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Aluminum Bromide Clusters

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Abstract: Mass spectra are presented of aluminum bromide clusters containing up to 30 atoms. Peaks in the mass spectra corresponding to $[(AlBr_3)_n]^+$ clusters are particularly strong for n equal to 2, 4, and 6. The structure and relative stability of neutral clusters were calculated by minimizing the total energy assuming purely ionic bonding. The calculations show enhanced stability for the $(AlBr_3)_{2n}$ species.

The stability of clusters of metal monohalides, $(MX)_n$, has been studied extensively both experimentally[1-5] and theoretically.[6,7] These studies have shown that clusters with certain sizes are highly stable. Mass spectrometric experiments on alkali halide clusters formed by bombardment of a solid with high-energy rare gas ions and atoms have indicated that clusters with the composition $[M_{14}X_{13}]^+$ are particularly stable. Calculations have shown that this cluster is most likely a small cube having the local symmetry of an NaCl lattice. The $[M_{14}X_{13}]^+$ cluster is highly stable even for CsI.

In the present investigation we have studied the metal trihalide $AlBr_3$. Evidence exists that the bonding in this molecule is at least partly covalent. The principal molecule found in the gas phase is the dimer Al_2Br_6. It is usually argued that the high stability of the dimer is due to the 4-fold coordination of Al giving it a complete octet of electrons. We will show that both the structure and the stability of the dimer and larger clusters can also be understood with a purely ionic model of the bonding.

Experimental Section

The technique used to produce clusters is based on that described by Sattler et al.[5] Anhydrous $AlBr_3$ was evaporated from a heated quartz crucible placed in a liquid nitrogen cooled chamber filled with 1 mbar of He gas. Clusters and small particles condense out of the high-temperature vapor on contact with the cold He gas. The clusters and gas flow through a small 3-mm diameter hole into a differentially pumped intermediate chamber and then enter the final vacuum chamber having a pressure of 5×10^{-6} mbar as a collimated beam. The clusters were ionized with 70-eV electrons and mass analyzed with a quadrupole mass spectrometer operated with a constant mass width Δm of 8 amu over a range of 0–2000 amu.

Results

Figure 1 is a mass spectrum of the cluster ions formed by the electron ionization of $AlBr_3$ vapor quenched in He gas. The spectrum appears complex at first glance because of fragmentation and the presence of water. However, the peaks are easy to assign. All the peaks repeat themselves at an interval corresponding to the mass of the $AlBr_3$ molecule. Therefore, it is necessary to identify the peaks in only one period in order to understand the complete spectrum. The peaks due to $[(AlBr_3)_n]^+$ have been shaded. These peaks are not the strongest in the spectrum. Neighboring peaks are at least one order of magnitude more intense. In addition, the strength of the $[(AlBr_3)_n]^+$ peaks does not decrease monotonically with increasing n, but alternates. The peaks are weak for odd n and strong for even n.

The strongest peak in each period can be unambiguously assigned to the cluster $[Al_nBr_{3n-1}]^+$. Why is this peak more than 1 order of magnitude more intense than the peak due to the stoichiometric cluster $[Al_nBr_{3n}]^+$? In an ionic picture of the bonding it is consistent to speak of Br electrons and Al electrons. The electrons most easily removed belong to the Br ions. After ionization the neutral Br atom interacts with the remaining ions in the cluster only through a relatively weak monopole-induced dipole term. This interaction is insufficient to compete with the large amount of energy converted to vibrational motion during the ionization process. The neutral Br atom is lost, resulting in a cluster with composition $[Al_nBr_{3n-1}]^+$.

Three peaks in each period of the mass spectrum in Figure 1 have been marked with arrows. These are due to the stoichiometric cluster ion with zero, one, and two Br ions removed. A weaker peak corresponding to the removal of three Br ions has not been marked explicitly. Each of these peaks is in turn the first member of a series of peaks separated by a mass interval of either 17 or 18 amu, corresponding to the addition of either OH^- or H_2O to the cluster. The low resolution of the mass spectrometer does not allow us to distinguish between these two possibilities. For example, the set of peaks near 1200 amu arise from the cluster Al_5Br_{15} minus two Br^- ions plus zero, one, and two OH^- or H_2O units.

