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We report the observation of large (n up to ~25) acetylene and methylacetylene cluster ions- the largest yet reported from ionization of neutral $(C_2H_2)_n$ or $(CH_3CCH)_n$ clusters. The cluster ion intensity distributions of both systems display prominent magic numbers at n = 3. This finding is indicative of intra-clusters ion-molecule reactions giving rise to what are most likely benzene and trimethylbenzene ions from $(C_2H_2)_n^+$ and $(CH_3CCH)_n^+$ cluster ions, respectively. The acetylene cluster ion intensity distributions observed under efficient clustering conditions are further characterized by unexpected features, most notably a sharp break at n = 7 and a strong magic number at n = 14. The mass spectra of methyl-acetylene display a less dramatic break at n = 7 and a weak magic number around n = 10. These surprising structures may arise as a result of the formation of particularly stable covalently bonded molecules ions. In view of the unique properties of carbon it is possible that these ions possess spherical cage geometries reminiscent of the fullerenes.

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Positive Ion Chemistry of Acetylene and Methylacetylene Clusters. Formation of Benzene and $C_{2n}H_{2n}^+$ Ions via Intracluster Polymerization Reactions

by

M. Todd Coolbaugh, Stephine Gumina, Gopal Vaidyanathan, and James F. Garvey*

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Intracluster Polymerization Reactions within Acetylene and Methylacetylene Clusters Ions.

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Abstract. We report the observation of large (n up to ~25) acetylene and methylacetylene cluster ions- the largest yet reported from ionization of neutral $(C_2H_2)_n$ or $(CH_3CCH)_n$ clusters. The cluster ion intensity distributions of both systems display prominent magic numbers at n = 3. This finding is indicative of intracluster ion-molecule reactions giving rise to what are most likely benzene and trimethylbenzene ions from $(C_2H_2)_n^+$ and $(CH_3CCH)_n^+$ cluster ions, respectively. The acetylene cluster ion intensity distributions observed under efficient clustering conditions are further characterized by unexpected features, most notably a sharp break at n = 7 and a strong magic number at n =14. The mass spectra of methylacetylene display a less dramatic break at n = 7 and a weak magic number around n = 10. These surprising structures may arise as a result of the formation of particularly stable covalently bonded molecular ions. In view of the unique properties of carbon it is possible that these ions possess spherical cage geometries reminiscent of the fullerenes.

† Alfred P. Sloan Foundation Fellow 1991-3.

A) Introduction

Gas phase clusters present the experimentalist excellent opportunities to study processes of chemical importance in greatly simplified environments. One such process which has begun to attract recent interest is ionic polymerization reactions. Clusters allow one to study ionic reactions in a solvated environment without complications due to the need to maintain electroneutrality, i.e. there is no need to consider effects due to neutralization reactions or counterions. It is also possible to investigate the chemistry of single ions. Although the the use of a molecular beam cluster source results in a distribution of cluster sizes, essentially all of the reaction products observed in the cluster mass spectrum (CMS) arise from reactions of a single ion within the cluster. The study of polymerization reactions in clusters permits one to gain insight into the importance of several factors in determining the course of reaction. Studying the reactivity patterns as a function of cluster size has shown the crucial role solvent molecules play in the intracluster polymerization reactions by stabilizing the highly excited intermediates formed by the first few addition reactions.

We have studied the positive ion chemistry of several olefin van der Waals clusters (ethene, 1,1-difluoroethene and propene).[1-3] The small clusters show ample evidence of the effects of solvent induced changes in the ion chemistry, particularly the stabilization of highly energetic intermediates. We have also presented results indicating that sequential ion-molecule addition reactions (intracluster cationic "polymerization"[4]) take place within the cluster ions.[1-3] The findings of these studies are entirely consistent with previous bulk phase studies and suggest that clusters can provide insight into the initial stages of ionic polymerization. Several other groups are now also investigating intracluster polymerization reactions, both cationic[5] and anionic.[6]

We have recently begun an investigation of the cluster ion chemistry of the alkynes acetylene (ethyne, ACE) and methylacetylene (propyne, MACE). Ionic polymerization reactions involving these molecules have been implicated in the formation of polyaromatic hydrocarbons (PAH's) in flames[7] and during

pyrolysis of alkynes.[8]

We will be reporting here the largest acetylene "cluster" ions observed to date. The CMS of the alkyne clusters show evidence of ionic intracluster polymerization reactions, the CMS of both acetylene and methylacetylene displaying magic numbers at n = 3 which may be indicative of the formation of benzene and trimethylbenzene ions, respectively. The CMS of acetylene also displays several features at higher sizes, most intriguing of which is a magic number at n = 14. This feature may indicate the formation of a particularly stable, covalently bound ion.

B) Experimental

The experimental setup has been described in detail elsewhere[9] and is shown schematically in Fig. 1. In brief, it consists of a continuous molecular beam cluster source of the Campargue design coupled to a chamber housing a mass spectrometer. The cluster beams were generated by expansion of gas through a 250 μm sonic nozzle. The pertinent expansion conditions- pressure (P_0) and temperature (T_0)- are reported in the figure captions.

