Energetics and Structure of Cluster Ions Inferred from Abundance Distributions

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If cluster ions are formed with excess energy and allowed to cool by evaporation, anomalies in the ensuing abundance distributions I_n often reveal corresponding anomalies in the evaporation (or dissociation) energies D_n. Anomalies in D_n, in turn, often provide a clue to the geometric structure. The correlation between I_n and independently computed D_n can be quite compelling.

This talk will focus on Cs^+ or coronene clusters $(C_{24}H_{12})_m^+ = Cor_m^+$ solvated in hydrogen. The corresponding neutral precursors are formed by passing He nanodroplets through a pickup cell containing Cs or coronene vapor and another cell containing H_2. The doped droplets are ionized by electron impact and extracted into a mass spectrometer.

Fig. 1 displays the abundance distribution of $(H_2)_nCs^+$ [1]. Abrupt drops in the abundance are observed at $n = 8$, 12, 32, 44, and 52. Three of these, 12, 32, and 44, are identical to anomalies in the distribution of He_nAr^+ which had been assigned [2] to three solid-like nested solvation shells of icosahedral symmetry (an icosahedral shell inside a dodecahedral shell inside an icosahedral shell). That conjecture has been corroborated by a path-integral Monte Carlo study [3]. The origin of anomalies at $n = 8$ and 52 remains to be explained.

The abundance of Cor^+ solvated in hydrogen (Fig. 2a) features an abrupt drop at $n = 38$ which likely corresponds to a structure in which all molecules occupy commensurate sites, i.e. 2 c-sites, 2*6 i-sites, and 2*12 o-sites with an overall D_{6h} symmetry. Additional anomalies at $n = 32$ and 36 indicate that formation of vacancies in the crowded solvation shell can reduce stress.

For the coronene dimer ion the drop in the abundance shifts to $n \approx 51$. It shifts by about another 11 units for the coronene trimer, and another 10 for the tetramer. We assign these shifts to a columnar structure in which adjacent coronenes are parallel displaced, forming terraces that offer additional strong adsorption sites. The cartoon in Fig. 2b illustrates the dimer structure. The experimental value for the number of adsorption sites per terrace, approximately six, barely depends on the number of coronene molecules. The displacement estimated from this number (6)

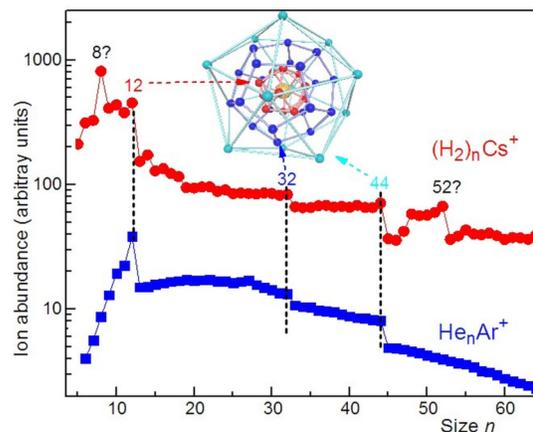exceeds the value reported in several theoretical studies of the bare, neutral coronene dimer.

Fig. 1. Abundance of ions solvated in H_2 and He [1,2].
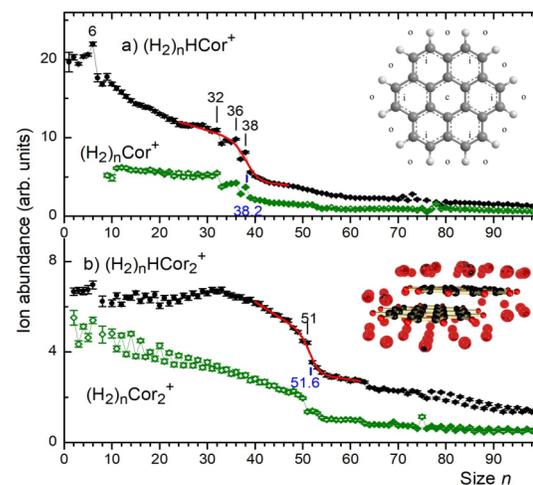

Fig. 2. Abundance of coronene monomer and dimer ions solvated in hydrogen [4].

References

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