

Electronic excitation and ionic dissociation of the vanillin molecule: photoionization with flavor

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Synopsis: The electronic properties of vanillin molecule were investigated by different excitation and ionization techniques. The ionic fragmentation mechanisms were studied using time-of-flight mass spectrometry as a function of the energy of the incident radiation in the valence energy region and the inner and core levels. It was established as a general feature that the ruptures related to the oxygen atoms are predominant at all energies. The resonances and ionization potential of the oxygen 1s was also determined by NEXAFS spectra.

The major component of natural vanilla is 4-hydroxy-3-methoxybenzaldehyde better known as vanillin (Fig. 1), one of the most used and important flavoring material worldwide. The vanilla is extracted from the bean or the pod of the tropical *Vanilla orchid* (mainly *Vanilla planifolia* Andrews, syn. *V. fragrans* (Salisb. Ames)).¹ Our research group has recently discussed the electronic excitation and ionic fragmentation of volatile natural products, such as limonene,² carvone,³ camphor⁴ among others.



Fig 1. Vanilla plant and vanillin molecular structure.

In the present work, the core electronic excitation and fragmentation of the vanillin molecule has been studied using the NEXAFS and PEPICO techniques. Soft X-rays from the TGM and SGM beamlines at the Brazilian Synchrotron Light Laboratory were used to ionize the sample, and the cations resulting from the photofragmentation process, were characterized according to their mass/charge ratios using a time-of-flight mass spectrometer. For the sake of comparison, TOF mass spectra were also obtained using a He(I) lamp, to access the valence region. An electron gun, tuned at an energy of 800 eV was also employed with the same purpose. Details concerning our experimental methodology may be found in the afore mentioned papers.

The NEXAFS spectrum of the vanillin molecule (Fig. 2) has been studied around the O 1s edge (525 – 555 eV). Since the vanillin molecule features oxygen atoms in three different chemical

environments (C-O-H, C-O-CH₃ and C=O) several bands would be expected. However, within our experimental resolution, a single resonance was observed at 531 eV, being assigned mainly to a O 1s $\rightarrow \pi^*_{C=O}$ transition.

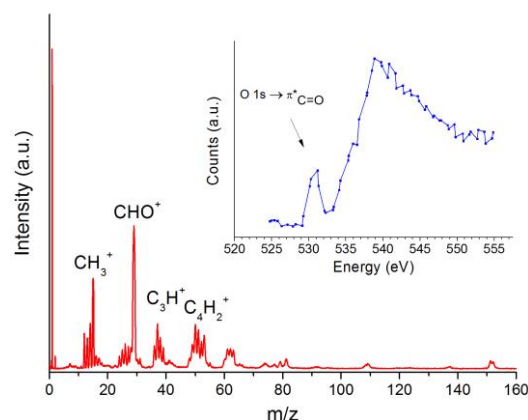


Fig 2. PEPICO spectrum measured at 531 eV and NEXAFS (insert) spectrum around the O 1s energy region for the vanillin molecule.

The TOF-MS spectra, measured either in a PEPICO using a He I Lamp (12 and 21.20 eV), synchrotron radiation (130, 310, 531 and 550 eV) or using an electron gun (800 eV) showed as a common feature ruptures involving the oxygen atoms. For example, the main fragments observed at all energies are H⁺, CH₃⁺, CHO⁺, C₆H₅O⁺, C₈H₇O₃⁺ and C₈H₈O₃⁺. Although the degree of molecular fragmentation increases steadily with increasing photon energy, essentially the same fragments are observed. A preference for site-specific dissociation of the oxygen atom is suggested.

References

- [1] J. Nicholas *et al* 2003 *Phytochem.* **63**, 505.
- [2] R. B. de Castillo *et al* 2007 *J. Elect. Spectr. Rel. Phenom.* **155**, 77. [3] R. B. de Castillo *et al* 2014 *J. Elect. Spectr. Rel. Phenom.* **192**, 61. [4] R. B. de Castillo *et al* 2014 *Rapid Commun. Mass Spectrom.* **28**, 1769.

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