The acetylene (Scott, 99.6%, dissolved in acetone) was expanded neat after passing through an activated charcoal filter (Matheson 454) to remove as much acetone vapor as possible. This purification step is absolutely necessary in order to observe neat acetylene clusters since the acetone impurity in the beam leads to the nearly exclusive observation of mixed acetylene/acetone cluster ions.[10] The methylacetylene (Applied Gas Technology, 10% in He) was used without further purification. Propadiene and isobutene were listed as being present in trace amounts.

After being skimmed and collimated, the neutral cluster beam enters the ionizer of a mass spectrometer (Extrel C50; capable of unit mass resolution to 1500 amu) where a small fraction of the neutral species are ionized *via* electron impact (emission current 0.65 mA), mass filtered and detected with a particle detector. The electron impact energy (E_e) is reported in the figure captions.

C) Results

Fig. 2 displays a portion of a typical acetylene CMS obtained with expansion conditions which may be expected to lead to efficient clustering. Under these conditions it is possible to observe ions with formulae $(C_2H_2)_{n\leq25}^+$. Even after purification, cluster ions containing acetone impurities still constitute a significant fraction of the total ion signal, particularly at higher masses. We have previously reported results of a study of these cluster ions.[10]

Fig. 3 displays plots of the intensities of the acetylene cluster ions *vs.* cluster size, n, for several different sets of expansion conditions. It is clear that expansion conditions favoring the production of larger neutral clusters lead to the emergence of a very prominent magic number in the $(ACE)_n^+$ ion intensity distributions at n = 3. As we will discuss below, this observation was not a great surprise. The same cannot be said of the magic number at n = 14 which is apparent in Fig. 3. A number of other reproducible features are found in the high pressure acetylene cluster ion intensity distributions. The most dramatic of these is the break at n = 7. Many of the CMS show slight maxima or breaks at n = 10 and 12, although these features are not nearly as prominent or reproducible as the features at n = 3 and 14.

These results have been duplicated on a number of different occasions. Isobaric interferences due to acetone or acetone fragments do not occur in the mass range under consideration. We have found that the intensities of the ions assigned as arising from neat acetylene clusters are inversely proportional to the concentration of acetone present in the expansion. Generation of neat acetylene cluster ions from acetylene/acetone heterocluster ions is very unlikely since the ionization energy of acetone is much lower than that of acetylene. Our previous studies of acetylene/acetone clusters indicate that the charge becomes trapped on an acetone molecule and leads to production of $C_7H_{10}O^+$ cyclic ions.[10]

Fig. 4 displays a portion of a typical methylacetylene CMS taken under

conditions of efficient clustering. Fig. 5 displays plots of the intensities of the acetylene cluster ions *vs.* cluster size, n, for several different sets of expansion conditions. In this case a magic number at n = 3 is observed. We were unable to observe a magic number at n = 14 in the methylacetylene CMS. A break may be discerned at around n = 7. The majority of the methylacetylene CMS show a break around n = 10.

D) Discussion

1) The n = 3 Magic Number Ions. The main limitation of any single stage mass spectrometric experiment such as we have employed in the present experiments is the lack of direct structural information, i.e. knowledge of an ion's m/z may only uniquely determine the ion's empirical composition. Of course in many instances knowledge concerning the neutral precursor(s) may allow certain possible structures to be postulated while others are ruled out. In the case of a cluster mass spectrum a further complication arises since now there is often more of a question concerning the nature of the bonding forces within the cluster, i.e. covalent vs. van der Waals or hydrogen bonding.

Acetylene and methylacetylene clusters are thermodynamically unstable with respect to polymerization reactions. However, such reactions are unlikely because of large activation reactions. Such reactions may be expected to be quite facile in $(ACE)_{n-1}ACE^+$ and $(MACE)_{n-1}MACE^+$ clusters since the activation barriers are much smaller for ion-molecule reactions, i.e. an acetylene or methylacetylene ion "solvated" within such a cluster will certainly react with one of the surrounding molecules. This ion product may also be capable of reacting with the surrounding molecules. One of the more interesting questions which arises in connection with these clusters then concerns the extent of these "polymerization" reactions within the clusters.

We have previously studied the cluster mass spectra of several olefinic molecules which were characterized by the emergence of prominent magic numbers under experimental conditions expected to favor efficient clustering.[1-3] In

the cases of ethene and 1,1-difluoroethene, for example, we observed that the $C_8H_{16}^+/C_8H_8F_8^+$ (i.e. n = 4) ions were formed with highest probability while a dramatic drop in ion intensity beyond the n = 5 ions was observed. These results were rationalized in terms of the kinetics of the intracluster ionic addition ("polymerization") reactions.[1-3] Monomer molecules will add to the reactive ion in the cluster until such time as an unreactive ion is formed- that is, until a kinetic bottleneck in the reaction sequence is reached. Following this, the highly excited product ion formed within the cluster 'boils' off a large number of unreacted monomer molecules leading to a high probability of observing the bare molecular ions and the emergence of the magic numbers in the CMS.

