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**Mass Spectrometric Investigation of
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Magic Numbers and Structural Implications**

by

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Mass Spectrometric Investigation of 2 - Methoxyethanol And 2 - Ethoxyethanol Clusters: Magic Numbers and Structural Implications.

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Abstract

In this paper we present the results of our mass spectrometric investigations for van der Waals clusters of 2 - methoxyethanol and 2 - ethoxyethanol. The cluster mass spectra were acquired for a variety of expansion conditions and electron energies. The protonated alkoxyethanol cluster ions $(AE)_nH^+$ form the dominant cluster ion series. A number of fragment ions, that may arise from an unprotonated and/or a protonated alkoxyethanol molecular ion, were solvated by additional alkoxyethanol molecules. The $(AE)_n(H_2O)_mH^+$ ions were observed with significant intensities only for $n \geq 5$ in neat as well as mixed alkoxyethanol/water expansions. It was also found that $(AE)_n(H_2O)_mH^+$ cluster ions which satisfy the condition $n = 2(m + 2)$, for $m = 1$ and 2 , have enhanced ion intensities. The various models that may explain the behavior of $(AE)_n(H_2O)_mH^+$ are discussed.

1) Introduction

The study of van der Waals clusters has received considerable attention in recent years.¹⁻⁴ The reason stated most often for studying van der Waals clusters is to bridge the conceptual gap between gas phase and condensed phase systems.⁵ The study of gas phase cluster ions by mass spectrometry has enabled the variations in chemical reactivities and stabilities of ions to be probed as a direct function of the degree of solvation.^{6 - 13} In a few cases, chemical reactions which have no counterpart in conventional bimolecular gas phase chemistry have been observed within the uniquely stabilizing cluster environment.^{7,8(a),11,13} Although the cluster mass spectra of a large number of van der Waals clusters usually exhibit an exponential decrease in the intensity of cluster ion sequences with increasing cluster size, the cluster mass spectrum (CMS) of certain molecular systems have displayed intensity anomalies (magic numbers) which are taken as an indication of the stabilities of cluster ions.^{8(a),9,14-16} Typically, magic numbers do not always manifest themselves as prominent peaks, but more often appear as discontinuities in the smooth cluster ion intensity distributions. Magic numbers have been attributed to (a) the completion of a solvation shell;^{8(a),17,18} (b) the onset of hydrogen bonded cyclic ions from chain-like structures;¹⁴ and (c) the formation of large clathrates that encage the

ionic moiety.^{15,16}

Ethers, alcohols, and water, as well their mixtures, have become the focus of a large number of investigations as these systems exhibit a large propensity for hydrogen bonding. Cluster ions of the type $(M)_n(H_2O)_mH^+$ where M has a proton affinity greater than water has been the subject of numerous investigations.^{9,10,18-23} Studies involving mixed expansions of ethers^{10,18}, ketones^{18,23}, and acetonitrile²², with water indicate a tendency for the central ion core to change from MH^+ to H_3O^+ at a particular cluster size. The intensity distributions of such cluster ions $(M)_n(H_2O)_mH^+$ exhibit strong magic numbers which have been explained using structures which have protonated water and water clusters as their ion core. A number of molecules which have proton affinities higher than water but are capable of acting as proton acceptors only have exhibited this kind of behavior.

Studies involving mixed clusters of alcohol with water are of considerable interest as alcohols are capable of acting as both proton donors and proton acceptors. Kebarle and coworkers¹⁹ have investigated the thermodynamics for clustering in methanol/water system using high pressure mass spectrometry (HPMS). Although the range of cluster sizes investigated for $(CH_3OH)_n(H_2O)_mH^+$ was small ($n+m \leq 6$), the degree to which alcohol was preferred was found to decrease with increasing cluster size leading Kebarle

and coworkers to predict that water would be the preferred solvent for $(n+m) \geq 9$. Stace and coworkers^{20,21} determined the branching ratios for the metastable dissociation of alcohol/water clusters $(\text{ROH})_n(\text{H}_2\text{O})\text{H}^+$ and reported that water loss is more predominant from smaller clusters whereas alcohol is lost to a greater extent from larger clusters. This changeover was reported to occur over the size range $n = 8 - 10$ depending on the identity of the alcohol. The size determinations for the switch in the preferred solvent was stated to have an error of $n \pm 1$. Even though the studies by Stace and coworkers are only qualitative in that they gain no thermodynamic information from their studies, the results obtained from free jet expansions was quite similar to that obtained in equilibrium experiments.

In a recent report involving mixed expansions of alcohols and water, we reported that the cluster ions $(\text{ROH})_n(\text{H}_2\text{O})\text{H}^+$ were observed only for $n \geq 7$ and found to have enhanced stability at $n = 9$.⁹ This observation was in general agreement with the predictions of Kebarle and the observations of Stace regarding the size at which a changeover in the solvent preference. We speculated that mixed cluster ions $(\text{ROH})_n(\text{H}_2\text{O})\text{H}^+$ for $n \geq 7$ arise from the complete solvation of a H_3O^+ ion core by an "open" ring of alcohol molecules, first at $n = 7$ and then closure of this ring at $n = 9$. In addition a similar structural model was also invoked to explain the enhanced stability

of $(\text{ROH})_{10}(\text{H}_2\text{O})_2\text{H}^+$. The structures proposed for $(\text{ROH})_9(\text{H}_2\text{O})\text{H}^+$ and $(\text{ROH})_{10}(\text{H}_2\text{O})_2\text{H}^+$ are consistent with earlier studies where H_3O^+ was suggested to form the ion core in mixed cluster ions even for systems having components with a higher gas phase proton affinity than that of water. These structures are also qualitatively similar to the ones proposed in previous studies where H_3O^+ and Cs^+ were suggested to be encaged in gas phase clathrates formed by extensive intermolecular hydrogen bonding.^{15,16}

In the last decade, water clusters have been generated by various techniques and the $(\text{H}_2\text{O})_{21}\text{H}^+$ clusters were found to be exceptionally stable.¹⁶ It was conjectured that the H_3O^+ is solvated by a cage of 20 water molecules. The structure of this species has been confirmed more recently by Castleman and coworkers¹⁶ through titrating the free hydrogen atoms extending away from the clathrate cage with trimethylamine (TMA) taking advantage of the fact that TMA can only act as a proton acceptor. Castleman and coworkers¹⁵ have also reported magic numbers in the intensity distribution of $\text{Cs}(\text{H}_2\text{O})_n\text{H}^+$ which they suggest arises from a Cs^+ being encaged within large water clusters.

The studies conducted by Castleman and coworkers,^{11,16} using a fast flow reactor, provided strong evidence against magic numbers resulting from non-equilibrium growth kinetics. It has also been pointed out that the

intensity distribution of cluster ions generated in flow reactors are similar to that observed in supersonic expansions followed by electron induced or photoionization. This suggests that studies involving (a) generation of neutral clusters by free jet expansion followed by electron impact or photoionization, and (b) setups where the desired ion can be expanded along with the solvent of interest, provide information which is qualitatively similar. Even though the studies where cluster ions are produced by adiabatic expansions are limited by the fact that they yield no thermodynamic data, the nonequilibrium conditions enable generation of much larger cluster ions than those observed in HPMS setups.

The reactivity and stability (magic numbers) of cluster ions generated in neat as well as mixed expansions of various classes of monofunctional compounds have been investigated extensively. However, there have not been many systematic investigations of van der Waals clusters composed of bifunctional compounds. As the reactivity and stability of van der Waals clusters composed of alcohols, ethers and their mixed expansions with water have been investigated extensively and is fairly well understood, we chose to study neat expansions of 2 - methoxyethanol and 2 - ethoxyethanol as well as mixtures of these two liquids with water. While the overall objective was to investigate the influence of solvation on chemical reactions in bifunctional

compounds, the principle aims were as follows: (1) to determine whether the presence of a hydroxyl and an ether group in the same molecule would affect the intensity distribution of cluster ions of the type $(AE)_n(H_2O)H^+$ (i.e. would these cluster ions be observed with significant intensity for small values of n as in the case of ethers ($n \leq 4$)^{10,18} or would they be observed only in larger clusters as in the case of alcohols^{9,11}); and (2) to determine whether the intensity distribution of $(AE)_n(H_2O)_mH^+$ shows any evidence of enhanced stability for a particular cluster size.

2) Experimental

The general experimental setup has been described in detail in an earlier publication.²⁴ The neutral cluster beam is generated by a continuous Campargue-type beam source²⁵ using a 250 μ nozzle 5 mm from a conical skimmer. This cluster beam is skimmed and collimated by a second skimmer before entering the chamber containing the mass spectrometer (EXTREL, C-50). A small fraction of this beam is ionized by a collinear electron ionizer and the ions are accelerated into the quadrupole mass filter and detected by a particle analyzer. The electron energy in this study was varied in the range 15.0 - 70.0 eV with the emission current being held constant at 0.65 mA.

Neat 2 - methoxyethanol and 2 - ethoxyethanol clusters, as well as mixed clusters of alkoxyethanols with H_2O , were generated by passing He through a reservoir containing these liquids. The stagnation pressure (P_0) of Helium used in this study was varied in the range 0.8 to 1.8 atm. while the pressure in mass spectrometer chamber varied in the range 2.0 to 7.5 X 10^{-7} torr respectively.

In all the experiments conducted during this study Helium (Irish, 99.995%) was used as the carrier gas. 2 - methoxyethanol (Aldrich, Certified 99.9 %), 2 - ethoxyethanol (J.T. Baker, Certified 99.9 %) and triply distilled water were used after repeated freeze-pump-thaw cycles to remove any dissolved gases. The gas handling system and the mass spectrometer were routinely baked out to reduce the level of background signals from H_2O , N_2 and O_2 .

Collision induced dissociation (CID) experiments were performed in a triple quadrupole mass spectrometer (TQMS) (VGTRIO-3). The first (Q1) and third (Q3) quadrupoles require both rf and dc potentials to provide mass filtering and resolution and have an upper mass detection limit of 2000 amu. The collision cell (Q2) requires only rf potentials to guide the ions from Q1 through the collision cell ($E_{lab} = 0.1 - 100$ eV). The alkoxyethanol samples were introduced through a heated liquid injection

port. The pressure in the ion source was in the range 9.0×10^{-6} to 2.0×10^{-5} torr during this process. This enables the generation of $\text{ROCH}_2\text{CH}_2\text{OH}^+$, $[\text{ROCH}_2\text{CH}_2\text{OH}]\text{H}^+$ and $[\text{ROCH}_2\text{CH}_2\text{OH}]_2\text{H}^+$ in addition to smaller fragments in copious amounts. The electron energy was set to 70.0 eV and source was maintained at 200 °C. Helium was used as the collision gas in Q2 and the pressure in the collision cell was maintained at 1.6 mtorr for all the studies reported in this work.

