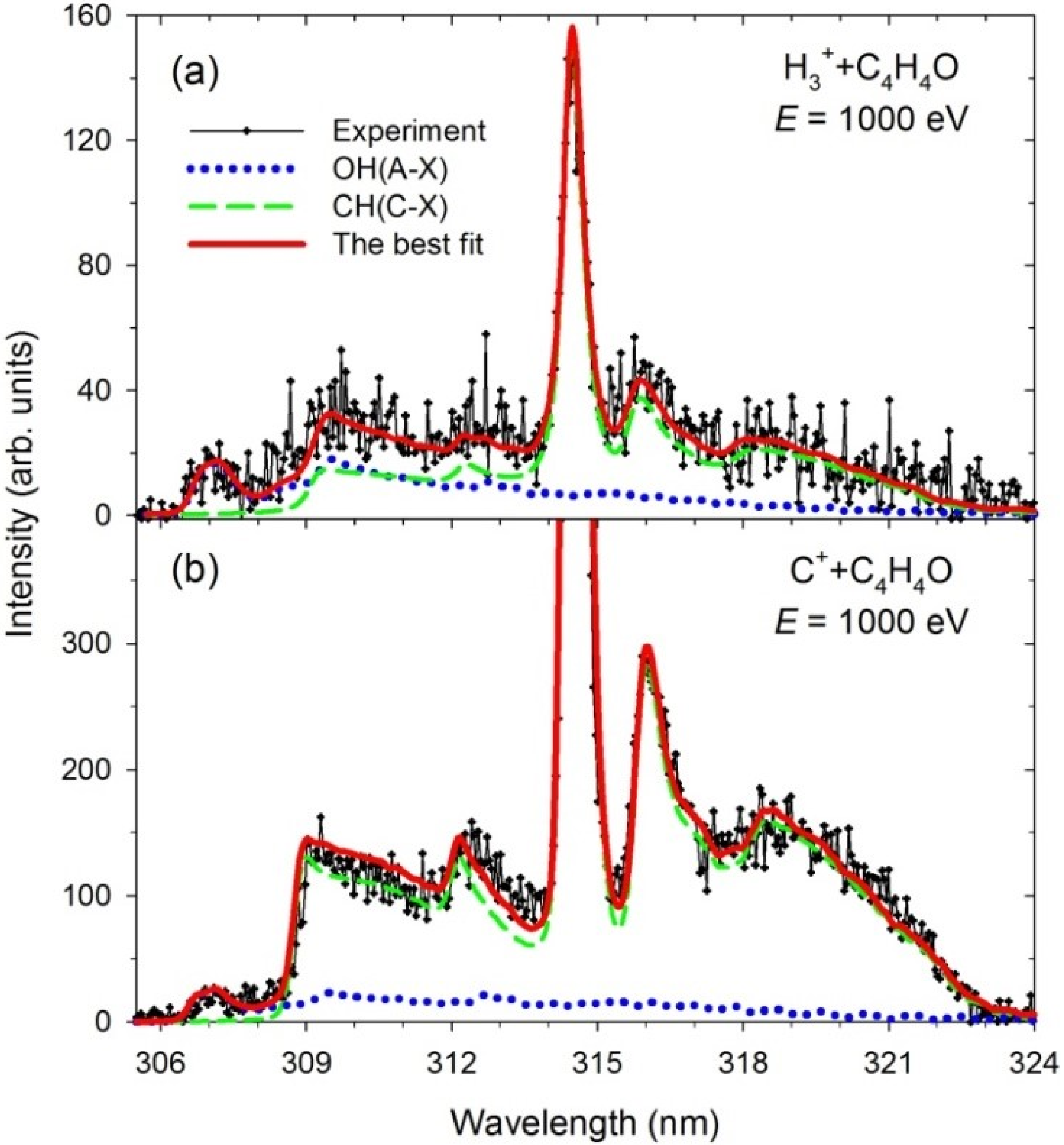
Division of Complex Systems Spectroscopy, Institute of Physics and Applied Computer Science, Faculty of Applied Physics and Mathematics, Gdansk University of Technology,
ul. G. Narutowicza 11/12, 80-233 Gdańsk, Poland
E-mail: *tomasz.wasowicz1@pg.edu.pl*

In the present communication, the fragmentation of the gas-phase furan molecules in collisions with the H_3^+ and C^+ cations has been measured by exploiting collision-induced emission spectroscopy (CIES). In particular, the formation of the $OH(A^2\Sigma^+)$_radicals has been observed among other fragments. Because they are not structural components of furan molecules, observation of their $A^2\Sigma^+ \rightarrow X^2\Pi$ bands indicates the intramolecular hydrogen migration prior to the cation-induced dissociation. The present results show that the cation-induced isomerization is possible in furan and depends on the particular projectile. The dissociation mechanisms leading to the OH formation are also discussed.