A similar line of reasoning may be appropriate in connection to the alkyne clusters. In the case of acetylene, formation of benzene is a well known "energy trap" in the polymerization sequence[11] and it is perhaps not surprising to observe a strong magic number emerge at n = 3 in the CMS as larger neutral clusters are produced. The gas phase analog of this termolecular reaction is shown in reaction (1).

$$C_2H_2^+ + 2\ C_2H_2 \rightarrow c\text{-}C_6H_6^+ \qquad \Delta H^\circ = -8.23\ eV^{12} \qquad (1)$$

Further support for this hypothesis may be derived from the work of Ng *et al.* who studied the single photon ionization of $(ACE)_3$.[14] The conclusion drawn from these studies was that the acetylene trimer ions isomerized to the same structure(s) as benzene ions produced with the same amount of internal energy. The observation of undissociated $C_6H_6^+$ ions in our experiments is a direct consequence of the production of large acetylene cluster ions since the large exothermicity of the ionic addition reactions must be dissipated by the evaporative loss of monomers from the cluster. This conclusion is consistent with the recent findings of Booze and Baer[15] who have shown that the $C_6H_6^+$ ion signal observed following ionization of neutral acetylene clusters arises entirely from dissociative ionization of higher order clusters.

The observation of the strong n = 3 magic number in the acetylene CMS alone does not provide conclusive evidence that the $C_6H_6^+$ magic number ions possess the benzene structure. However, the apparent low reactivity of the observed $C_6H_6^+$ ion,[16] the fact that this structure can be formed without any rearrangements and the fact that the benzene ion is the lowest energy $C_6H_6^+$ isomer would all seem to favor the benzene structure.

Applying these same criteria to the methylacetylene system leads one to the conclusion that one should observe a magic number at n = 3 in this system corresponding to the production of trimethylbenzene ions (Eqn. 2 depicts analogous gas phase reaction). This finding is in accord with the experimental findings.

$$C_3H_4^+ + 2\ C_3H_4 \rightarrow c\text{-}C_9H_{12}^+ \qquad \Delta H^\circ = -(7.87 - 8.09)\ eV^{12,13} \qquad (2)$$

Some support for this conclusion may be drawn from the trimer and tetramer ion "fragment" regions of the methylacetylene CMS. As can be seen in Fig. 3, the most abundant non-stoichiometric cluster ions correspond to loss of CH_3 radicals from the $(MACE)_{3,4}^+$ clusters. $(MACE)_3^+$ also displays weaker peaks corresponding to loss of C_2H_5 (or C_2H_4 +H) and losses of 1, 3 and 5 H atoms. All of these fragments are consistent with production of trimethylbenzene ions. Under weaker expansion conditions the qualitative features of the CMS and trimethylbenzene mass spectra[17] match rather closely in the 85 - 120 amu range.

2) The Higher Magic Numbers.

i) Acetylene. The observation of a relatively strong magic number for n = 14 in the acetylene CMS is intriguing. In view of the highly reactive nature of the cluster components it seems extremely improbable that this ion represents a solvated acetylene ion, i.e. $(ACE)_{13}C_2H_2^+$. At least some amount of polymerization has certainly taken place in the cluster. In view of the obvious propen-

sity of $C_6H_6^+$ ions to form from acetylene clusters, it might be suggested that the ACE_{14}^+ ion represents an $(ACE)_{11}C_6H_6^+$ ion. This assignment is not particularly satisfactory in as much as it is not clear why eleven acetylenes solvating a central benzene ion would possess such extraordinary stability. Nor does is it seem possible to explain the sharp break in the ion intensity distributions observed at n = 7, which implies increasing stability for the $(ACE)_{n>7}^+$ ions, since it is also not clear why there would be such a change in stability between a fourth and fifth acetylene molecule solvating a benzene ion.

Although the CMS alone does not provide sufficient information to allow us to come to any definitive conclusions regarding the natures of the $(ACE)_{n>3}^+$ ions, it may be useful to consider the present results in light of the known gas phase chemistry of acetylene. Unlike ethene, which undergoes only limited ion-molecule addition/polymerization reactions, acetylene has been found to undergo very facile addition reactions leading to polymeric products, giving products with $n >> 7$.[18] The gas phase radiolysis of acetylene has also attracted a good deal of attention over the years. Two main products were observed in the high pressure radiolysis of acetylene: benzene and a solid polymeric product referred to as cuprene, the latter in the form of small, nearly perfect spheres.[19-21]

This much more efficient polymerization of acetylene observed under radiolysis suggests that the $(C_2H_2)_{14}^+$ ion which is observed in our experiments is a covalently bonded species, i.e. $C_{28}H_{28}^+$. At the same time it would suggest that the $(ACE)_n^+$ ions with $3 < n < 15$ are likewise covalently bound ions. This conclusion is also supported by the behavior of ion intensity distributions shown in Fig. 3 wherein the n = 3 and n ≈ 14 magic number ions are seen to arise simultaneously as expansion conditions increasingly favor the formation larger clusters. This observation would not be expected if the $(ACE)_{14}^+$ ion were a weakly bound complex consisting of acetylene molecules solvating a benzene ion. In this case the extremely large energy release accom-

panying the formation of the benzene ion would be expected to lead to a wide range of expansion conditions over which only the bare benzene ion would be observed A magic number due to formation of a fully solvated benzene ion would be expected to arise from much larger clusters. All of the available evidence thus suggests that the $(ACE)_{14}^+$ ion is a $C_{28}H_{28}^+$ molecular ion.