3) Results and Discussion

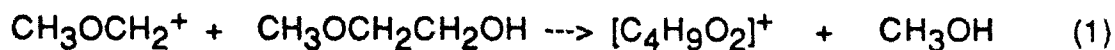
(A) Reactivity:

(i) Neat Expansions of 2- methoxyethanol:

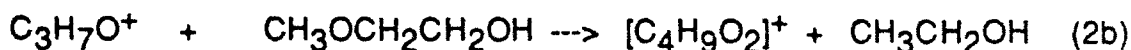
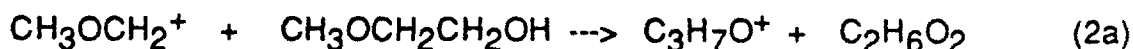
The CMS for neat expansions of 2 - methoxyethanol exhibit a number of different cluster ion series as can be seen in Figure 1. The protonated 2 - methoxyethanol cluster ions, i.e. $(\text{ME})_n\text{H}^+$, form the dominant cluster series and are labelled as "a_n". Small amounts of unprotonated cluster ions , i.e $(\text{ME})_n^+$, were also seen for the smaller cluster sizes , i.e n = 1 - 3. This is particularly interesting as protonated cluster ions are almost exclusively observed in neat expansions of molecules that are capable of hydrogen bonding. The $(\text{ME})_n(\text{H}_2\text{O})\text{H}^+$ were also observed and are labeled as "b_n". This cluster ion series was observed with significant intensity only for $n \geq 5$.

Additional cluster ion sequences, too numerous to be labelled individually in Figure 1, are listed in Table 1.

An ion was observed at $m/z = 89$. This ion may be attributed to either (a) a cluster ion where a CH^+ fragment is solvated by a 2 - methoxyethanol molecule, or (b) a molecular ion with the empirical formula $\text{C}_4\text{H}_9\text{O}_2^+$. Caserio and coworkers^{26,27} had observed an ion at this mass and suggested the following ion-molecule reaction as the route for the formation of this ion:



Eyler and coworkers²⁸ also suggest that this ion may arise from two consecutive reactions involving $\text{C}_3\text{H}_7\text{O}^+$ ($m/z = 59$) cation as follows:



(ii) Neat expansions of 2 - ethoxyethanol:

The CMS obtained for neat expansions of 2 - ethoxyethanol are very similar to that obtained for neat 2 - methoxyethanol expansions in that they also have protonated cluster ions, $[\text{EE}]_n\text{H}^+$, (labelled as " a_n " in Figure 2) as the dominant cluster ion series and small amounts of unprotonated cluster ions, $[\text{EE}]_n^+$, were observed for smaller cluster sizes. Other cluster ion series that can be seen in Figure 2 but are not labelled are listed in Table 2.

The $(EE)_n(H_2O)H^+$ were observed with significant intensity only for $n \geq 5$.

An ion was observed at $m/z = 103$. This ion may be a CH^+ fragment associated with an 2 - ethoxyethanol molecule or arise from reactions analogous to the reactions (1) and (2).

(B) Origin of $(ME)_n(H_2O)H^+$ and $(EE)_n(H_2O)H^+$ Cluster Ions:

The $(ME)H^+$ ($m/z = 77$) was generated in the ion source of the TQMS and the MS-MS spectrum for the collision induced dissociation (CID) of this ion were obtained using He as the collision gas. A typical CID spectrum for this ion obtained from 10.0 eV (lab) collisions is shown in Figure 3. The most intense ions in this spectra are observed at $m/z = 59$ and 45 corresponding to the loss of either a single H_2O or CH_3OH molecule from the protonated methoxyethanol molecular ion. Additional peaks observed at $m/z = 33$ and 19 may correspond to protonated methanol $CH_3OH_2^+$ and the H_3O^+ ion respectively.

The CID spectrum of protonated 2 - ethoxyethanol molecule, $(EE)H^+$, ($m/z = 91$) is shown in Figure 4. Prominent ions are seen at $m/z = 73$ and 45 corresponding to the loss of a H_2O and a C_2H_5OH molecule from the protonated 2 - ethoxyethanol molecule respectively. Ions observed at $m/z = 47$ and 19 may be assigned as $C_2H_5OH_2^+$ and H_3O^+ respectively.

The 2 - methoxyethanol (< 0.005% H₂O) and 2 - ethoxyethanol (<0.07 % H₂O) used in this study have only traces of water while the gas handling lines and the mass spectrometer chambers were baked out to reduce moisture content to a minimum. This leads us to conclude that the [ME]_n(H₂O)H⁺ and [EE]_n(H₂O)H⁺ observed in the CMS for neat expansions of 2 - methoxyethanol and 2 - ethoxyethanol arise from intracuster ion-molecule reactions.

(B) Magic Numbers and Structural Implications for [AE]_n(H₂O)_mH⁺ Cluster Ions:

The variations in the intensity distribution of cluster ions belonging to the series [AE]_n(H₂O)H⁺ in neat expansions of 2 - methoxyethanol and 2-ethoxyethanol are shown in Figures 5 and 6 respectively. The form of the intensity distribution for this cluster ion series remains the same for a wide variety of stagnation pressures of He and electron impact ionization energies. The CMS acquired when mixtures of alkoxyethanol and small amounts of water were expanded through the nozzle lead to a large enhancement in the intensities of ions of [AE]_n(H₂O)H⁺ cluster ions. The CMS for mixed expansions of alkoxyethanols with water are shown in Figure 7. The intensities of the heterocluster ions, [AE]_{n≥6}(H₂O)H⁺, is comparable if not greater

than greater than the intensities of protonated alkoxyethanol $(AE)_{n \geq 6}H^+$ in mixed expansions as can be seen from Figure 7. Figures 8 and 9 show the variations in the intensity of $(AE)_n(H_2O)H^+$ cluster ions with increasing cluster size for mixed expansions of 2 - methoxyethanol and 2 - ethoxyethanol as a function of energy and stagnation pressure respectively. The overall profile of the intensity distribution is identical for the $(AE)_n(H_2O)H^+$ cluster ions formed from neat expansions. This leads us to suggest that the addition of small amounts of water does not significantly perturb the cluster distribution and the large increase in the intensity of $(ROEtOH)_{n \geq 5}(H_2O)H^+$ is a reflection of the overall stabilities of these cluster ions. In all the plots showing the intensity distributions of $(AE)_n(H_2O)H^+$ ions as a function of cluster size, these ions are only observed in significant amounts for $n \geq 5$ and exhibit a maxima at $n = 6$.

The observation of mixed cluster ions $(AE)_n(H_2O)H^+$ in substantial quantities only for $n \geq 5$ in neat as well as mixed expansions is qualitatively similar to the intensity anomalies observed for $(ROH)_n(H_2O)H^+$ and $NH_4^+[NH_3]_n(H_2O)_m$ cluster ions, in that these ions are observed with significant intensity only beyond a certain value of n , i.e. water is the preferred solvent above a critical size. As the proton affinity of alcohols is greater than that of water, the proton is expected to be associated with the alcohol

molecule for small cluster sizes. Stace and coworkers^{20,21} rationalized the change in solvent preference for $(\text{ROH})_n(\text{H}_2\text{O})\text{H}^+$ by suggesting a structural model where methanol molecules hydrogen bond to form a $(\text{ROH})_3\text{H}^+$ core. This ion core would be associated with additional methanol molecules as charge enhanced hydrogen bonds between the ion core and methanol would be stronger than the water - methanol ion core interactions. As the cluster size increases, the methanol molecules would be further away from the ion core and the hydrogen bond strengths would decrease and eventually drop below that of the water - methanol core interaction and then the preferred solvent will change from methanol to water. Kebarle and coworkers²⁹ had also found that in $\text{NH}_4^+(\text{NH}_3)_n(\text{H}_2\text{O})_m$ cluster ions, ammonia is the preferred solvent in the first solvation shell while water is highly favored beyond in the first solvation shell. The solvent switch was rationalized by suggesting a NH_4^+ as the core and ammonia molecules by virtue of their higher proton affinity would hydrogen bond strongly to the ion core. At distances greater than the first solvation shell the weak ion dipole interactions are more important and water on account of its high dipole moment can solvate better than ammonia.

Extensive studies with bifunctional compounds such as diamines, aminoalcohols, diethers and alkoxyalcohols suggests that these molecules on

protonation form an internal hydrogen bond as shown in structure 1.³⁰ It has also been suggested that the internal hydrogen bond between the two functional groups should be linear for maximum stability.³¹ In bifunctional ethanes the constraints imposed by the molecular structure can distend and distort the angle of the hydrogen bond from its optimal geometry. Meot-Ner suggested that the exceptionally weak bonds and loose structure in $XCH_2CH_2YH^+$ may indicate that this cyclic ion (structure 1) is not permanent.³⁰ Solvation of the hydrogen bonded ion delocalizes the charge onto solvent molecules. Thus, solvation can not only weaken but in extreme cases displace the original intramolecular hydrogen bond. Based on thermochemical data it was suggested that monohydration or dimerization of protonated dimethoxyethane can bring about the opening of the intramolecular hydrogen bond.³⁰ This effect was noted in other diethers also as the internal bonding of the only $-OH^+$ can effectively block further clustering under moderate conditions.³¹ However, in other proton bridged bifunctional molecules, such as aminoalcohols and diamines having additional protonic binding sites, three or four more solvent molecules can solvate the protonated molecule before the internal hydrogen bond is opened.³⁰ Protonated methoxyethanol and ethoxyethanol could also form an internal hydrogen bond, even though on account of the non linear geometry of the hydrogen

bond, maximum stability may not be achieved. The presence of the -OH group may enable at least the dimerization to take place without the displacement of the internal hydrogen bond. The proton affinities of the methoxyethanol and ethoxyethanol are at least comparable to that of ethanol but may be higher.³² Thus based on proton affinity values alone it is quite likely that the protonated alkoxyalcohol molecule would be preferentially solvated by other alkoxyethanol molecules rather than water. However at greater distances from the protonated ion core, water molecules (1.85 D)³³ by virtue of a higher dipole moment than that of -OH (1.24 D)³⁴ and -OCH₃ (0.81 D)³⁴ bonds would interact more strongly with the ion core. We have compared the dipole moment of water with the bond dipole moments rather than the dipole moment of methoxyethanol (2.36 D in the gauche form)³³ because it is the individual bonds rather than the alkoxyalcohol molecule as a whole that would be interacting with the ion core.

As has been discussed earlier solvation of a protonated bifunctional molecule by additional solvent molecules can lead to the opening of the internal hydrogen bond. It appears that when the number of solvent molecules equals or exceeds the number of protonic sites available for additional hydrogen bonding, the internal hydrogen bond is displaced.³⁰ Though there is no report on the specific number of solvent molecules required for the ring

opening in protonated alkoxyalcohol molecules, it may not be unreasonable to expect the same behaviour in protonated alkoxyalcohol clusters; i.e. $\{AE\}_{n \geq 5}H^+$ may form chain like structures. Hence $\{AE\}_{n \geq 5}(H_2O)H^+$ would have long chains of alkoxyethanol molecules forming the inner shell around a protonated ROEtOH molecule with water being held in the outer shell. Even though the model discussed above explains the preference for alkoxyalcohol molecules for smaller cluster sizes and water for larger cluster sizes this does not explain the stability of $\{AE\}_6(H_2O)H^+$.

