

# Vibrational properties of colloidal semiconductor nanoclusters

P. Han and G. Bester

Colloidal semiconductor nanocluster research is a rapidly growing field driven by the attractive idea to tailor material properties by acting on the morphology of the structures. The modification of the optical properties by merely changing the diameter of colloidal quantum dots is one of the figureheads of nanostructure science. It is the intense research effort towards the fabrication of nanostructures with favorable properties that has helped to establish most of the knowledge base we rely on today. The modifications of the electronic and optical properties by changing the size of the nanoclusters are rather well understood theoretically and well controlled experimentally. However, the effects of temperature on the electronic and optical properties of nanoclusters and hence their vibrational properties remains largely on open question. A solid understanding of the physical processes involved is a decisive step for real world applications, in which the physical properties such as temperature broadening, loss of quantum coherence and relaxation of charge carriers are key components. We have recently calculated confinement and surface effects on the vibrational properties of III-V and II-VI colloidal nanoclusters based on first-principles density functional theory (DFT) [1]. We described how the molecular-type vibrations, such as surface-optical, surface-acoustic, and coherent acoustic modes, coexist and interact with bulk-type vibrations, such as longitudinal and transverse acoustic (LA, TA) and optical (LO, TO) modes. We could link the vibrational properties to structural changes induced by the surface and highlight the qualitative differences between III-Vs and II-VIs. We also derived a set of empirical interatomic potentials for zinc blende III-V semiconductors based on DFT calculations. These potentials allow us to study the surface relaxation and the vibrational properties of nanoclusters with experimental sizes, i.e. typically thousands of atoms [2].

The nanoclusters we studied are constructed by cutting a sphere, centered on a cation with  $T_d$  point group symmetry, from the zinc blende bulk structure and removing the surface atoms having only one nearest-neighbor bond. The surface dangling bonds are terminated by pseudohydrogen atoms  $H^*$  with a fractional charge. We use *ab initio* DFT to optimize the geometry and to calculate the vibrational eigenmodes. The wave function of the lowest unoccupied molecular orbital (LUMO) states of  $Ga_{531}As_{532}H_{412}^*$  nanocluster is plotted in Figure 1.

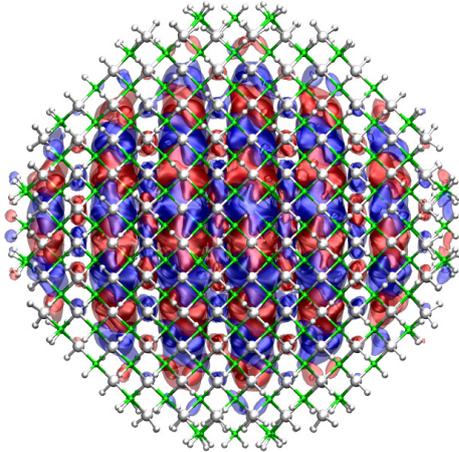


Figure 1: The wave function of the lowest unoccupied molecular orbital (LUMO) state for a  $Ga_{531}As_{532}H_{412}^*$  nanocluster with isosurface corresponding to 75% of the maximum value. The colors blue and red indicate the phase of the wave functions.

We have calculated the vibrational properties for a series of nanoclusters made of InP, InAs, GaP, GaAs, CdS, CdSe, and CdTe. In this report, we select InP and CdS clusters as representatives to describe the confinement and surface effects on the vibrational properties. The results are given in Figure 2 and allows us to make three observations: First, the III-V materials (illustrated by InP) show a blueshift of LO-, TO-, and LA-derived cluster modes with decreasing size, while II-VI materials (illustrated by CdS) show no such shifts. Second, the surface modes tend to completely fill the acoustic-optic phonon gap in II-VIs, in contrast to the situation in III-Vs. These modes have purely optical character and can be described as “surface optical” modes. Moreover, the surface modes, which vibrate with frequencies below the lowest core modes, have purely acoustic character and can be described as “surface acoustic” modes. Third, the “broadening” of the bulk optical phonon branches induced by the confinement is larger for II-VIs than for III-Vs. These three effects can be understood from the geometry of the relaxed nanoclusters. We plot in Figure 2 (k)-(n) the nearest-neighbor distances of relaxed III-Vs and II-VIs as a function of the distance of the respective bond to the cluster center. From Figure 2 (k)-(n), we see that for III-Vs the surface shells show a successive reduction of bond length, going outward, while II-VIs show a large bond-length distribution. The overall reduction of bond length in III-Vs along with the positive Grüneisen