We can only propose conjectures concerning the structure(s) of the n = 14 magic number ion and the origin of its enhanced stability. One possibility is that the n = 14 magic number may arise as a consequence of the geometry of the neutral clusters, i.e. the neutral clusters may take a form which does not allow more than 14 molecules in the cluster to react. This is improbable since the observation of stoichiometric clusters implies that the initially formed product ions are stabilized. Stabilization must occur by transfer of energy into the cluster modes which leads to rapid heating and evaporative losses of monomers from the cluster ion- i.e. the cluster ions would retain their 'memory' of the neutral cluster structure for only a very short time.

In all likelihood, the enhancement of the n = 14 cluster ion, as well as the rather unusual shape of the ion intensity distribution for n > 6, must be attributed to the kinetics of the intracluster polymerization reactions. The acetylene cluster ion intensity distributions then indicates that the ionic polymerization reaction sequence in an acetylene cluster ion is very likely to be halted by the formation of a benzene ion (see above); i.e. benzene formation represents an efficient kinetic bottleneck. Not all of the polymerization reactions are quenched at this point. In some finite number of clusters the ionic reactions are able to form ions of higher molecular weight. The occurrence of a further magic number at n = 14 would then imply an additional kinetic bottleneck at this point in the reaction sequence.

The cause of this second bottleneck is not apparent. Our previous experience with intracluster polymerization reactions suggests that this magic number may be associated with formation of an ion which is particularly stable towards reaction with the monomer. In the case of the olefin clusters and the n = 3 magic number ions in acetylene and methylacetylene, the stability is appar-

ently associated with formation of cyclic ions. Thus there is some grounds to postulate that the same is true of the $C_{28}H_{28}^+$ ion.

There are, of course, a huge number of possible structures for this ion, yet we can present a few suggestions consistent with the data presented here. First, it is known that polyaromatic hydrocarbons are produced from gas phase reactions of acetylene under a variety of conditions.[7,8] It is logical then to consider polycyclic structures for the $(ACE)_n^+$ clusters. If the reactions take place without rearrangements, as suggested by the methylacetylene data (see above), then a significant number of sp^3 carbons will be present in the ions. At the same time it has been established that carbon has a unique proclivity to form spheroidal cage molecules, e.g. the fullerenes[22] and possibly metallo-carbohedrenes.[23] In view of these facts we would suggest the possibility of the $C_{28}H_{28}^+$ magic number ion possessing a spheroidal cage structure.

The break observed in the $(ACE)_n^+$ ion intensity distribution at n = 7, Figs. 2 and 3, may reflect a transition in the structures of the ions formed by the intracluster polymerization processes. This possibility is suggested by theoretical studies by Ohnishi et. al.[24] These workers calculated stable structures for semiconductor clusters based on a potential which implicitly accounts for the directionality of interactions between sp^3 hybridized atoms. Application of the results of this model to the $C_{2n}H_{2n}^+$ clusters should be valid since the number of hydrogens present requires many of the carbons to be sp^3 hybridized. The calculations show that the stable structures based on five membered rings are characterized by a changeover from 2D structures to 3D hollow sphere structures. This switch occurs between 15 and 16 atoms. This would correspond to n = 7 and 8 in the present experiments. The break in the ion intensity distributions may then reflect the production of unreactive closed spherical molecules.

If the $C_{28}H_{28}^+$ molecule is in fact a spherical cage molecule, then it would most likely consist of 20 five-membered and four six-membered rings. The magic number behavior suggests that the probability of forming larger ions within acetylene cluster ions is much lower. We cannot offer an explanation for

this observation. This effect may arise as a consequence of the structure(s) taken by the ions formed at an early stage of the polymerization process which may incorporate one or more six-membered rings.

ii) Methylacetylene. Methylacetylene clusters do not display the same magic number at n = 15 as do the acetylene clusters. They do however show evidence of a break at n =7 and a possible magic number at n = 10. Methylacetylene should polymerize as efficiently as does acetylene so it is very likely that the $(MACE)_n^+$ (n > 3) clusters are probably also covalently bonded molecular ions. The reason for methylacetylene's differing reactivity pattern may be associated with the presence of the methyl group; similar large changes in the CMS were observed upon changing from ethene to propene. It is possible that the bulk of the methyl group decreases the probability of forming larger polymer ions within the clusters by blocking reactive sites or by hindering isomerization reactions leading to the formation of kinetically stable products.

E) Conclusions

Ionization of acetylene and methylacetylene cluster ions initiates intracluster polymerization reactions. The observation of magic numbers at n = 3 under conditions of efficient clustering is best explained in terms of formation of benzene and trimethylbenzene ions in acetylene and methylacetylene cluster ions, respectively. The formation of benzene ions, which are stable, relatively inert, cyclic molecular ions, represents a fairly efficient kinetic bottleneck in the intracluster polymerization reactions. The observation of further anomalous features, particularly in the acetylene cluster ion intensity distributions, is indicative of more extensive polymerization reactions. These ions, which may be thought of as hydrogenated carbon clusters $C_{2n}H_{2n}^+$, may possess very interesting structures. There is some evidence of a structural transition between the n = 7 and n = 8 cluster ions, possibly associated with a switch from 2D polycyclic molecular ions to closed spherical molecules. A prominent magic number at n = 14 (corresponding to generation of a $C_{28}H_{28}^+$ ion) in the acetylene CMS may be due to the formation of a closed spheroidal cation formed via

sequential reactions within the cluster.

Acknowledgements

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(4) Strictly speaking, the reactions observed in cluster ions would be better described as oligomerization reactions since in most cases they appear to give rise to low molecular weight products containing two to five monomer units.