There are several reasons why clusters containing an even number of $AlBr_3$ units might give rise to strong peaks in the mass spectrum. The simplest explanation is that since the vapor of $AlBr_3$ is known to consist primarily of dimers,[8,9] these dimers might be expected to act as building blocks in the formation of $(AlBr_3)_{2n}$ clusters. One objection to this explanation is that the strengths of the peaks corresponding to the fragments $[Al_nBr_{3n-1}]^+$ are independent of whether n is even or odd. An alternative explanation is that the $[(AlBr_3)_n]^+$ charged clusters have a higher stability if n is even. A third possibility is that the neutral clusters have a higher stability if n is even. In the following calculation we determine the stable configurations of neutral aluminum bromide clusters by minimizing the total energy.

Calculations

Because of the localized nature of the wavefunctions of ionically bonded materials it is possible to define a two-body interaction potential between ions. The total potential energy can be obtained by summing over the two-body terms,[7]

$$V = \frac{1}{2}\sum_{i,j} \frac{Z_i Z_j}{r_{ij}} + A \exp(-r_{ij}/\rho) \qquad (1)$$

The first term represents the Coulomb interaction between point charges Z_i and Z_j separated by a distance r_{ij}. The second term is a short-range Born–Mayer repulsive interaction. The calculational procedure is very simple.

First, decide how many ions are to be contained in the clusters. Place these ions anywhere in space. Then allow them to move, in the calculation, under the constraint that for each movement the total energy must be lowered, until it is not possible to move any ion in any direction without increasing the total energy. Then a stable or at least metastable configuration has been found. In this way, with only two parameters, A and ρ, we can calculate not only the shape of clusters of all sizes but also the binding

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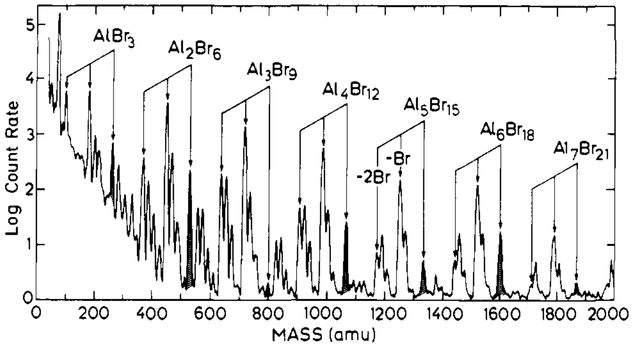

Figure 1. Mass spectrum of clusters formed by quenching the vapor over $AlBr_3$ in He gas.

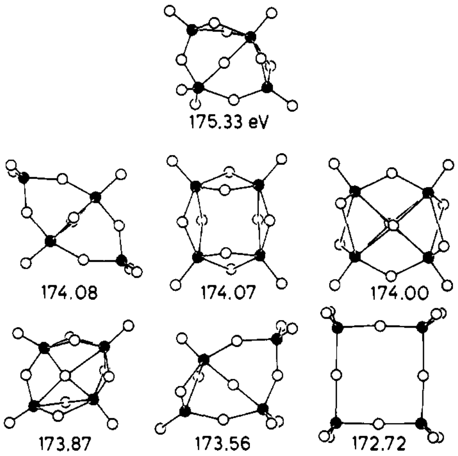

Figure 2. Stable configurations of Al_4Br_{12} clusters. The energy for dissociation into ions is given in eV.

