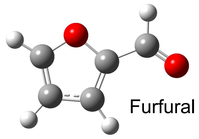
Dissociative Dynamics of Furfural

Gabrielle Anne Lapeña Laguisma,[1] Andras Bodi,[2] and Giovanni Meloni[1,*]

1. Department of Chemistry, University of San Francisco, San Francisco, CA 94117; 2. Molecular Dynamics Group, Paul Scherrer Institut, Villigen 5232, Switzerland

Introduction

Furfural has been proposed as a promising platform for lignocellulosic biofuels.[1,2] In order to easily detect combustion species from furanic biofuels it is crucial to know and understand the photoionization behavior of furfural. Threshold photoionization experiments are performed using the imaging photoelectron-photoion (iPEPICO) coincidence instrument at photon energies between 9 and 16 eV. The fragments of $C_5H_3O_2^+$ (*m/z* = 95), *m/z* = 39, and *m/z* = 29 are observed from the dissociative photoionization process. Data is reported in the form of time-of-flight distributions and breakdown diagrams, used to obtain experimental appearance energies and dissociation rates.



Method

The apparatus will briefly be described here but has been explained in detail elsewhere.[3] Experiments were conducted at the imaging photoelectron photoion coincidence (iPEPICO) endstation at the vacuum ultraviolet (VUV) X04DB bending magnet beamline of the Swiss Light Source (SLS). Samples were introduced effusively at room temperature into the experimental chamber, with typical pressures of ranging between 5.00×10^{-7} – 1.10×10^{-6} bar, then subsequently ionized by incident monochromatic VUV radiation produced from the SLS. Photoelectrons are velocity map imaged onto a position sensitive delay line anode. Their detection begins the time window measurement of cationic species. The distribution of electrons detected in coincidence with a particular cation creates a mass-resolved photoelectron spectrum.[3,4]

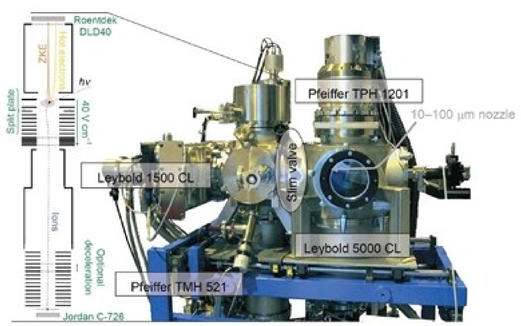


Figure 1. Overview of iPEPICO apparatus

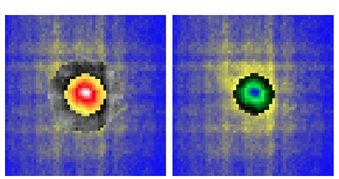


Figure 2. False color photoelectron velocity map image at a photon energy of 13.89 eV. Hot electron (yellow) contamination is removed by a subtraction process of a weighted fraction of the ring area from center spot.

Results

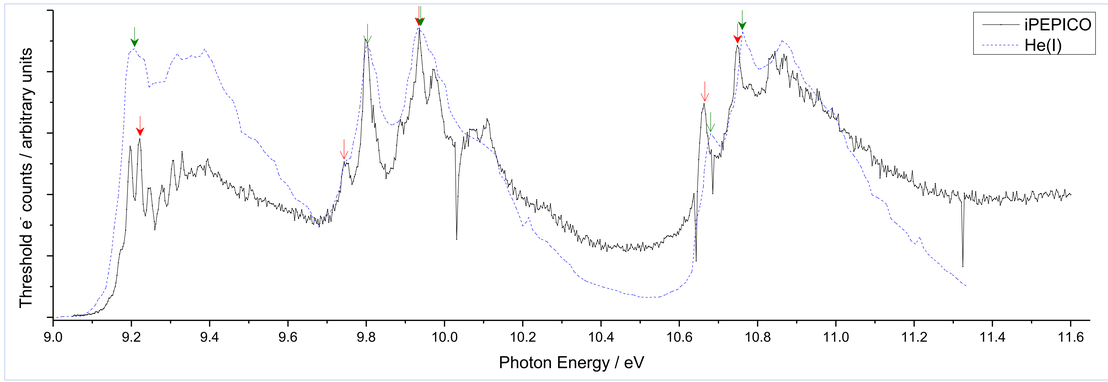


Figure 3. Threshold photoelectron (TPE) spectrum of furfural at room temperature taken with the iPEPICO apparatus (black) and a literature reported He(I) spectrum (blue). Arrows indicate the iPEPICO (red) and He(I) spectrum (green) ionization energies.