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13) The overall exothermicity of Rxn (2) is dependent on the exact structure of the trimethylbenzene ion, the heats of formation being 187, 190 and 192 kcalmol^{-1} for the 1,2,4-, 1,3,5- and 1,2,3-trimethylbenzene ions, respectively.[14]

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Figure Captions

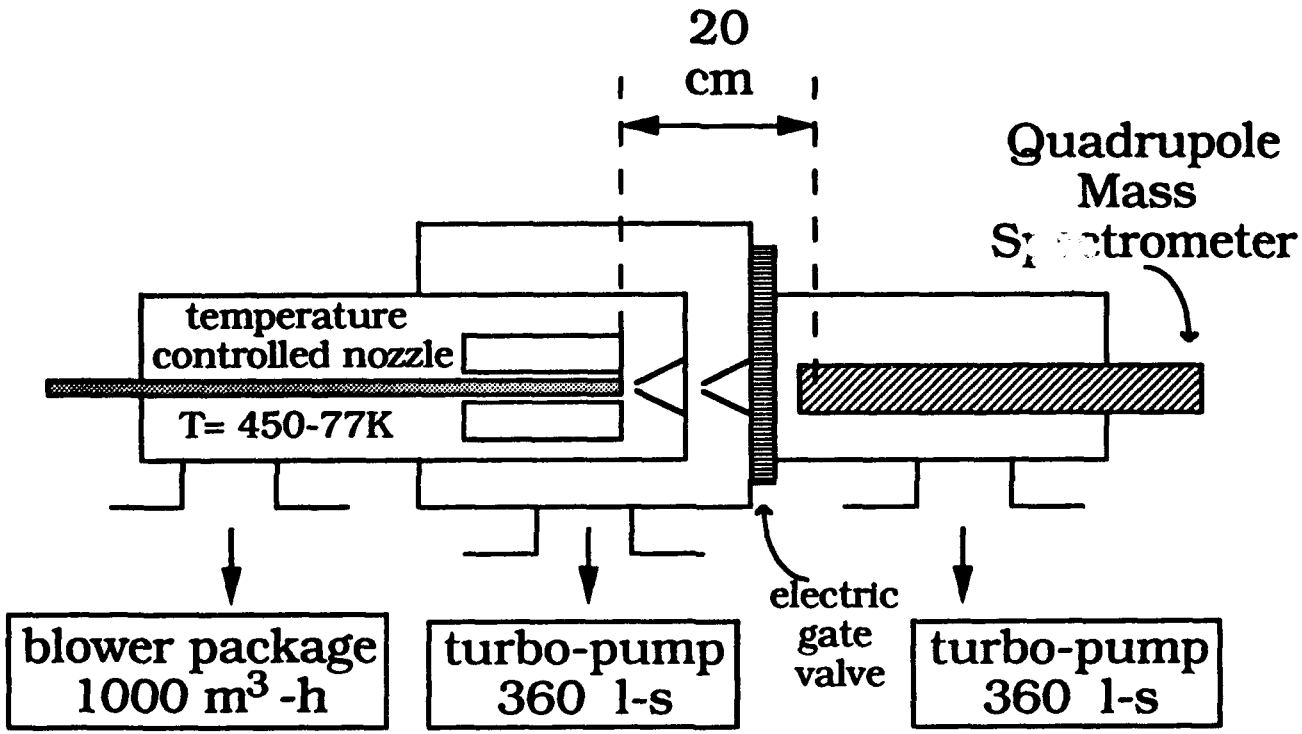
Figure 1. Schematic representation of the molecular beam cluster source and mass spectrometer.

Figure 2. A typical 70 eV acetylene cluster mass spectrum. The expansions conditions were P_0 = 1.8 Atm. and T_0 = 259.5 K. The asterisks mark the positions of stoichiometric acetylene clusters, $(C_2H_2)_n^+$.

Figure 3. Plots of $(C_2H_2)_n^+$ ion intensities vs. n for several sets of expansion conditions. Data has been corrected for background noise and contributions to ion signals due to ^{13}C isotope. All data was obtained with 70 eV electron energy. Expansion conditions are: a) P_0 = 1.5 Atm., T_0 = 275.8 K; b) 1.3 Atm., 268 K; c) P_0 = 1.5 Atm., T_0 = 268 K; d) P_0 = 1.8 Atm., T_0 = 268 K.

Figure 4. A typical 50 eV methylacetylene cluster mass spectrum. Expansion conditions were P_0 = 1.5 Atm. and T_0 = 259.6 K.