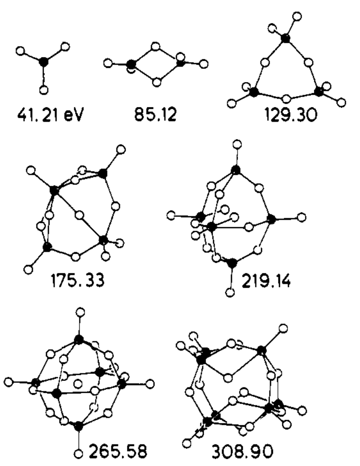

Figure 3. The most stable configurations of Al_nBr_{3n} for $n = 1$ to 7. The energy for dissociation into ions is given in eV.

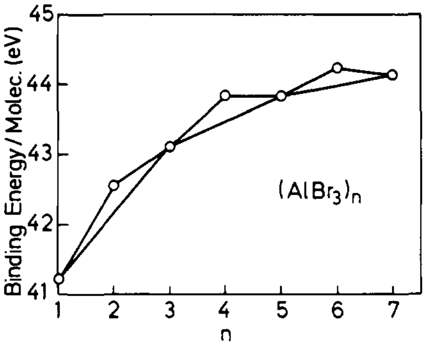

Figure 4. Binding energy per molecule for the most stable configuration of a given size.

energy, the vibrational frequencies, the free energy, and the infrared absorption. The assumption made here is that A and ρ are independent of cluster size and shape.

For each cluster size there exists more than one stable configuration. It is rather difficult to systematize the search for minima in the total energy surface. In fact, it remains more or less a matter of intuition. The best we can do is to make calculations for a large number of initial configurations. Each initial configuration will, of course, converge to some stable configuration. Usually, this stable configuration will be known from previous trials. Occasionally, a new stable configuration will be found.

The parameters A and ρ have been chosen to yield the known interatomic distances[10] in the $(AlBr_3)_2$ dimer. Explicitly, Z takes on the value 3 for Al and -1 for Br. A is chosen to be 4.0×10^{-9} erg and ρ, 0.31 Å.

Discussion

Relatively high energy (70 eV) electrons have been used in this work to ionize the clusters. Thus, we were able to obtain high ion yields. However, under these conditions fragmentation of the parent clusters must be expected. For this reason, in the past, we have been careful to draw conclusions concerning the stability of the charged fragments only. In the case of $[(AlBr_3)_n]^+$ clusters we are presented with a new problem. How should we distribute the negative charge removed from the cluster on ionization? Until now we have found no unique answer to this question. Therefore, results are presented for the calculated stable configurations of neutral clusters only. Such calculations indicate the relative stability of not only the parent cluster but also the ionized cluster if the charge is uniformly removed from all negative ions.

The multiplicity of metastable forms of a cluster is illustrated in Figure 2. In all cases the composition of the cluster is Al_4Br_{12}. However, through variation of the initial coordinates seven minima have been located in the energy surface. Notice that the most stable configuration is not that with the highest symmetry or densest packing. For the configurations shown in Figure 2, the Al ions all lie in the same plane. We have also found shallow minima for tetrahedral arrangements of the Al ions. However, the most stable of these had less than 174 eV of binding energy.

The most stable configurations for clusters containing one to seven molecules are shown in Figure 3. Starting with the cluster containing five molecules, a three-dimensional arrangement of the Al ions becomes energetically favored. The hexamer with highest symmetry consists of an almost spherical hollow shell of ions with a nonbridging bromine ion extending outward from each Al site. Energy is gained, however, if the symmetry is lowered by placing one of these dangling bromine ions at the center of the shell (Figure 3).

Figure 4 shows the total binding energy per molecule for the most stable configuration of a given size. Notice that the points tend to alternate about a smooth fit. Even values of n show high stability and odd values low stability, in qualitative agreement with the mass spectrum.

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Registry No. $AlBr_3$, 7727-15-3; Al_2Br_6, 18898-34-5; Al_3Br_9, 88211-74-9; Al_4Br_{12}, 88211-75-0; Al_5Br_{15}, 88229-01-0; Al_6Br_{18}, 88229-02-1; Al_7Br_{21}, 88211-76-1.

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