Meot-Ner studied the solvation of protonated aminoethanol and ethane diamine by water and suggested that the stabilization of $\{NH_2CH_2CH_2OH\}(H_2O)_2H^+$ results from a cyclic structure involving intermolecular hydrogen bonding with the two water molecules bridging the $-NH_3^+$ and $-OH$ groups.³⁰ The stability of this bridged structure could result from the fact that the hydrogen bonds in this structure can have a nearly linear geometry. The proton may very easily shift to a water molecule so that the ion may be considered to be $\{NH_2CH_2CH_2OH\}(H_5O_2)^+$; i.e the proton switches from aminoethanol to the water portion of the heterocluster ion. Such a switch has also been suggested by Deakyne and Meot-Ner²² in $\{CH_3CN\}_2(H_2O)H^+$ even though the proton affinity of CH_3CN is 21.7 kcal/mol greater than that of water. The study of metastable decompositions

in other $\{M\}_n\{H_2O\}_mH^+$ where M is an ether^{10,18} or a ketone^{18,23} have also been rationalized by invoking the proton switch model, i.e. protonated water and water clusters form the ion core. The enhanced stability of $\{CH_3OCH_3\}_n\{CH_3OH\}H^+$ at $n = 2$ was also rationalized in terms of the proton switch model, i.e. the protonated methanol, $CH_3OH_2^+$, forms the ion core even though the gas phase proton affinity of methanol is lower than that of dimethylether.^{8(a)}

We have found that neat expansions of dimethoxyethane also exhibit enhanced stability for $\{CH_3OCH_2CH_2OCH_3\}_n\{H_2O\}H^+$ at $n = 3$.³⁵ Thus it appears that even though $CH_3OCH_2CH_2OCH_3$ molecules have a higher proton affinity than water and two sites capable of acting as proton acceptors, the proton is associated with the water molecule. This would enable the H_3O^+ to form the ion core and thus maximise the number of $CH_3OCH_2CH_2OCH_3$ molecules to hydrogen bond to the central core. The intensity distribution of $\{CH_3OCH_2CH_2OCH_3\}_n\{H_2O\}H^+$ cluster ions, suggest maximum stability at $n = 3$ while the intensity of $n = 4$ was very much smaller. This is consistent with the observations of Stace and coworkers for $\{CH_3OCH_3\}_n\{H_2O\}_mH^+$.¹⁸ The form of the intensity distributions of $\{AE\}_n\{H_2O\}H^+$ are very much different from that of $\{CH_3OCH_3\}_n\{H_2O\}H^+$ and $\{CH_3OCH_2CH_2OCH_3\}_n\{H_2O\}H^+$ in that the intensity of the

alkoxyethanol/water heterocluster ions are significant only beyond $n = 5$ and maximise at $n = 6$. This trend may result from ethers being capable of acting only as proton acceptors whereas the alkoxyethanol molecules have two sites that can act as hydrogen bond acceptors and a site that can be a hydrogen bond donor.

An alternative model for $\{\text{ROEtOH}\}_n(\text{H}_2\text{O})\text{H}^+$ clusters may consist of a central H_3O^+ unit that can hydrogen bond directly to 3 alkoxyethanol molecules through the ether end (ethers have a higher proton affinity than alcohols) and that still leaves the $-\text{OH}$ groups free for additional hydrogen bonding. This model not only explains the difference in the intensity distributions of $\{\text{AE}\}_n(\text{H}_2\text{O})\text{H}^+$ from that of either $\{\text{CH}_3\text{OCH}_3\}_n(\text{H}_2\text{O})\text{H}^+$ and $\{\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3\}_n(\text{H}_2\text{O})\text{H}^+$ but also enables us to understand the enhanced stability of mixed alkoxyethanol/water cluster ions at $n = 6$. Thus $\{\text{AE}\}_6(\text{H}_2\text{O})\text{H}^+$ ions may have structures as shown in structure 2. It is also quite possible for cluster ions shown in structure 2 to form bridged structures by additional hydrogen bonding interactions as shown in Figure 10. The intermolecular hydrogen bonding among the various alkoxyethanol molecules shown in Figure 10 are nearly linear and hence would not impose strain on the structure but may impart considerable stability to the cluster ion structure. Examination of space filling models shows that in all cases

the alkyl groups lie outside the hydrogen bonded rings. Hence, the proposed structures are independent of alkyl group in alkoxyethanols. The structural model shown in Figure 10 is very similar to the one we had proposed earlier to account for the enhanced stability of $\{\text{ROH}\}_9\{\text{H}_2\text{O}\}\text{H}^+$ and $\{\text{ROH}\}_{10}\{\text{H}_2\text{O}\}_2\text{H}^+$.⁹ The results obtained for $\{\text{ROH}\}_n\{\text{H}_2\text{O}\}_m\text{H}^+$ and $\{\text{AE}\}_n\{\text{H}_2\text{O}\}\text{H}^+$ are very similar in that water is present in these heterocluster ions are observed with significant intensities only beyond a critical size. This leads us to suggest that the formation of hydrogen bonded networks among the alkoxyethanol molecules solvating the central H_3O^+ may be a general feature in mixed cluster ions of the type $\{\text{M}\}\{\text{H}_2\text{O}\}\text{H}^+$, when M has the capacity to act as both as proton donor and proton acceptor. Such networks involving extensive hydrogen bonding have also been stated to be the reason for enhanced stability of large water clusters.¹⁶

Lastly, experiments were also conducted with larger amounts of water in mixed expansions of 2 - methoxyethanol so that cluster ions of the type $\{\text{ME}\}_n\{\text{H}_2\text{O}\}_m\text{H}^+$ would also be generated.³⁶ Based on the above model, where the central H_3O^+ ion is solvated by two shells of 2 - methoxyethanol molecules to yield enhanced intensity for $\{\text{ME}\}_6\{\text{H}_2\text{O}\}\text{H}^+$ ion, one would expect a magic number at cluster sizes which satisfy the condition $n = 2(m+2)$. As can be seen from Figure 11, the intensity distribution of

$\{\text{ME}\}_n\{\text{H}_2\text{O}\}_2\text{H}^+$ shows a magic number at $n = 8$ and may have a central ion core shown in structure 3 with two shells of 2 - methoxyethanol molecules bonded to each free hydrogen bonding position. It can also be seen from Figure 11 that the intensity of $\{\text{ME}\}_4\{\text{H}_2\text{O}\}_2\text{H}^+$ is negligible while the intensity is maximum for $\{\text{ME}\}_8\{\text{H}_2\text{O}\}_2\text{H}^+$. Thus the behavior of $\{\text{ME}\}_n\{\text{H}_2\text{O}\}_m\text{H}^+$ is consistent with the suggested model where a proton switch to a water molecule enables formation of a $\{\text{H}_2\text{O}\}_m\text{H}^+$ (where $m = 1,2$) ion core which is solvated extensively by the alkoxyethanol molecules.

5) Conclusions:

A number of cluster ion series were observed in the CMS obtained by electron impact ionization of neutral alkoxyethanol clusters. Intermolecular proton transfer reactions dominate the CMS as evidenced by the fact that the protonated cluster ions are the most abundant species in the CMS even though unprotonated $\{\text{AE}\}_n^+$ cluster ions are observed in small amounts. In addition to various fragments that may arise from an unprotonated and/or a protonated alkoxyethanol molecular ion solvated by additional alkoxyethanol molecules, we also observe $\{\text{AE}\}_n\{\text{H}_2\text{O}\}\text{H}^+$ cluster ions for $n \geq 5$. Based on CID studies we conclude that these arise from an intracuster ion-molecule reaction.

In this paper we have been able to probe the behavior of solvent molecules situated beyond the first solvation based on intensity measurements alone. Although these experiments do not yield any thermodynamic data, they enabled us to get a qualitative idea of the bonding characteristics in large cluster ions. The enhanced stability of $\{AE\}_n\{H_2O\}_mH^+$ ions for cluster sizes where $n = 2(m + 2)$ may be rationalized using a structural model where the proton switch to water enables the solvating AE molecules to hydrogen bond to the central core of $\{H_2O\}_mH^+$ cluster ions. It is also possible that the AE molecules are involved in extensive intermolecular hydrogen bonding to form bridged structure. The bridged structure proposed for these ions maximizes the number of hydrogen bonding positions, while minimizing the number of free hydrogen bonding positions bonds yet maintaining favorable bonding geometries. The "magic number" observed in the intensity distributions of $\{AE\}_n\{H_2O\}_mH^+$ ions strongly suggests that hydrogen bonding interactions are strong, selective and highly directional within clusters and dominate the stabilization of these species. We are currently investigating other bifunctional molecules where the two groups are separated by two or more methylene groups. A systematic study of bifunctional molecules having functional groups with varying proton affinities, dipole moments and different hydrogen bonding sites will enable us to obtain a better

understanding of the role of hydrogen bonding in polyfunctional environments which are the norm in biological systems.

Acknowledgements

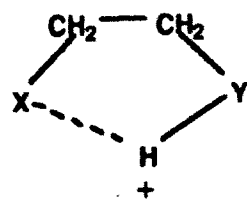
We gratefully acknowledge the financial support of this work provided by the Office of Naval Research and the Alfred P. Sloan Foundation.

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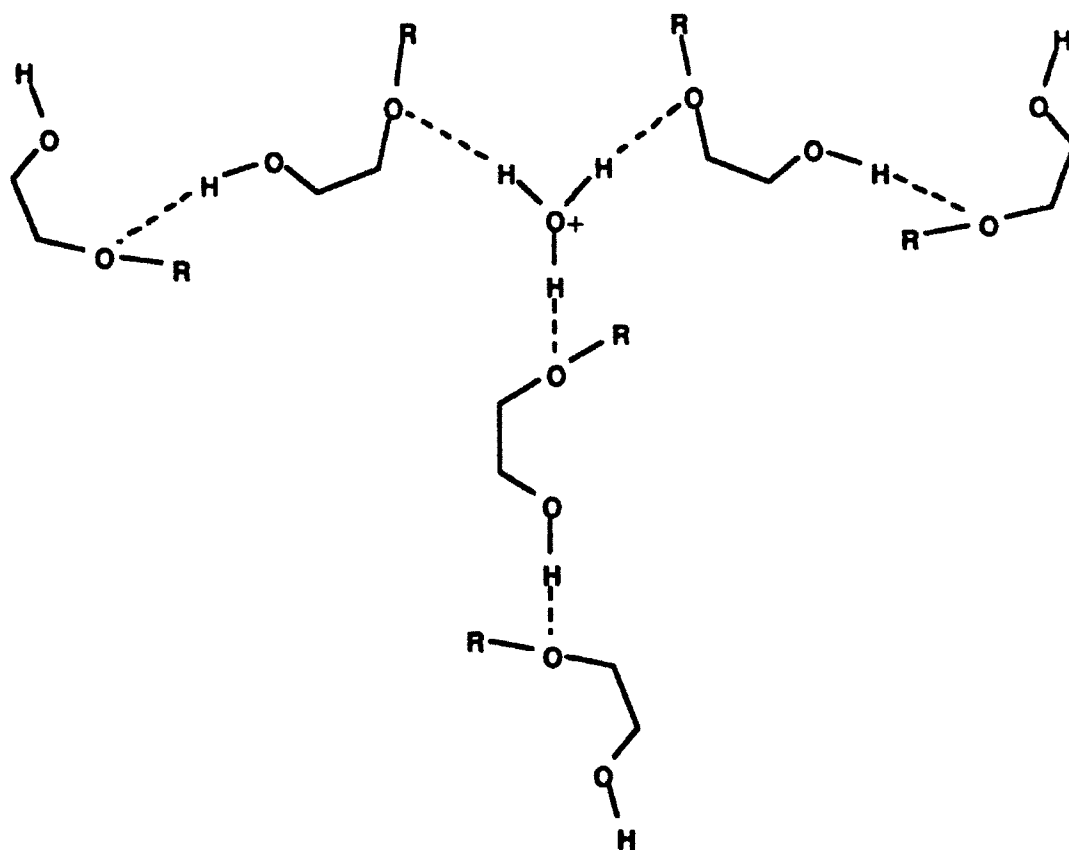
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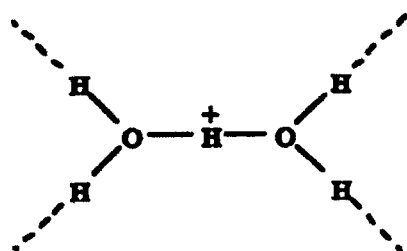
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structure I