Figure 5. Plots of $(C_3H_4)_n^+$ ion intensities vs. n for several sets of expansion conditions. Data has been corrected for background noise and contributions to ion signals due to ^{13}C isotope. All data was obtained with 50 eV electron energy. Expansion conditions are: a) P_0 = 1.5 Atm., T_0 = 259.6 K; b) 1.8 Atm., 259.6 K; c) P_0 = 2.1 Atm., T_0 = 259.6 K; d) P_0 = 2.7 Atm., T_0 = 259.6 K.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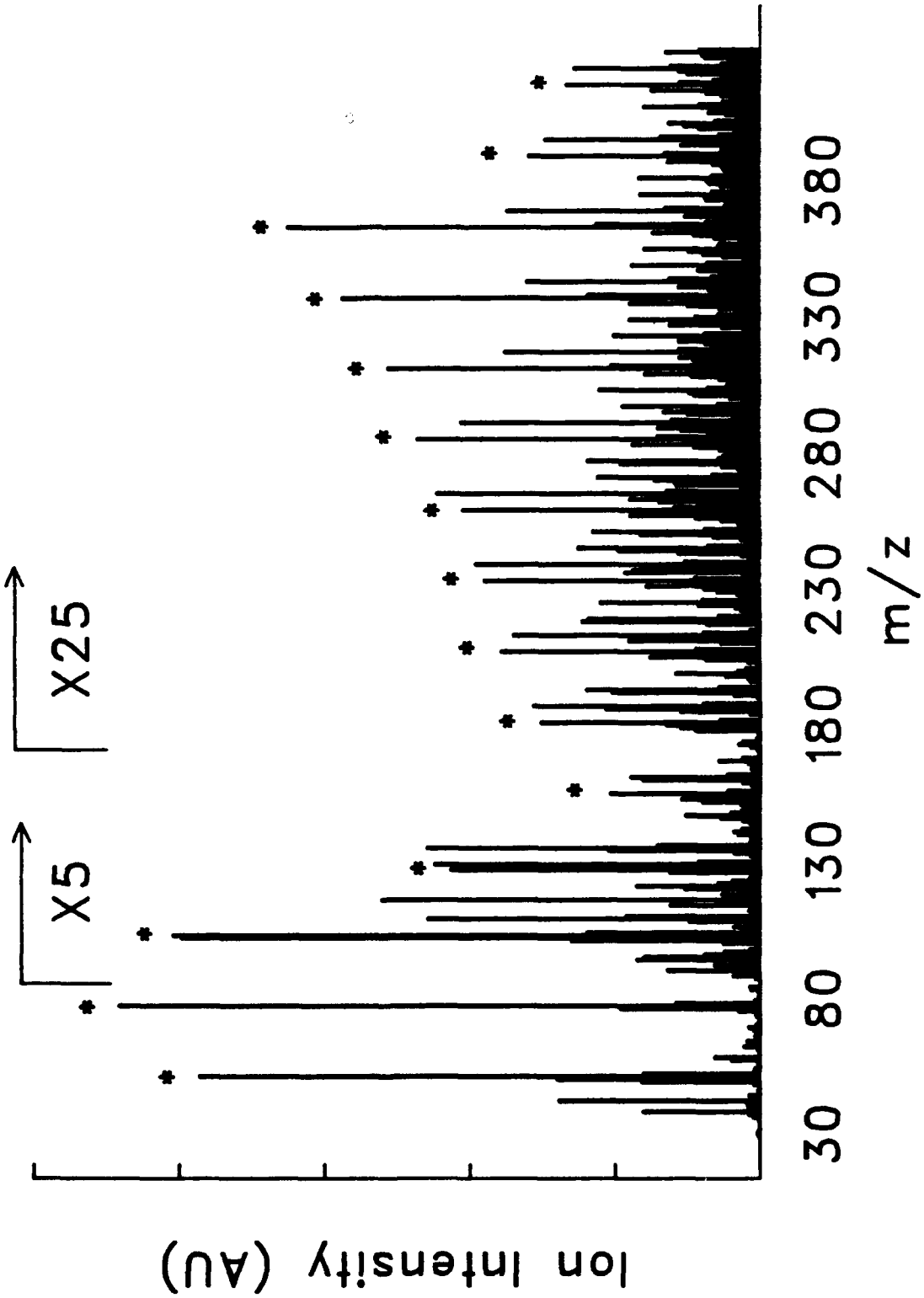
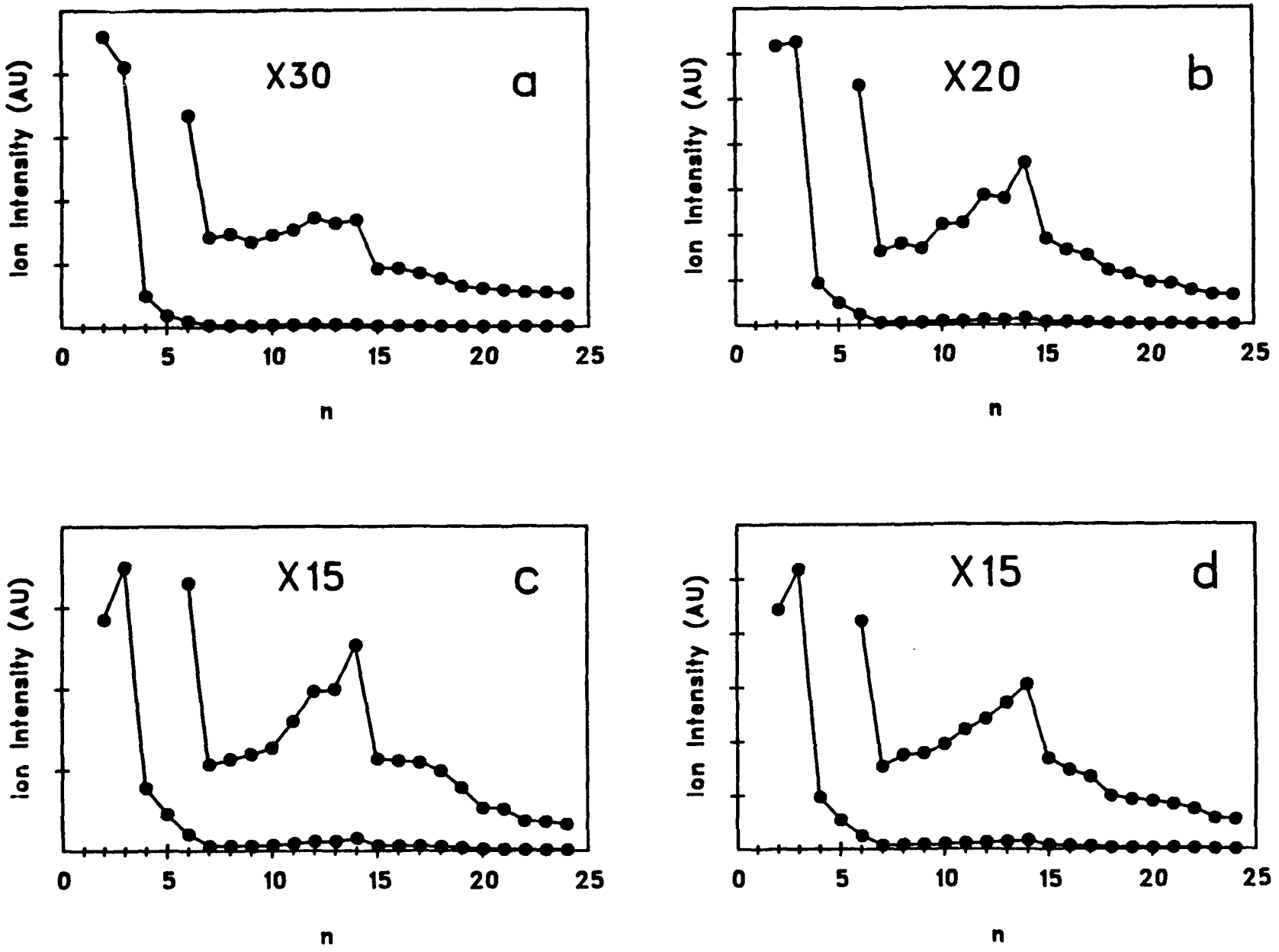


