lecture 6.1.2011

we had so far:

- details with respect to production and detection of clusters

now:

binding in clusters and their appearances in mass spectra

 a) undirected van-der-Waals bonding
 b) ionic bonding
 c) covalent bonds

Laser vaporization cluster source



the pulsed arc cluster source



Arc Cluster Ion Source (ACIS)



Methling et al., EPJD 16, 173 (2001)

Cu_N from the ACIS

with mass filter

80 V

250 V



Sputtering (Zerstäuben)



Fig. 1. Monte Carlo simulation of the trajectories of recoiling Cu atoms bombarded by 10 keV Ar⁺ ions at (a) normal incidence and (b) 70° (from ref. [5]).

The recoil trajectories are due to first-, second-, and higherorder collisions within the cascade. While the volume of the cascade caused by a single incident particle is quite large and extends nearly 100 Å into the solid, the area on the surface from which sputtered atoms are ejected about the impact site is only on the order of 40 Å in diameter.

Electrospray Ion Source



M. Yamashita and J. B. Fenn, Electrospray ion source. Another variation on the free-jet theme, J. Ph. Chem. 88, 4451 (1984)

J. B. Fenn, et al. Electrospray ionization for mass spectrometry of large Biomolecules. Science. 246, 64 (1989)

S. Brøndsted Nielsen *et al.*, Biomolecular ions in accelerators and storage rings, J. Ph. B: At. Mol. Opt.Phys. **37**, R25 (2004)

binding in clusters and their appearences in mass spectra

a) undirected bonding (Van-der-Waals)

b)ionic

c) covalent

d)metal

Neutral rare-gas clusters

Very weak bonding (van der Waals, or dispersion)

Mostly pair-wise (can be modelled by Lennard-Jones 6-12 potential) But three-body corrections are non-negligible Need low temperature to be stable (dimerization temperature is 11K for He, 281 K for Xe)

Molecular orbital diagram for He dimer



Bond order = 0

Charged rare-gas clusters

Molecular orbital diagram for singly charged He dimer



calculation of the structures

- two-body central forces (which is the main restriction)
- N-particle problem, 3N-6 inner coordinates rN
- conjugated momenta **p**^N

Hamilton function

$$H(\boldsymbol{p}^{N},\boldsymbol{r}^{N}) = \sum_{i} \boldsymbol{p}_{i}^{2}/2m + V(\boldsymbol{r}^{N})$$

with \mathbf{r}^{N} vectors in the N-dimensional configuration space

V d W: Lennard Jones Clusters



O Spherically-symmetric, pairwise additive model

С

$$U(\mathbf{r}^{N}) = \sum_{i=1}^{N} \sum_{j < i} u_{ij}(r_{ij}) \qquad u_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

Force
$$\mathbf{F}_{i} = -\sum_{j \neq i} \frac{\mathbf{r}_{ij}}{r_{ij}} \frac{du_{ij}}{dr_{ij}} \qquad \frac{\mathbf{r}}{r} \frac{du_{LJ}}{dr} = \mathbf{r} \frac{48\varepsilon}{\sigma^{2}} \left[\left(\frac{\sigma}{r}\right)^{14} - \frac{1}{2} \left(\frac{\sigma}{r}\right)^{8} \right]$$

Section of a potential energy surface



Example: stable and metastable configurations



B 88 33 83 A ġ ALL A S. 路 88 œ × 8 A E. B B ST -R æ 478 480

Fig. 11. Tetrahedral Lennard-Jones isomers for N = 13. The first and last 43 isomers from the total of 483 are selected, again in order of decreasing binding energy. Note the N = 13icosahedron top left and the Boerdijk spiral, which proves to have by no means the least possible binding energy.

Hoare

local energy minima



Figure 4. Local energy minima found for clusters containing 13 to 147 atoms. For each cluster size, the zero of energy is taken to be the energy of the apparent ground state. For clusters containing 55 or more atoms, we found minima of higher energy that are not shown.



Thomas Fennel

Mackay icosahedra





magic numbers

Fig. 5. The first five Mackay icosahedra. N = 13, 55, 147, 309, and 561, respectively.

geometric shell structure of rare gas clusters



Icosahedral vs. FCC cluster growth



(a)



(b)

GAP (c) The rare-gas crystals are FCC !

Icosahedra maximize the number of nearest-neighbour attractive interactions: it is greater than for a FCC/HCP cluster.

13-atom cluster : Icosahedra has 5 NN FCC has only 4 NN

However, packing of hard spheres as icosahedra gives frustration.

Cross-over between 800 and 10000 atoms

Geometrical Packing of Magnesium Clusters



Diederich et al., Rostock

free-energy landscapes

Example: the free energy landscape for protein folding



Folding occurs through the progressive organization of ensembles of structures [shown here for the src-SH3 domain (**left**)] on a funnel-shaped free energy landscape (**right**). Conformational entropy loss during folding is compensated by the free energy gained as more native interactions are formed. Kinetics is determined by the local roughness of the landscape, relative to thermal energy. Key interactions in early folding (dashed circle) coincide, for this protein, with experimentally determined regions.

application to isomerization in clusters

Visualization: Disconnectivity Graphs

At a given energy, minima can be divided into 'basins' whithin which minima are mutually accessible via transition states lying lower than this energy. Minima in different basins cannot interconvert at this energy.

Lowering the energy causes basins to split as the threshold descends below the connecting transition states.

In a disconnectivity graph, basins are calculated at a series of energies, plotted on a vertical scale. Each basin is represented by a node at the appropriate level. Lines join parent nodes to their daughters in the level below

Adjacent are some schematic potential energy curves and the corresponding graphs. Below are results for Lennard–Jones (LJ) clusters.



disconnectivity graphs





landscape. The lowest–energy 150 minima out of a database of 6000 are plotted above.