structure II



structure III

Figure Captions

Figure 1: Typical cluster mass spectrum for neat expansions of 2 - methoxyethanol with ionizing energy of 70.0 eV and a stagnation pressure of helium of 0.8 atm. The peaks corresponding to the dominant cluster ion series $(\text{ME})_n\text{H}^+$ are labeled as "a_n". The peaks corresponding to the cluster ion series $(\text{ME})_n(\text{H}_2\text{O})\text{H}^+$ are labeled as "b_n". A number of other cluster ion series are also observed and are listed in Table 1.

Figure 2: Typical cluster mass spectrum for neat expansions of 2 - ethoxyethanol with ionizing energy of 70.0 eV and a stagnation pressure of helium of 0.8 atm. The peaks corresponding to the dominant cluster ion series $(\text{EE})_n\text{H}^+$ are labeled as "a_n". The peaks corresponding to the cluster ion series $(\text{EE})_n(\text{H}_2\text{O})\text{H}^+$ are labeled as "b_n". A number of other cluster ion series are also observed and are listed in Table 2.

Figure 3: Example of MS-MS spectrum for the collision induced dissociation of $(\text{ME})\text{H}^+$ with 1.6 mtorr helium as collision gas and 10.0 eV collision energy.

Figure 4: Example of MS-MS spectrum for the collision induced dissociation of $\{\text{EE}\}\text{H}^+$ with 1.6 mtorr helium as collision gas and 10.0 eV (lab) collision energy.

Figure 5: Plot of $\{\text{ME}\}_n\{\text{H}_2\text{O}\}\text{H}^+$ ion intensities as a function of n for various (a) stagnation pressures of He at 30.0 eV, and (b) electron energies with 1.0 atm helium as carrier gas in neat 2 - methoxyethanol expansions.

Figure 6: Plot of $\{\text{EE}\}_n\{\text{H}_2\text{O}\}\text{H}^+$ ion intensities as a function of n for various (a) stagnation pressures of helium at 30.0 eV, and (b) electron energies with 1.0 atm helium as carrier gas in neat 2 - ethoxyethanol expansions.

Figure 7(a): Typical cluster mass spectrum for mixed expansions of 2 - methoxyethanol/water with ionizing energy of 70.0 eV and a stagnation pressure of helium of 0.8 atm. The peaks corresponding to the dominant cluster ion series $\{\text{ME}\}_n\text{H}^+$ are labeled as " a_n ". The peaks corresponding to the cluster ion series $\{\text{ME}\}_n\{\text{H}_2\text{O}\}\text{H}^+$, $\{\text{ME}\}_n\{\text{H}_2\text{O}\}_2\text{H}^+$, and $\{\text{ME}\}_n\{\text{H}_2\text{O}\}_3\text{H}^+$, are labeled as " b_n ", " c_n ", and " d_n " respectively.

Figure 7(b): Typical cluster mass spectrum for mixed expansions of 2 - ethoxyethanol/water with ionizing energy of 70.0 eV and a stagnation pressure of helium of 0.8 atm. The peaks corresponding to the dominant cluster ion series $(EE)_nH^+$ are labeled as "a_n". The peaks corresponding to the cluster ion series $(EE)_n(H_2O)H^+$ are labeled as "b_n".

Figure 8: Plot of $(ME)_n(H_2O)H^+$ ion intensities as a function of n for various electron energies with 1.0 atm helium as carrier gas in mixed expansions of 2 - methoxyethanol and water.

Figure 9: Plot of $(EE)_n(H_2O)H^+$ ion intensities as a function of n for various stagnation pressures of He at 30.0 eV with 1.0 atm helium as carrier gas in mixed expansions of 2 - ethoxyethanol and water.

Figure 10 : A proposed structure for the $(AE)_6(H_2O)H^+$ cluster ion. This specie is the most prevalent of all cluster ions in the series $(AE)_n(H_2O)H^+$ and is proposed to be an H_3O^+ cation surrounded by a complete solvation shell of 6 alkoxyethanol molecules.. The dark circles correspond to carbon atoms, the shaded circles correspond to oxygen atoms and

the open circles are hydrogen atoms. Chemical bonds are indicated by 'sticks' while hydrogen bonds are indicated by thin lines. Only hydrogens which are directly involved with hydrogen bonding are shown.

Figure 11: Plot of $(ME)_n(H_2O)_2H^+$ ion intensities as a function of n for various electron energies with 1.0 atm helium as carrier gas in mixed expansions of 2 - methoxyethanol and water.

Table 1.

List of ions observed in the monomer to dimer region of the CMS for neat

2 - methoxyethanol expansions:

m/z	Ion
76	(ME) ⁺
77	(ME)H ⁺
89	(ME)CH ⁺ / C ₄ H ₉ O ₂ ⁺
102	(ME)C ₂ H ₂ ⁺
103	(ME)C ₂ H ₃ ⁺
107	(ME)CH ₃ O ⁺
108	(ME)CH ₄ O ⁺
109	(ME)CH ₅ O ⁺
119	(ME)C ₂ H ₃ O ⁺
120	(ME)C ₂ H ₄ O ⁺
121	(ME)C ₂ H ₅ O ⁺
122	(ME)C ₂ H ₆ O ⁺
123	(ME)C ₂ H ₇ O ⁺
135	(ME)C ₃ H ₇ O ⁺

Table 2.

List of ions observed in the monomer to dimer region of the CMS for neat

2 - ethoxyethanol expansions:

m/z	Ion
90	(EE) ⁺
91	(EE)H ⁺
103	(EE)CH ⁺ / C ₅ H ₁₁ O ₂ ⁺
116	(EE)C ₂ H ₂ ⁺
117	(EE)C ₂ H ₃ ⁺
121	(EE)CH ₃ O ⁺
133	(EE)C ₂ H ₃ O ⁺
135	(EE)C ₂ H ₅ O ⁺
136	(EE)C ₂ H ₆ O ⁺
137	(EE)C ₂ H ₇ O ⁺
149	(EE)C ₃ H ₇ O ⁺
150	(EE)C ₃ H ₈ O ⁺
162	(EE)C ₄ H ₈ O ⁺
163	(EE)C ₄ H ₉ O ⁺