FIGURE 2, Goldstein et. al., "Intracluster [illegible]..."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b
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c
X15
d
Ion Intensity (AU)
n
0
5
10
15
20
25

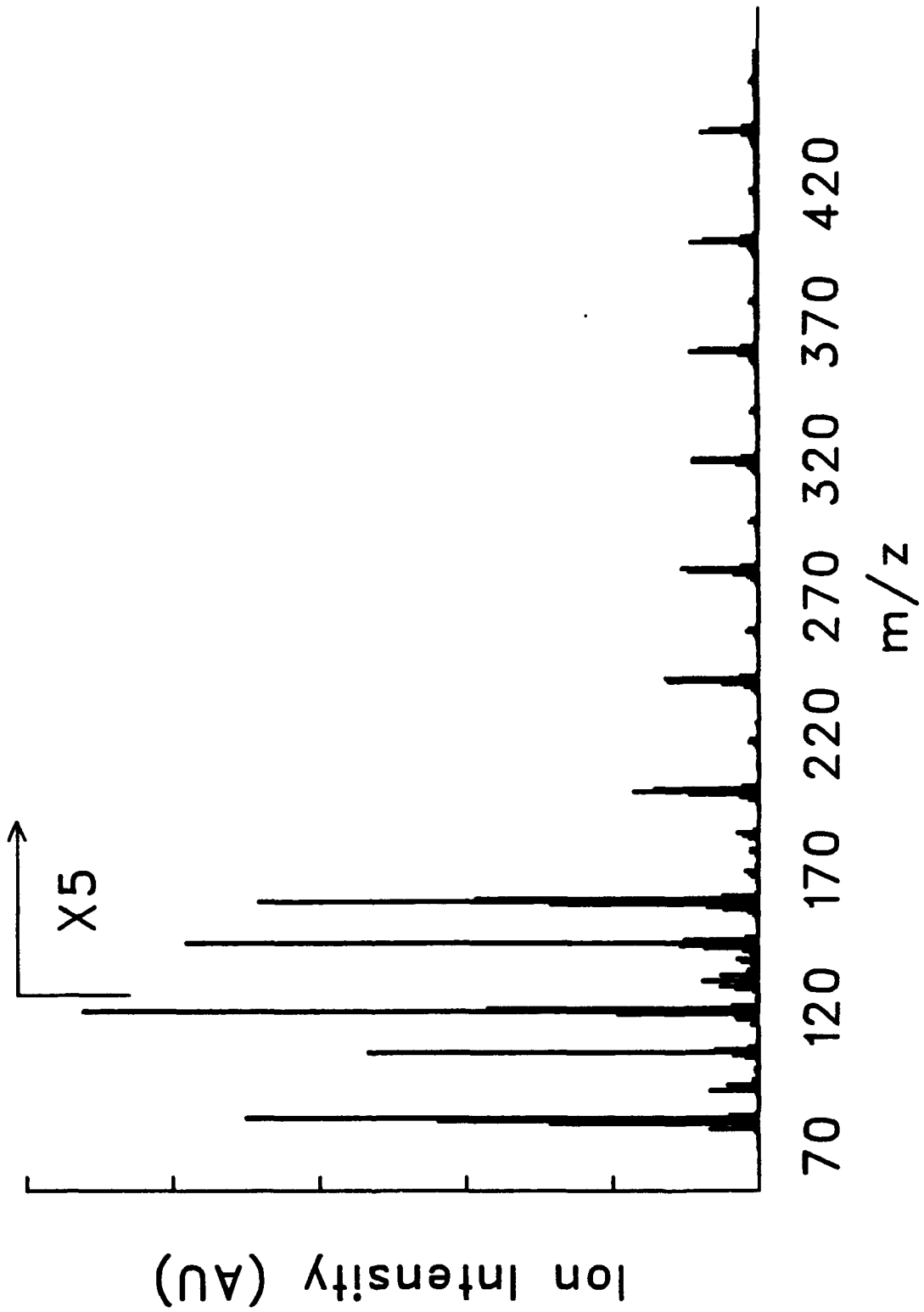
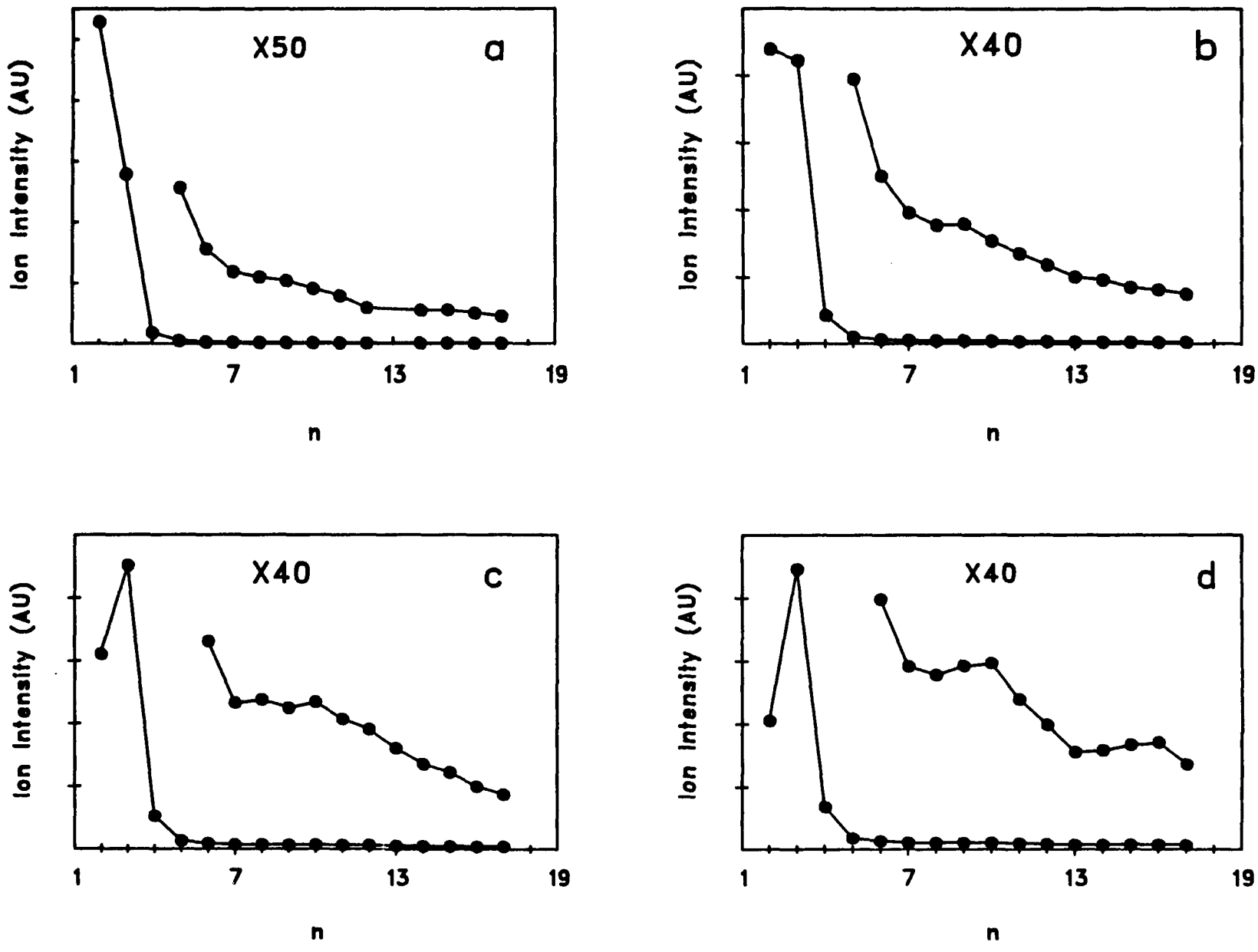


FIGURE 4, COOLBAUGH ET. AL., "INTRACELLULAR POLYHYDRATES."


X50
a
Ion Intensity (AU)
1
7
13
19
n
X40
b
Ion Intensity (AU)
1
7
13
19
n
X40
c
Ion Intensity (AU)
1
7
13
19
n
X40
d
Ion Intensity (AU)
1
7
13
19
n