Lowest 900 minima in a database of 6000 shown. All the minima are solid–like, as only the very lowest parts of the landscape have been covered.



http://brian.ch.cam.ac.uk/index.html





David Wales et al.

proteins



David Wales et al.

binding in clusters

a) undirected bonding (Van-der-Waals)

b)ionic

c) covalent

d)metal

additional terms to the interaction potential:



- monopole dipole interaction
- dipole-dipole interaction
- self energy of the dipole

ionic bonding in alkali halides





Ionic lattice structure

T.P. Martin

Fig. 5. Mass spectrum of $Na(NaI)_n^+$ clusters. The interval between the oscillations corresponds to the number of atoms needed to cover one face of cuboid-shaped clusters.



Stable configurations for alkali halides with a small number of atoms



binding in clusters and their appearences in mass spectra

a) undirected bonding (Van-der-Waals)

b) ionic

c) covalent

d) metal bonding

Basics of covalent bonding: The Hydrogen molecule

- The classic case of <u>covalent bonding</u>, the hydrogen molecule forms by the overlap of the wavefunctions of the electrons of the respective hydrogen atoms in an interaction which is characterized as an exchange interaction. The character of this bond is entirely different from the <u>ionic bond</u> which forms with <u>sodium</u> <u>chloride, NaCl</u>. If you measure then energy balance when you form H+ and Hions and examine the attractive force between them, the energy required is positive for any value of ion separation. That is, there is no distance at which there is a net attractive interaction, so the bond cannot be ionic.
- The electron distribution around the protons of the hydrogen is described by a quantum mechanical wavefunction, and the wavefunction which describes the two electrons for a pair of atoms can be symmetric or antisymmetric with respect to exchange of the identical electrons. From the <u>Pauli exclusion principle</u>, we know that the wavefunctions for two identical fermions must be antisymmetric. The <u>electron spin</u> part of the wavefunction can be symmetric (parallel spins) or antisymmetric (opposite spins), but then the space part of the wavefunction must be the opposite. That guarantees that the entire wavefunction (the product of the spin and space wavefunctions) is antisymmetric. The two possibilities for the spatial wavefunctions for distant hydrogens are shown below.

basics of covalent bonding: the Hydrogen molecule



As shown above, when the hydrogen atoms are brought close together the symmetric spatial wavefunction leads to a bonding configuration of electrons and the antisymmetric one does not. The actual electron charge density is given by the square of the magnitude of the wavefunction, and it can be seen that the symmetric wavefunction gives a high electron density between the nuclei, leading to a net attractive force between the atoms (a bond).

basics of covalent bonding: the Hydrogen molecule

The exchange interaction (an entirely quantum mechanical effect) leads to a strong bond for the hydrogen molecule with dissociation energy 4.52 eV at a separation of 0.074 nm. The potential energy of the antibonding orbital shown gives some insight into why a third hydrogen atom cannot bond to the two atoms of the hydrogen molecule. It would be in an anti-bonding situation with one of the other hydrogen atoms and would therefore be repelled. We say that the bond in the hydrogen molecule is "saturated" because it cannot accept another bond.



For larger molecules or clusters: Quantum-chemical methods, e.g., Hückel approximation



Carbon: a model case for covalent bonding





the fullerenes

In 1985, identification by Kroto, Smalley, Curl and co-workers of the C_{60} molecule as being a truncated icosahedron, with very high symmetry (Ih) :

all 60 atoms are equivalent, and are three-fold coordinated.

Also, fullerenes with 70, 76, 78 (3 isomers), 84 (2 isomers), ... atoms.



(Named after the architect Buckminster Fuller)

Buckminster-Fulleren







"Buckminister-Fulleren"





Lanthan Atom in C_{60}

Small carbon clusters

Competition between rings and chains. Chains are more floppy (entropy favoured), but rings are energetically favoured above N=10.

Magic number for ionized carbon chains : 7,11,15 ...

Linear structures of C_3 and C_5 . The spectral lines due to the C_3 molecule were seen in 1881 in the spectrum of a comet, but not identified until 1951. C_5 identified in the infrared spectrum of a carbon star.

ACC.

mass spectrum of carbon clusters



mass spectra of silicon clusters

Charged clusters show magic number n=6, 10, 16 and 32, but a maximum in the spectrum is not followed by a deep minimum for n+1 atoms ! (Photofragmentation shows no monomer evaporation).



structure of Si clusters



Proposition of basic building blocks : distorted octahedral Si_6 and adamantane (a diamond fragment) Si_{10} . Actually, the calculated lowest energy structure for Si_{10} is the high density tetracapped trigonal prism.

Compared to carbon, reduced tendency to participate in π -bonding.

structure of hydrogenated Si clusters



Hydrogen atoms saturate the silicon clusters by taking up dangling bonds : more open, sp^3 structures.

metal chalcogenide clusters : ZnS mass spectrum



MoS platelet



Seifert et al.

Hydrogen bridge binding: molecular clusters, e.g. (H₂O)_N



Ring structures. One hydrogen per molecule involved in H bond. Near-planar structure of H bonds. Frustration for odd cycles. Tunneling splitting pattern of the vibration spectrum (like for ammonium)

Five-membered ring structure of the 20 water molecule cluster. Note that only six-membered rings are present in hexagonal ice.

structure of protonated water clusters



Most clusters consist of a number of water molecules surrounding a hydronium ion, H_3O^+ . The $(H_3O^+)(H_2O)_3$ moiety, with $C_{3\nu}$ symmetry, is the smallest unit where the inner hydronium is completely hydrogen bonded. The structure of $(H_3O^+)(H_2O)$ is however $H_2O\cdots H^+\cdots OH_2$