FIGURE 1

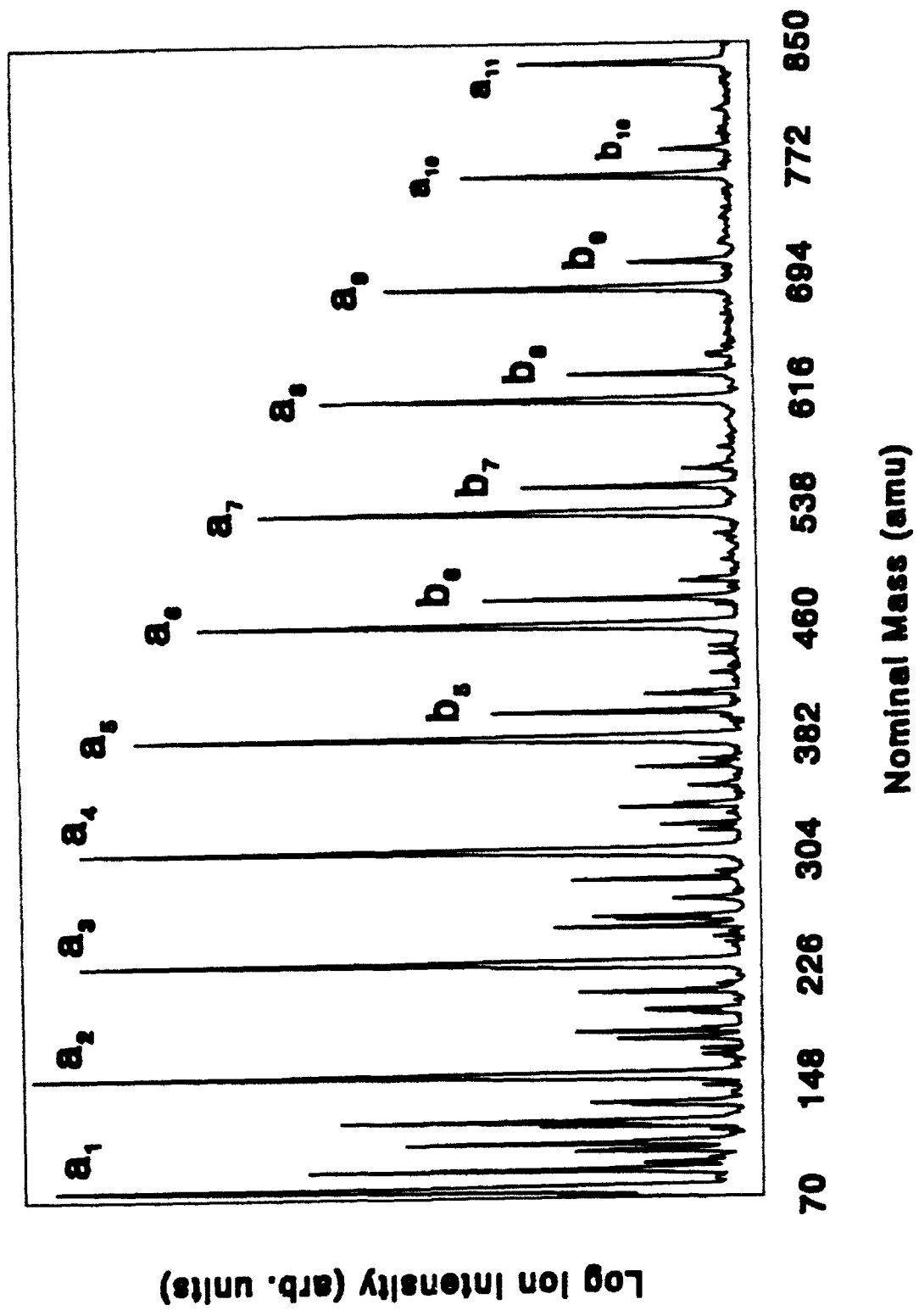


FIGURE 2

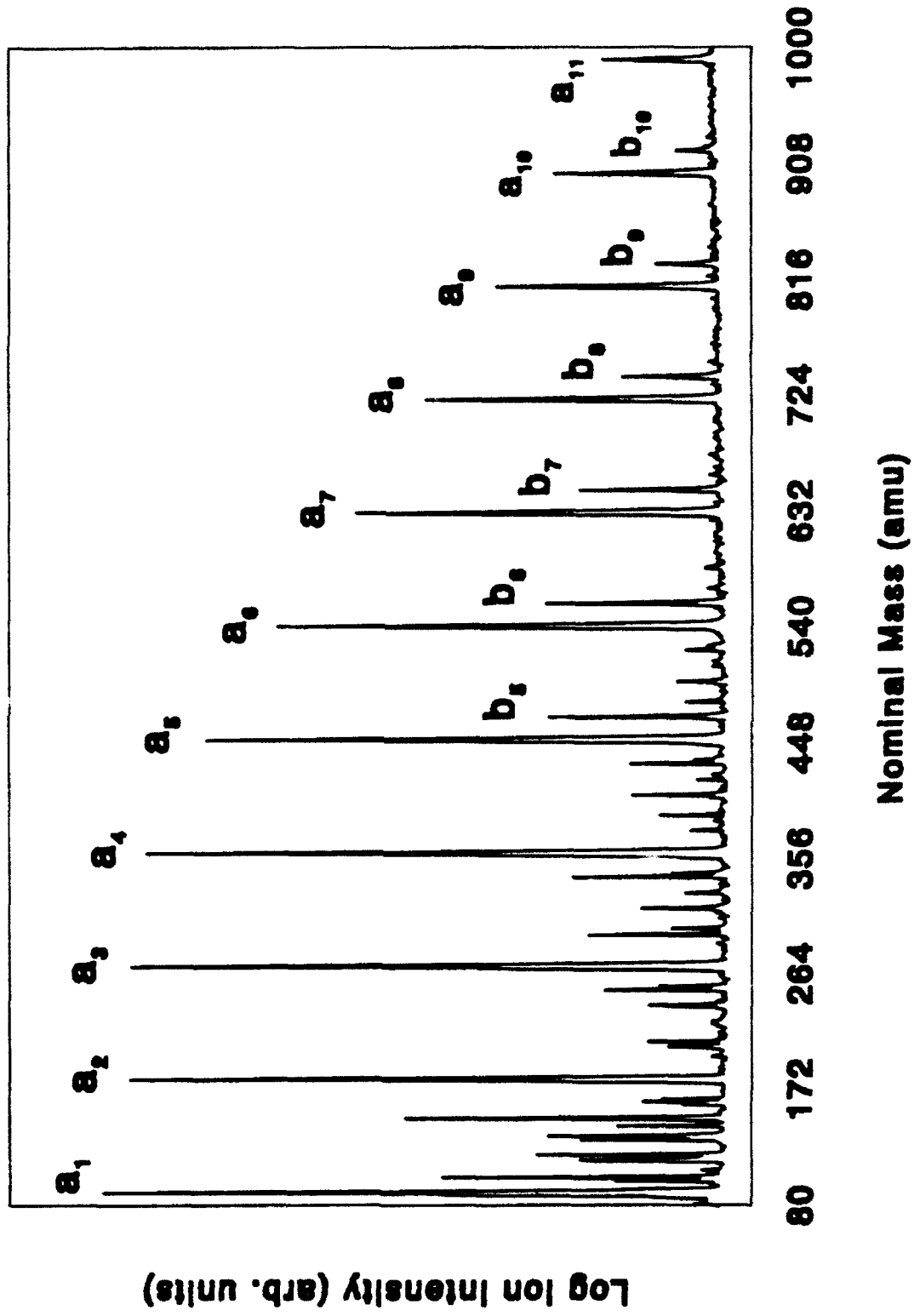


FIGURE 3

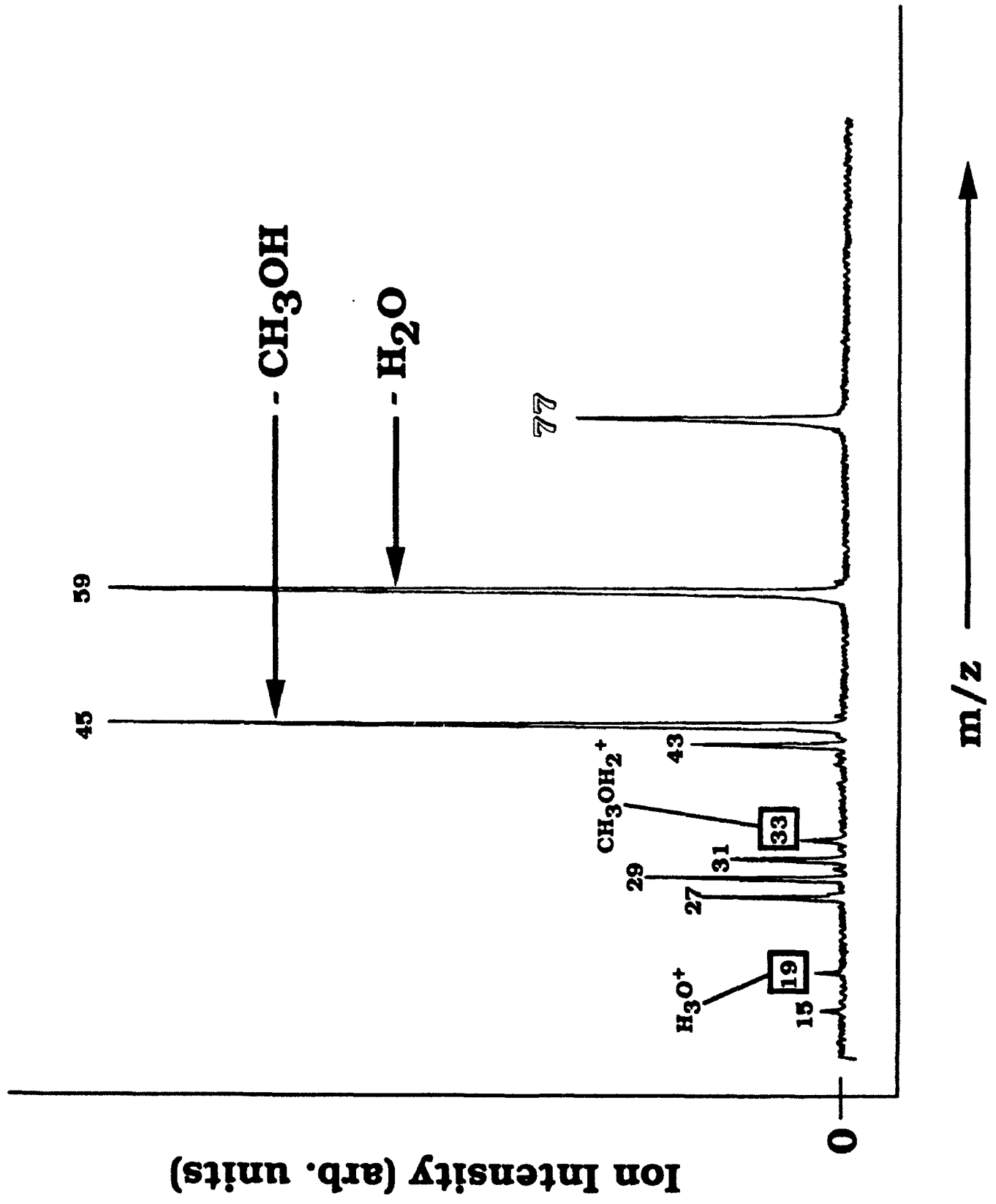
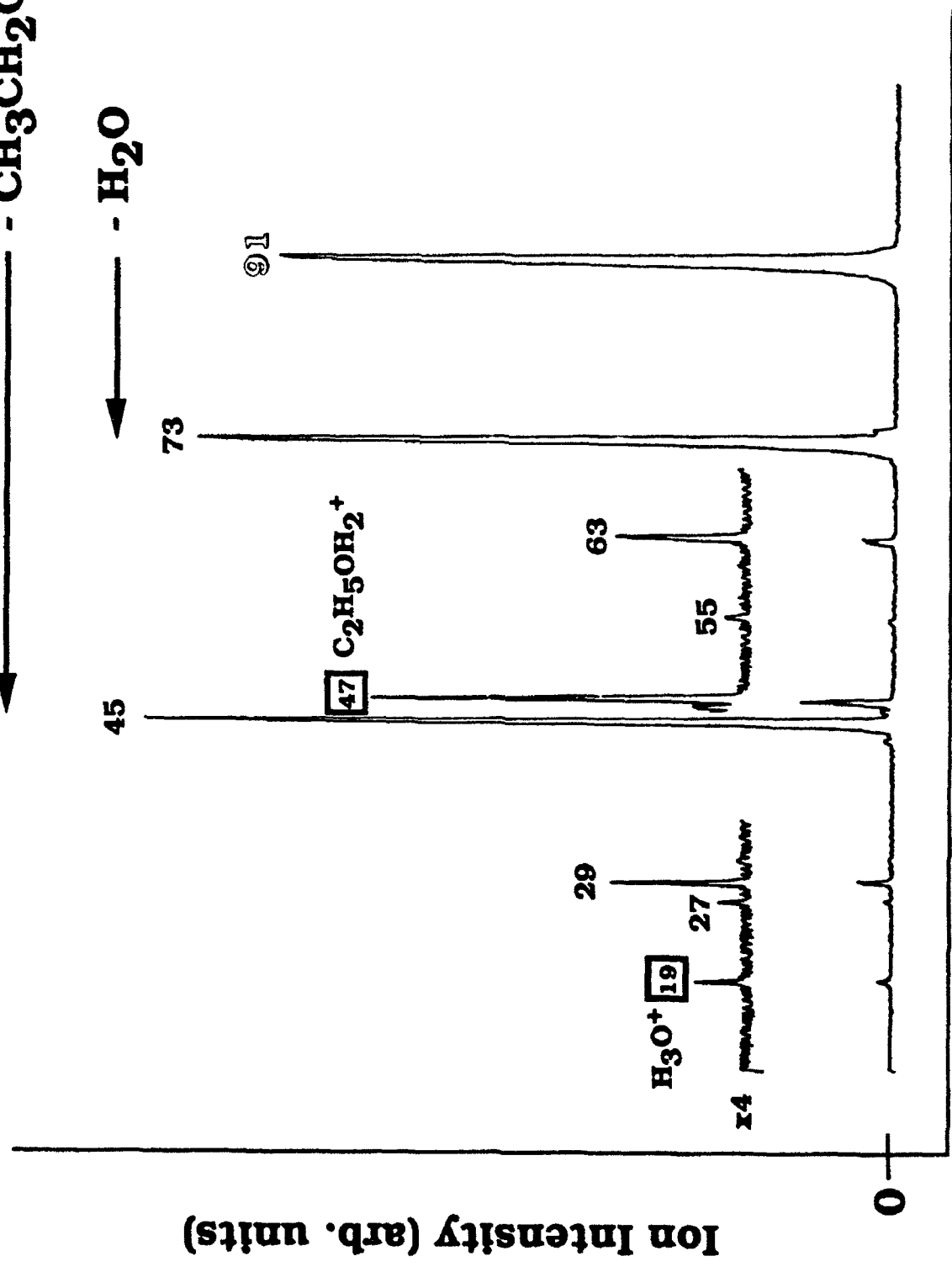


