CHAPTER 1

INTRODUCTION AND AIM OF THE WORK .

1.1. INTRODUCTION :-

In recent years the applications of mass spectrometry to the field of positive ions have been developed and increase continuously. Mass spectrometry is frequently used to acquire qualitative and/or quantitative infomations on the sample introduced into the instrument . That is,it is often employed as an analytical technique(1). Applications extend throughout chemistry, physics, geology, and biology and typical uses in chemical physics include : Mass spectra of molecules , energetic study of positive ions such as ionization energy (I), appearance energy (AE), electronic energy states (and in certain cases vibrational energy states), electron and proton affinities as well as structure of positive and negative ions(1).

One of the most important applications of mass spectrometry is to study ionization and fragmentation of organic molecules. Since the energy of ionization and fragmentation of organic molecules is dependent upon structures(2-4), it should be possible to use experimentally determined ionization and appearance energies as a source of information for structural elucidation of molecules(5). The importance of ion structures for both fundamental studies of ion reactions and determination of unknown molecular structures would make valuable a simple , direct method for ion structure identification and characterization(6).

In mass spectrometry the fragment ions are formed in a series of competitive and consecutive fragmentation of the molecular ion(7) . Elucidation of structure of the ions needs some information about the paths along which particular fragment ions are formed and also how many fragmentation steps are involved in their formation . Information concerning some individual steps involved can be gleaned from energetic considerations e.g. *thermodynamical threshold* (ΔE_{th}) *calculations* or from *observation of metastable ions*(7).

Inspection of the published work done on the mass spectra, ionization and fragmentation as well as structural elucidation of 1,2-Ethanediol,1,3-Propanediol and 1,4-Butanediol show that:

1- Mass spectrometric fragmentation of a series of diols , among them 1,2-Ethanediol, 1,3-Propanediol and 1,4-Butanediol are studied by **Blanck** et al(8). They(8) observed that the intensity of some ions containing oxygen atom e.g. $[CH_2OH]^+$ (m/z=31) decreases with increasing chain length . Also, they observed that an extensive labelling of 1,4-Butanediol with deuterium allows fragmentation modes to be proposed .

2- **Holmes** and **Lossing**(9) measured the ionization energy at threshold for 1,2-Ethanediol using monoenergetic electron beam, while **Ballard** et al.(10) measured the ionization energy at threshold as well as higher energy levels using photoelectron spectroscopy and ab initio MO calculations. On the other hand, for the best of the present author knowledge, no values are found in literature for the ionization energies as well as the higher energy levels for 1,3-Propanediol and 1,4-Butanediol.

3- The only reported value of appearance energy (AE) for m/z=31 fragment ion obtained from 1,2-Ethanediol was measured by **Holmes** and **Lossing**(11) using monoenergetic electron beam . The structure of the m/z=31 fragment ion produced from the presently studied precursors had not been studied before .

4- The structure of $[C_2H_3O]^+$ (m/z= 43) ion obtained from 1,2-Ethanediol was studied by **Weber** and **Levsen**(12) and **Terlouw** et al(13) using collisional activation (CA) mass spectra .

5- The only reported AE value for $[C_2H_5O]^+$ (m/z=45) fragment ion was that obtained from 1,3-Propanediol and measured by **Burgers** et al(14) using monoenergetic electron beam . On the other hand, the structure of $[C_2H_5O]^+$ (m/z=45) fragment ion obtained from 1,2-Ethanediol and 1,3-Propanediol was studied by **McLafferty** et al.(6) using collisional activation (CA) mass spectra, while **Burgers** et al.(14) studied the same frag-