

OPTIMIZATION OF MASS SPECTROMETRIC IONISATION EFFICIENCY DATA

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ABSTRACT. A new method is developed and tested to find out the excited electronic and vibrational energy levels (fine structure) of molecules from mass spectrometric ionisation efficiency data which were obtained by a conventional mass spectrometer ion source having normal electron energy distribution.

Electrons emitted in a conventional mass spectrometer ion source are not monoenergetic, therefore, evaluation of Ionisation Potentials (IP) and Appearance Potentials (AP) from experimental data creates some problems. This is even worse in the evaluation of Fine Structure (excited electronic and vibrational energy levels) from ionisation efficiency data [1]. This is overcome either by using specially designed monoenergetic ion sources which have their own problems (manufacture of special design, difficulty of operation, too much decrease of ion current), or by eliminating disturbing effects in the ionisation efficiency data by some deconvolution techniques [2,4,5,6,7,9].

In this study attempts were made to eliminate the deteriorating effects (mainly arising from electron energy distribution and noise) in the ionisation efficiency data by a deconvolution technique.

The technique was applied to the ionisation efficiency data of molecular nitrogen, oxygen and methylamine and its fragment and interesting results were obtained.

1. Introduction

Molecular and fragment ions, excited to various electronic levels may be formed with excess energy, and if the transferred energy is appropriate, excitation to different vibrational (and translational) energy levels is also possible. Difference between these energy levels can be detected by appropriate techniques [3]. Electrons emitted from a conventional mass spectrometer ion source obey the Maxwell energy distribution and have an energy spread. However it is possible to decrease this energy spread by some deconvolution techniques. Some of these deconvolution techniques are The First

Differential of the ionisation efficiency data [3,4], The Second Differential of the ionisation efficiency data [5]; Energy Distribution Difference Technique (EDD) [4]; Double EDD [6]; and The Inverse Convolution Technique [7]. The Inverse Convolution Technique proposed by Morrison gives very satisfactory results for ionisation efficiency data. This technique uses Fourier Transformation and has gained importance after the improvement of Fast Fourier transformation (FFT) [8]. Smoothing Technique of Savitzky and Golay [9] was also used by some experimenters to eliminate the effect of noise from experimental data. However, smoothing spreads the deteriorating effect of a bad data to a certain data region therefore prevents precise and satisfactory results [10].

In this study, spoiling effects of electron energy spread and noise on the mass spectrometric ionisation efficiency data were eliminated by using filters and FFT deconvolution.

The deconvolution technique used to eliminate a distorting effect from an experimental data can be explained as follows. The function of the distorting effect is formed. Inverse Fast Fourier Transform of both this function and the experimental data are obtained. Then Fast Fourier Transform of the experimental data are divided by the Fast Fourier Transform of the function of the distorting effect. Inverse Fast Fourier Transform of this function gives the signal data which is stripped from the distorting effect (figure 1).

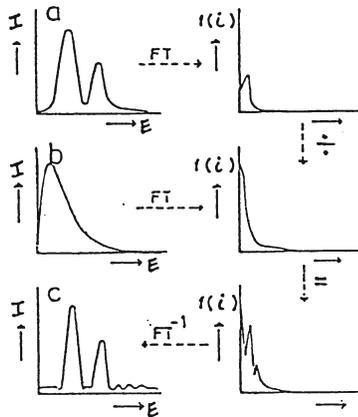


Figure 1. Improvement of experimental data by using the deconvolution technique.
a) deteriorated signal b) deteriorating signal, c) improved signal.

2.Experimental

The experiments were carried out by a CH7 model VARIAN MAT mass spectrometer connected to a PC-XT computer. The mass spectrometer has a conventional electron impact ion source, a magnetic sector analyser and a faraday cage detector. External vacuum measuring / control system was connected to the mass spectrometer. Also an isolated external electron energy control module which itself could be controlled by the computer was connected between the mass spectrometer and the computer, and electron energy could be increased by small (0.01V) steps. The collector of the mass spectrometer was also connected to the computer so that data could be stored and processed afterwards.