FIGURE 4



m/z

FIGURE 5(c)

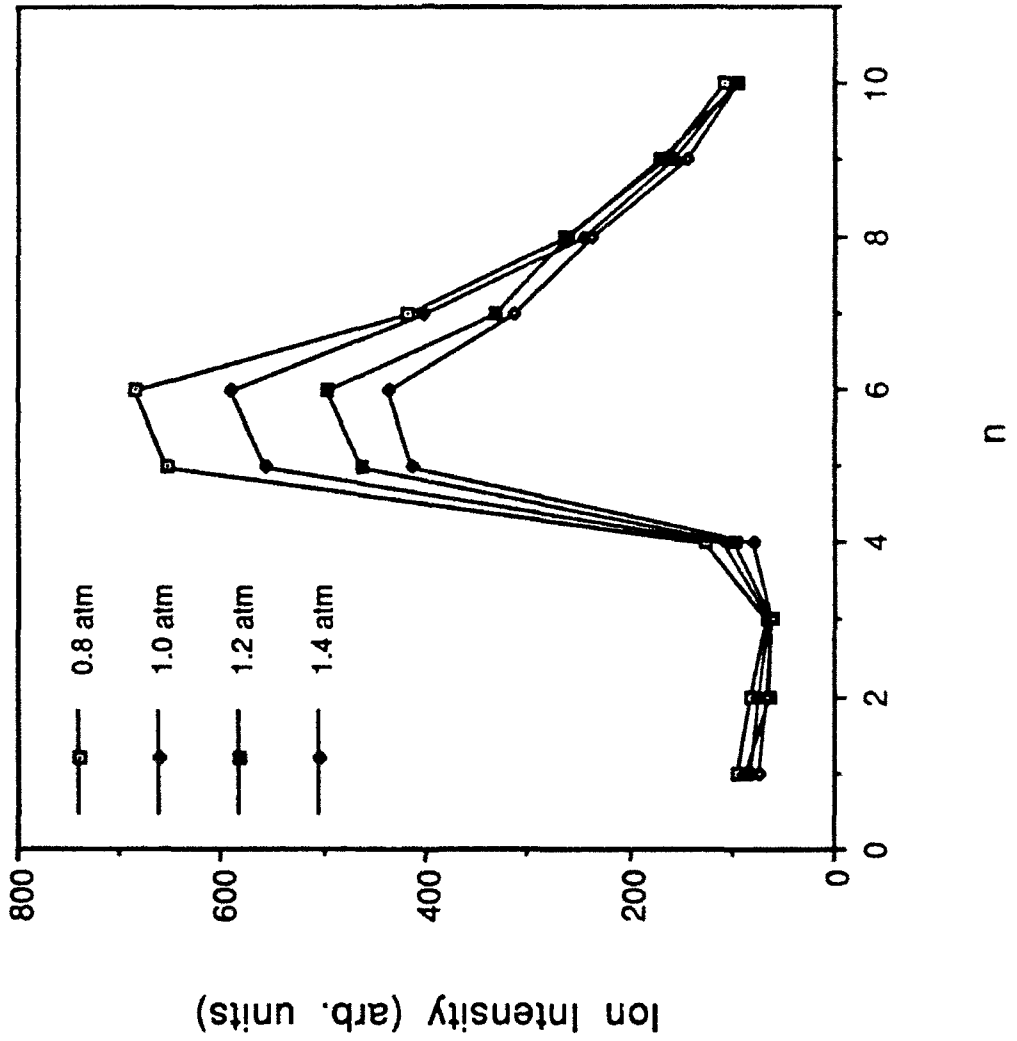


FIGURE 5(5)

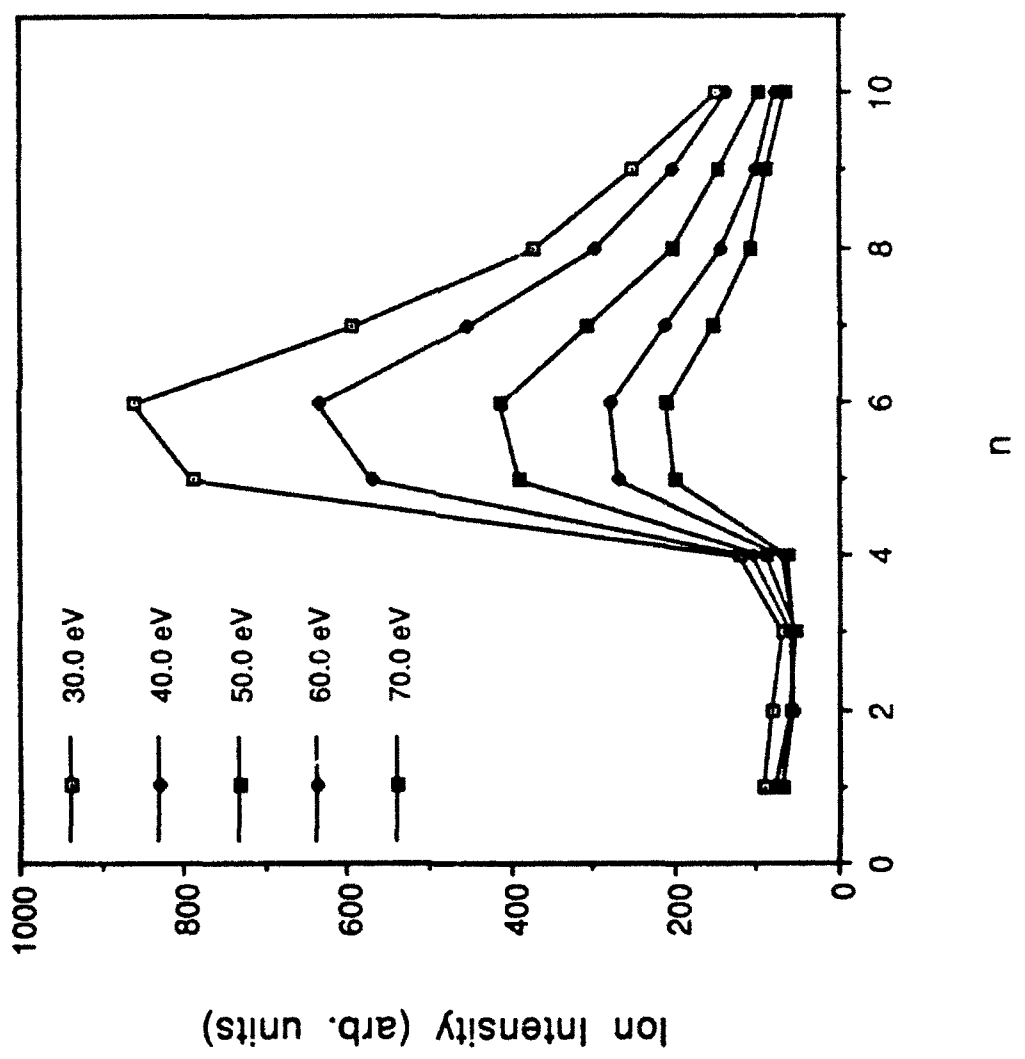


FIGURE 6(a)

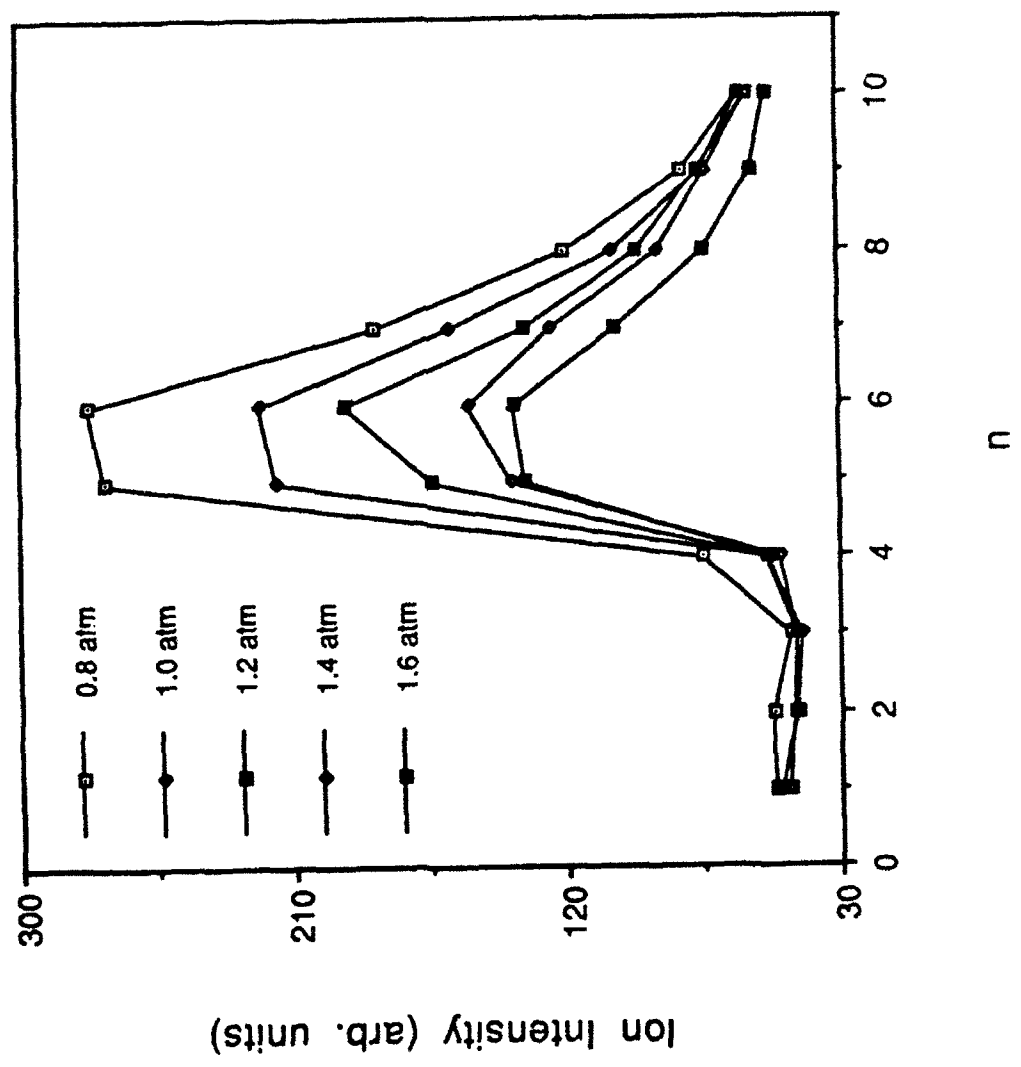


Figure 6(4)