Furan molecule



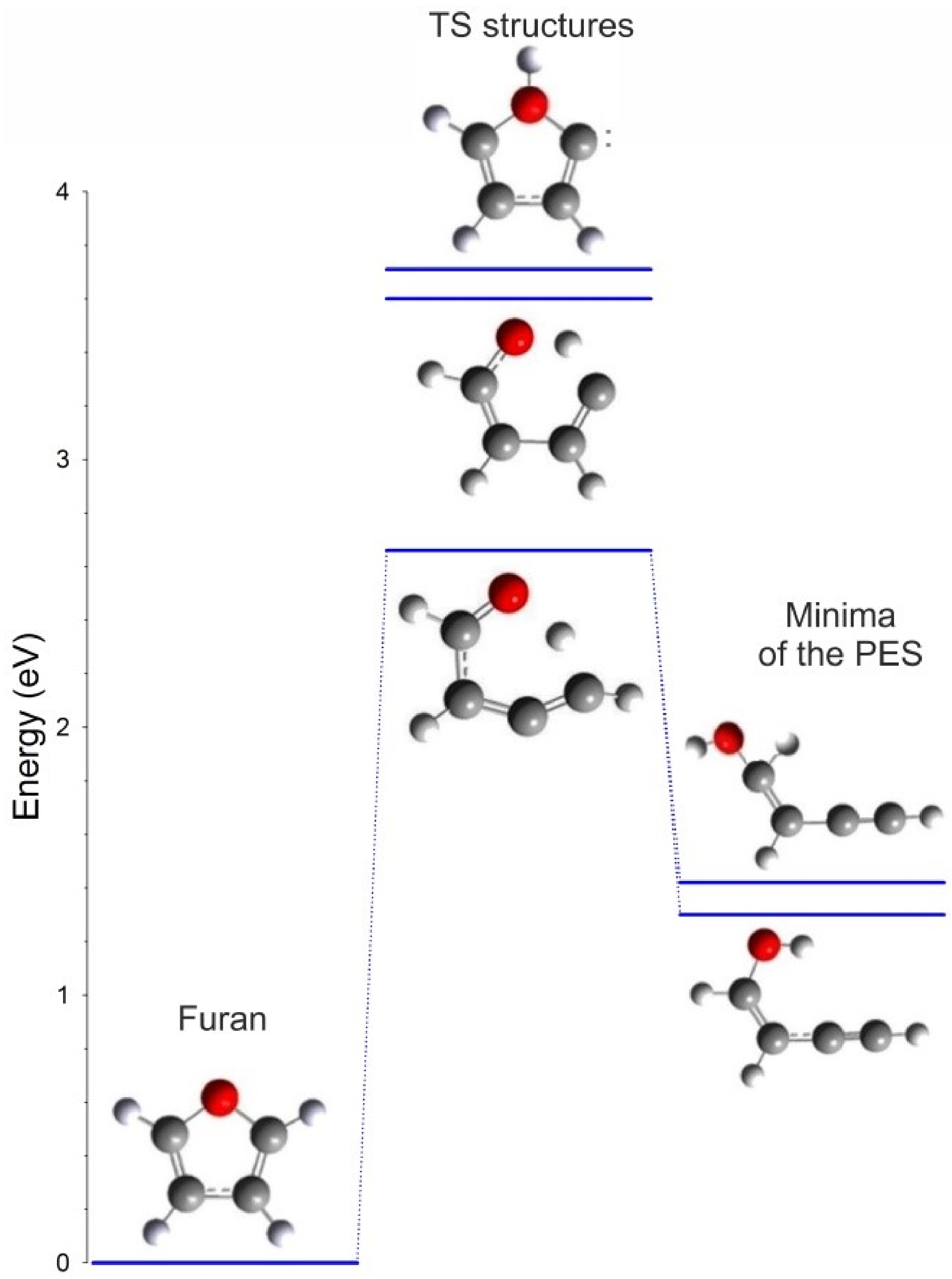
FRAGMENTATION SPECTRA



The figure shows the high-resolution optical fragmentation spectra measured for collisions between the H_3^+ and C^+ cations and furan molecules. Both spectra show spectral features of the molecular $OH(A^2\Sigma^+ \rightarrow X^2\Pi)$ $\Delta\nu = 0$, and $CH(C^2\Sigma^+ \rightarrow X^2\Pi_r)$ $\Delta\nu = 0$ bands. The spectrum obtained in the H_3^+ collisions (a) contains a much weaker signal than that obtained for C^+ impact (b). Moreover, the relative intensities of the features in both spectra are different.

ISOMERIZATION MECHANISMS

The figure shows the most likely isomerization pathways leading to the production of OH fragments [1], [2]. An H transfer from C(2) to O(1) may occur through three transition state structures (TS structures in the figure). The most likely mechanism in the OH formation involves the reaction pathway showing the lowest energy barrier located just 2.66 eV above furan canonical form and implies simultaneous 2,1- and 3,2-H shifts accompanied by a single C(2)–O(1) bond rupture (the lowest TS structure in the figure). Then this transition state structure can rearrange into two minima of the PES, i.e., stable alkyne–alcohol structures differing in energy by 0.12 eV [1]. Both open-ring molecules develop the –OH side terminal, which can serve as the last step in OH release.



SUMMARY

The most recent calculations [1], [2] predicted significant furan isomerization associated with the movement of hydrogen atoms alongside the furan's skeleton. Up to now, any of the suggested pathways have been observed to the best of our knowledge. In the present work, the fragmentation of the gas-phase furan molecules in collisions with the low-energy cations has been measured by exploiting collision-induced emission spectroscopy. In particular, the formation of the OH radicals has been identified among the fragmentation products. Because these radicals are not structural components of furan molecules, observation of their emission bands implies an isomerization process involving the intramolecular hydrogen migration prior to the cation-induced dissociation, thus confirming the calculations.

References

1. E. Erdmann, et al., J. Phys. Chem. A **122**, 4153−4166 (2018).
2. T. Li, et al., Energy Fuels **35**, 7819−7832 (2021).

Acknowledgements. This work is based upon work from COST Action CA20129 – Multiscale Irradiation and Chemistry Driven Processes and Related Technologies, supported by COST (European Cooperation in Science and Technology). The experiments were carried out at the University of Gdansk using a spectrometer for collision-induced emission spectroscopy. Therefore author thanks professors: A. Kowalski (Univ. of Gdansk) and B. Pranszke (Gdynia Maritime Univ.) for enabling the present measurements.