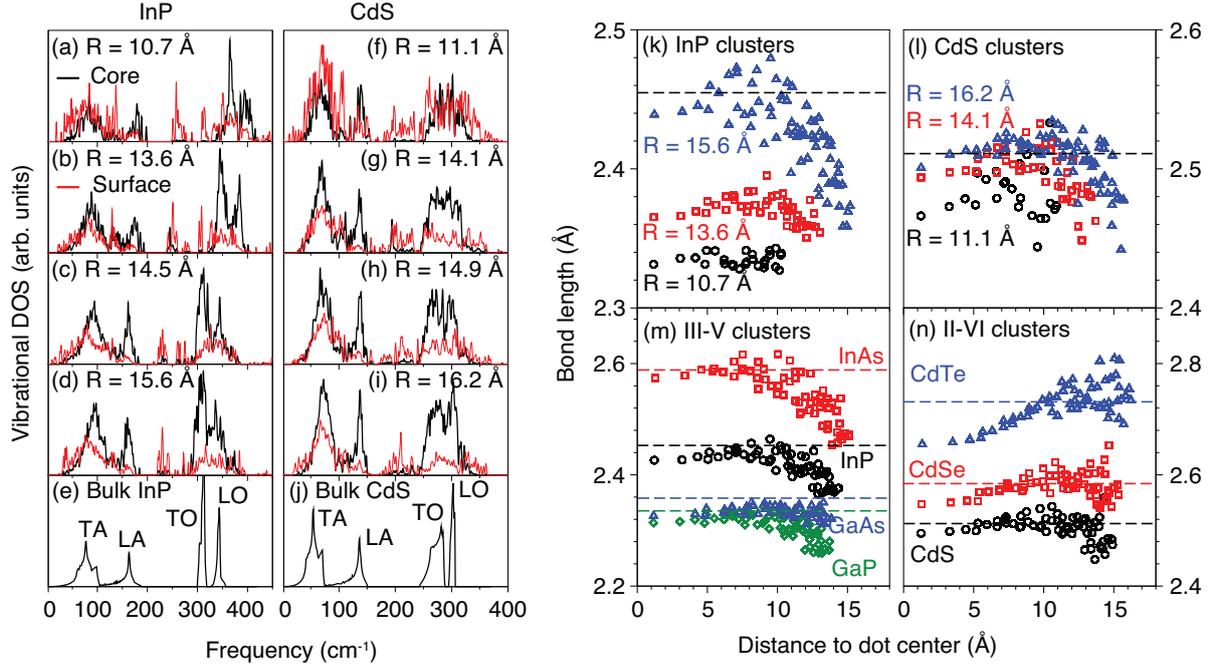


Figure 2: Vibrational density of states (DOS) contributed by core atoms (black) and surface atoms (red) for (a)-(d) InP clusters, (e) bulk InP, (f)-(i) CdS clusters, and (j) bulk CdS. Bond-length distribution as a function of their distance to the dot center for (k) InP, (l) CdS, (m) III-Vs, and (n) II-VIs. LDA bulk bond lengths are given as dashed lines.

parameters (describing the change in phonon frequencies with volume) explains the blue shift of the LO-, TO- and LA-derived cluster modes (first observation above). The lack of shift in the TA modes stems from the small negative Grüneisen parameter for this branch. We attribute the large bond-length distribution at the surface of II-VIs to the long-range ionic interaction and connect it to the broadening of optical branches and the filling of the phonon-gap (second and third observations above).