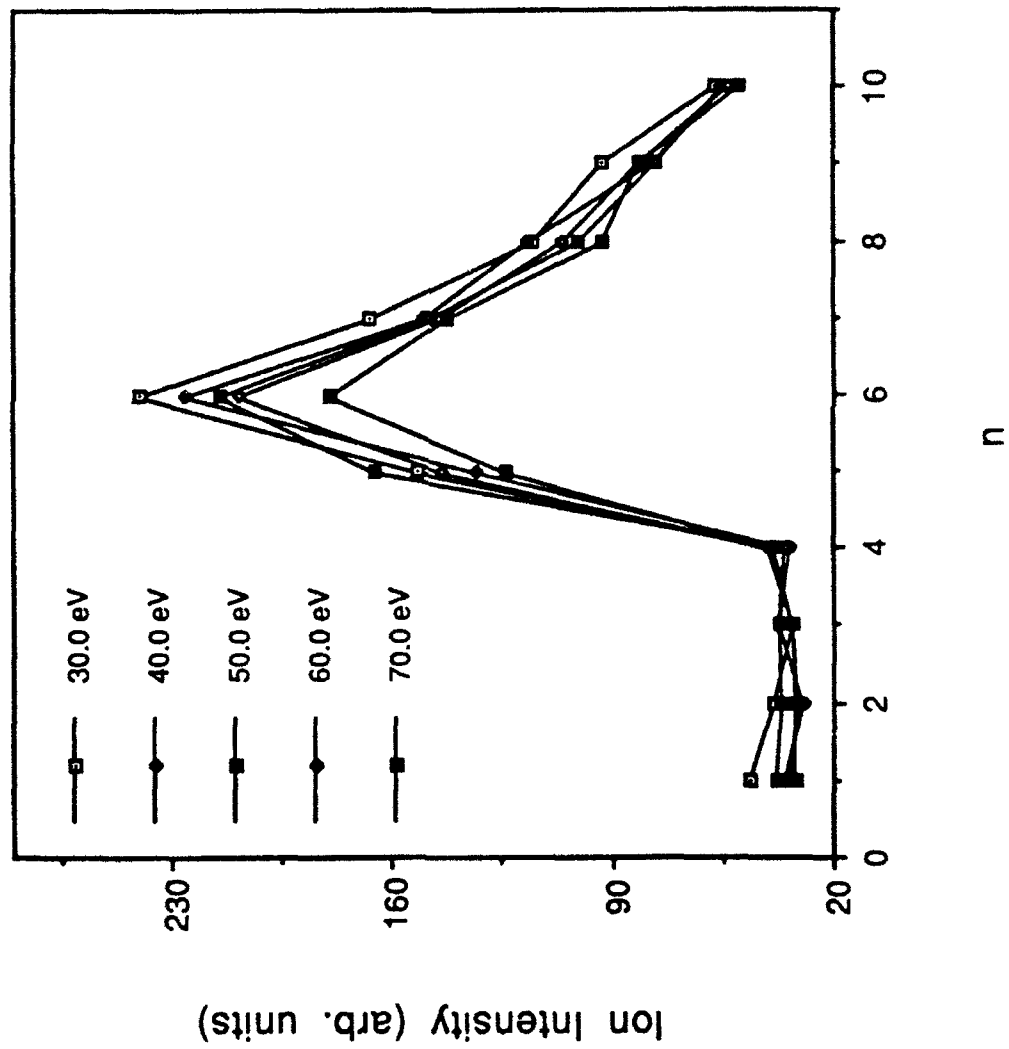
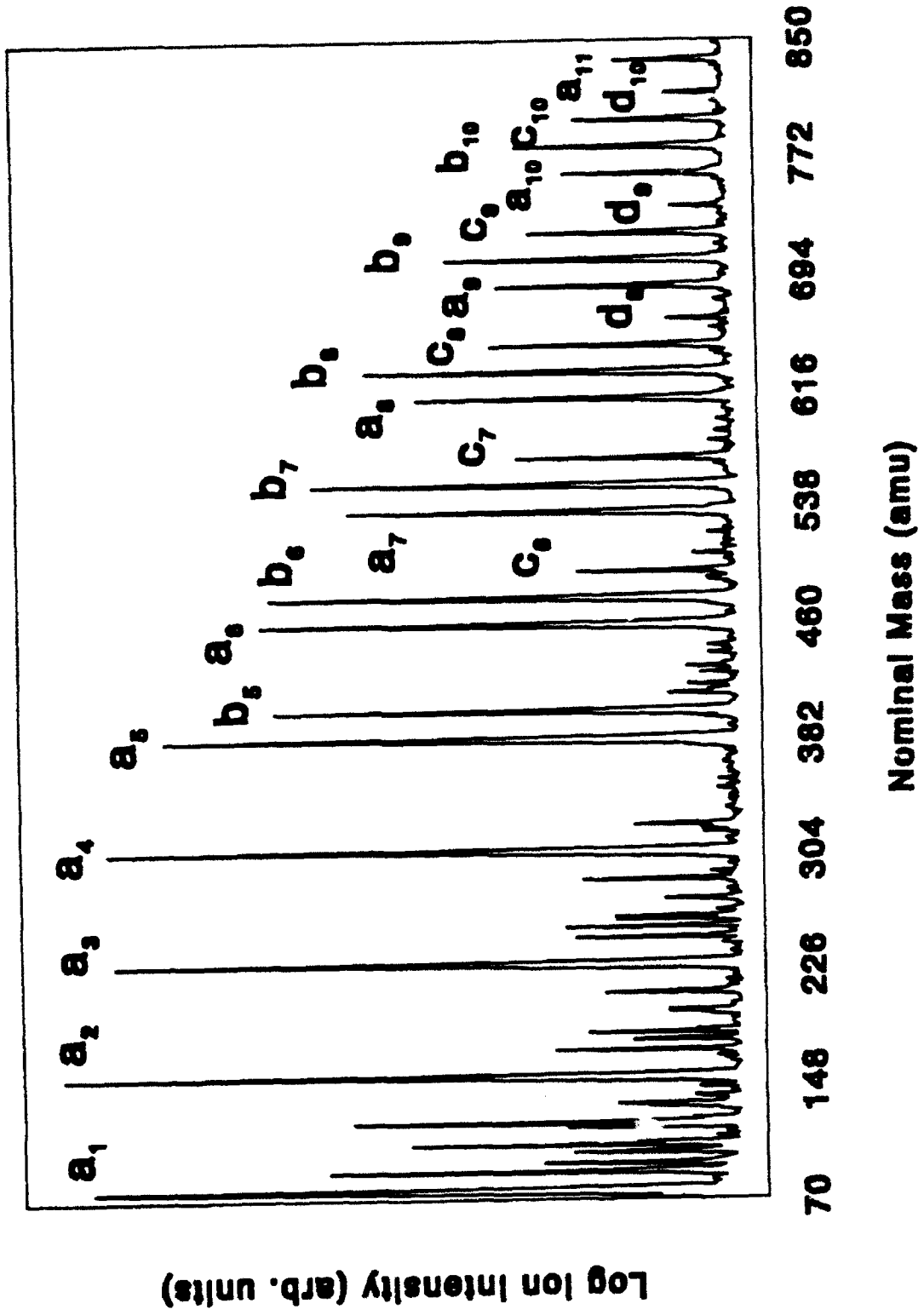


FIGURE 7 (a)