Table 1. Experimental ionization energies[a]

iPEPICO / eV	He(I)[b] / eV
9.2215	9.22
9.9358 (9.7437)	9.94 (9.80)
10.7482 (10.6633)	10.76 (10.67)

[a] Vertical values, adiabatic values in parentheses.
[b] Klapstein et al.

Figure 4. Threshold breakdown diagram of furfural collected with iPEPICO setup at room temperature is plotted in **(a)**. Open shapes show experimentally determined abundances, whereas solid lines show the modelling results. The breakdown diagram is fitted simultaneously with the daughter ion center of gravity (CoG). The daughter CoG points and continuous CoG fit, plotted in **(b)**, are based on photon energy scan and threshold photoionization.

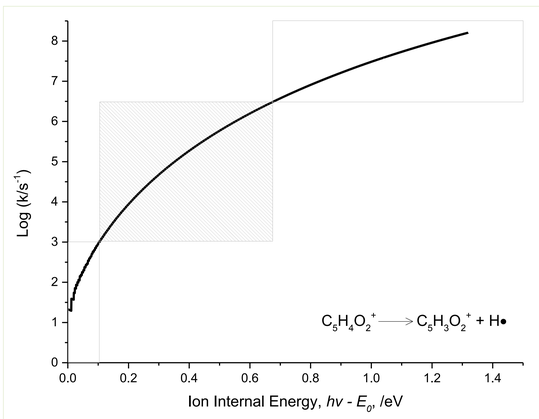


Figure 5. Best fit curves determined by RRKM rate theory for the dissociation channel of $C_5H_4O_2^+$ to $C_5H_3O_2^+$. Shaded area indicates experimental window of directly measurable rates.

Conclusions

Ionization energies of furfural were accurately determined from the TPE spectrum. Experimental values were found to be comparable with those reported in literature. [5]
Below 12 eV, the formation of $C_5H_3O_2^+$ was observed as a result of the formyl hydrogen loss. The 0 K appearance energy of $C_5H_3O_2^+$ was derived to be 11.057 ± 0.033 eV.

Future Work

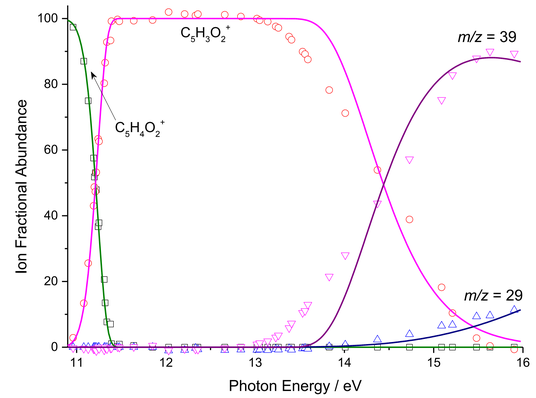


Figure 6. Threshold breakdown diagram of furfural ion dissociations.

The dissociation channels of furfural have been modelled between photon energies of 10.9 to 16 eV. However, modelling results are not reproduced faithfully with the breakdown diagram at higher energies due to the difficulty in finding the appropriate transition state (TS) structures. More TS geometries are currently under investigation.

Acknowledgements

This research is supported by the American Chemical Society – Petroleum Research Fund Grant #51170 UNI6, the University of San Francisco via Faculty Development Fund, and the Swiss Federal Office of Energy (BFE contract 101969/152433). The experimental work reported was carried out at the VUV beamline of the Swiss Light Source.

References

1 Lange, J.-P.; van der Heide, E.; van Buijtenen, J., Price, R. ChemSusChem, 2012, 5, 150-166.
2 Dutta, S.; De, S.; Saha, B.; Alam, I. Catal. Sci. Technol., 2012, 2, 2025-2036.
3 Johnson, M.; Bodi, A.; Schulz, L.; Gerber, T. Nucl. Instrum. Methods Phys. Res., Sect. A, 2009, 610, 597-603.
4 Bodi, A.; Johnson, M.; Gerber, T.; Gengeliczki, Z.; Sztáray, B. Rev. Sci. Instrum., 2009, 80, 034101.
5 Klapstein et al. Can. J. Chem., 1990, 68, 747.