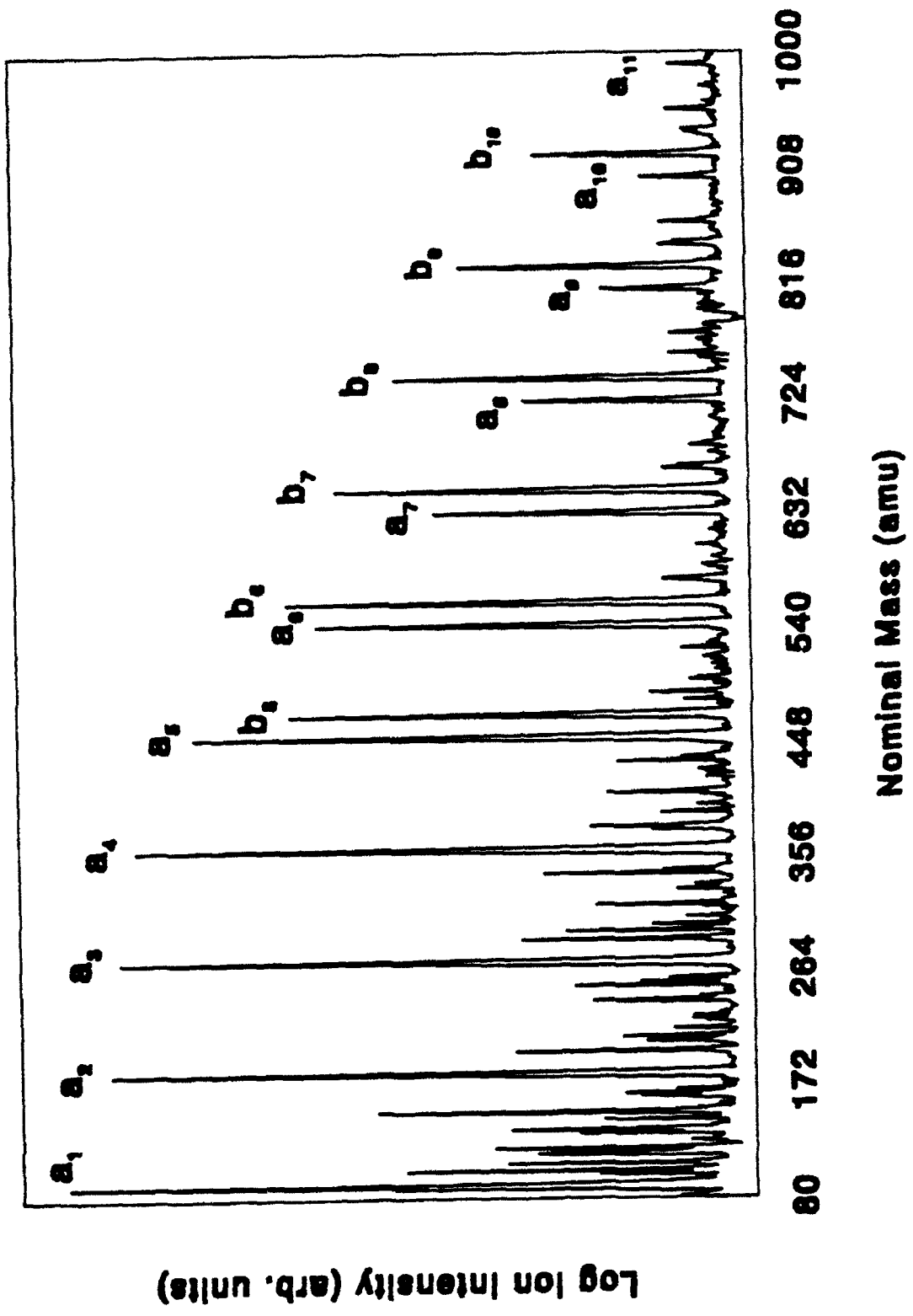


Figure 3

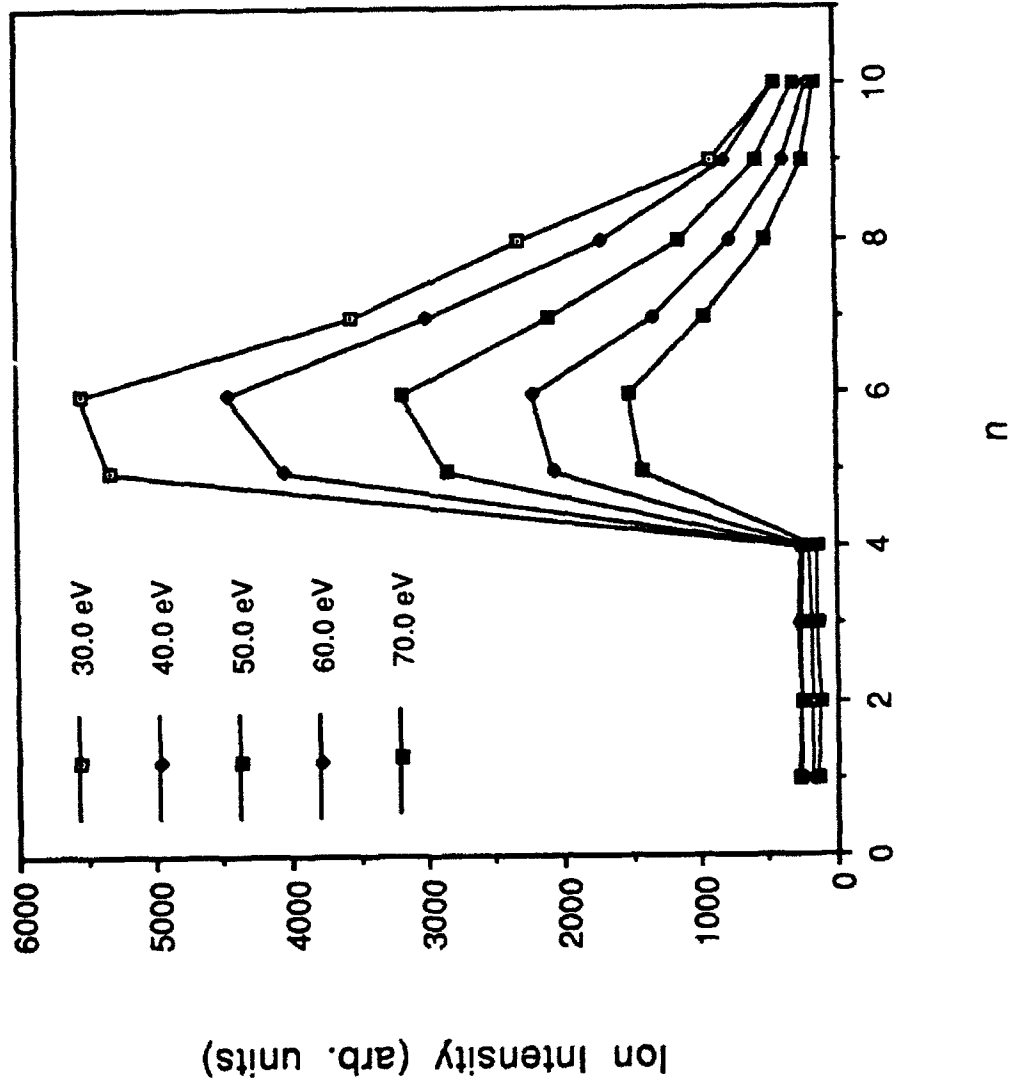
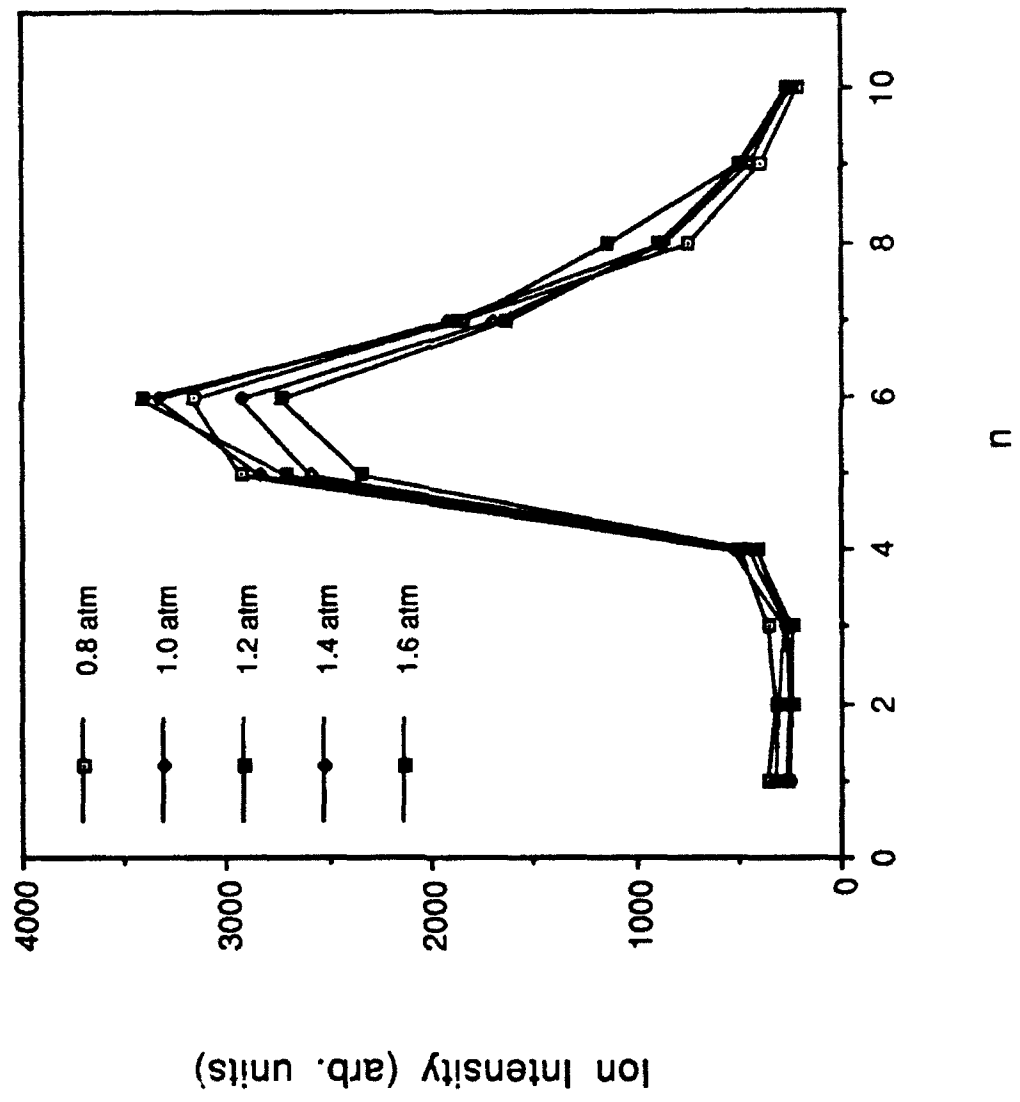


FIGURE 7



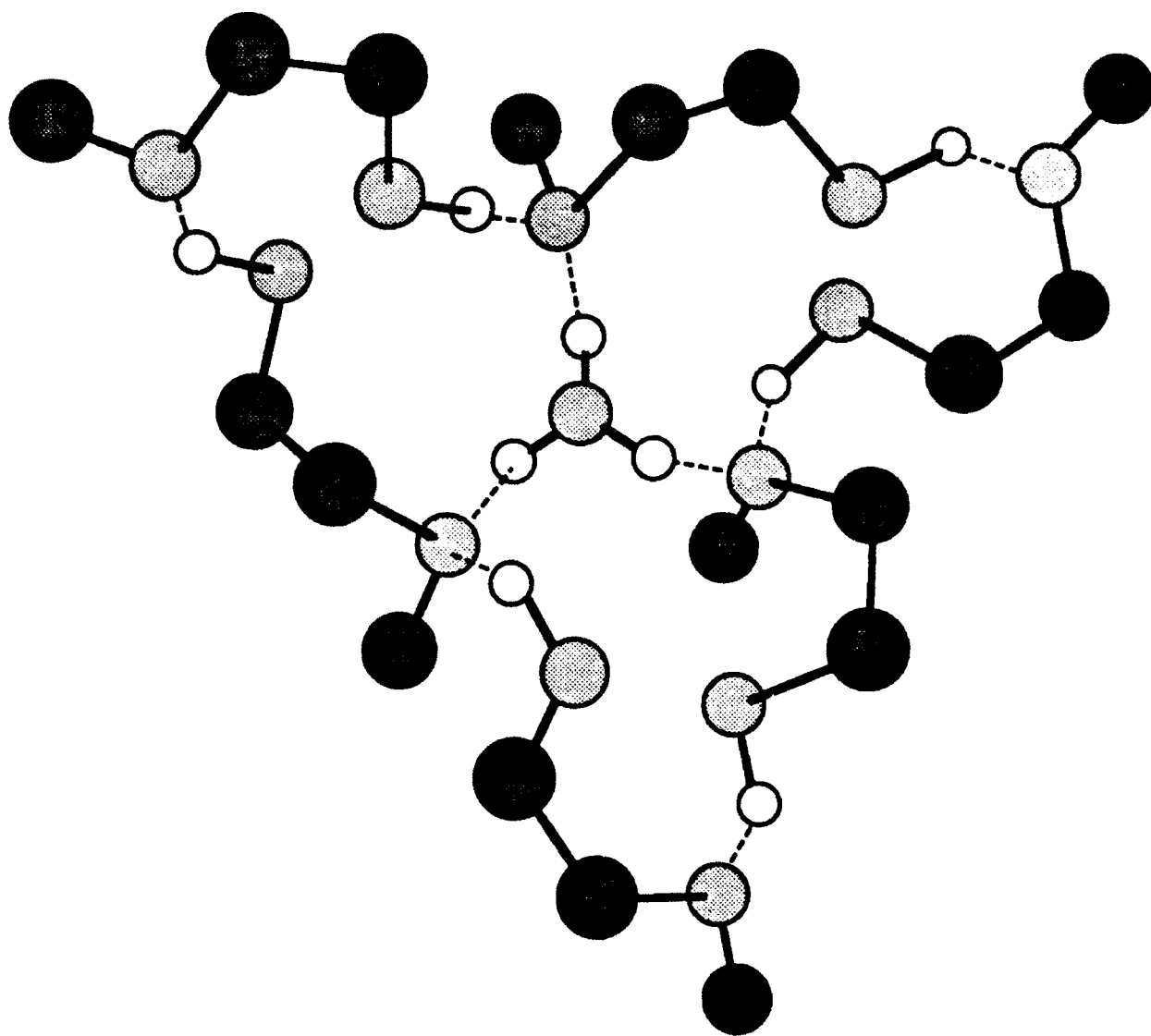


FIGURE 10

FIGURE 11