After looking at the vibrations on the medium and high frequency regions, we now focus on the confinement effects on the interesting low frequency part of the spectrum. Similarly to classical waves confined in one

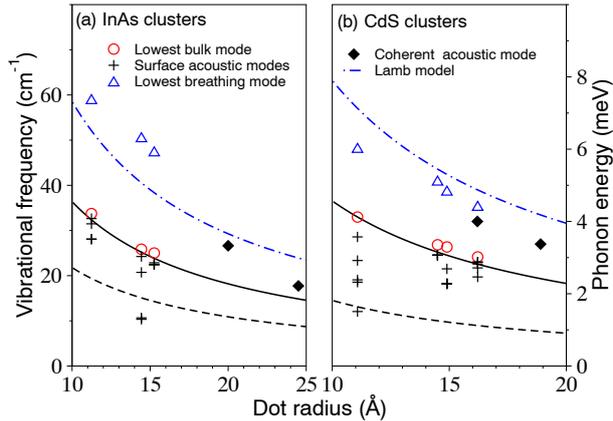


Figure 3: Size-dependent low frequency vibrational modes for (a) InAs and (b) CdS. Lowest modes with bulk character (circles), surface acoustic modes (crosses), lowest breathing modes (triangles), and experimental results [D. Oron *et al* Physical Review Letters **102**, 177402 (2009), L. Saviot *et al* Physical Review B **57**, 341 (1998).] for the coherent acoustic modes (diamonds). Lowest spheroidal mode according to the Lamb model (dashed-dotted line), according to the confined bulk model using the sound velocity of the TA- (solid lines) and LA-branch (dashed lines).

dimension, the vibrational frequency of the longest wavelength in a nanocluster can be described as  $f_{min} = v/2d$ . Here,  $v$  is the velocity of sound and  $d$  is the diameter of the cluster. In Figure 3, we plot the size-dependent lowest frequencies  $f_{min}$  calculated from the longitudinal and transverse sound velocities as solid and dashed curves. As circles and crosses we plot the lowest core and surface modes obtained from the DFT calculations. We see that the lowest modes with dominant bulk character follow closely the analytic  $1/R$  dependence. The surface modes have the lowest frequency since they can run over the surface of the cluster. They are however strongly affected by the morphology of the surface and their frequencies are not monotonous with cluster size. One last important type of modes are the so called *coherent acoustic modes*. These are breathing modes, where all the atoms vibrate in phase. These modes have been observed via Raman spectroscopy, far-infrared absorption spectroscopy, and resonant high-resolution photoluminescence spectroscopy, and are now the center of attention

when the manipulation of spins and the spin-decoherence in nanoclusters is investigated. We plot our results as triangles in Figure 3, the experimental results as diamonds and the results of the Lamb model as dashed dotted line. Our results are in good agreement with the experimental results (although our clusters sizes are still somewhat smaller than experiment in the case of InAs) and with the simple Lamb model.

In summary, we have performed *ab initio* DFT calculations to study the confinement and the surface effects on the vibrational properties of III-V and II-VI colloidal nanoclusters with up to thousand atoms. We can identify the following confinement and surface effects. (i) The LA, TO and LO-derived cluster modes of III-V clusters significantly blue shift with decreasing cluster size. For II-VI clusters this shift is absent but the broadening of bulk derived modes is significant and the gap between optical and acoustic phonons is filled by surface modes. (ii) We can clearly ascribe these observations to the large relaxation of the clusters dominated by: an inward relaxation of the surface penetrating deep inside the cluster in case of the III-Vs and a large distribution of bond length at the surface of II-VIs. These strong confinement effects tend to disappear for clusters with more than 1000 atoms. (iii) We find surface optical modes in the phonon gap and surface acoustic modes as the lowest frequency modes. The *coherent acoustic phonons* are identified and found to be in good agreement with results from the Lamb model and experiment. In addition, we have derived a set of empirical interatomic potentials for the surface relaxation and vibrational mode calculation of III-V nanoclusters. These potentials allow us to extend our research to the realm of nanoclusters with up to ten thousand atoms.

#### References:

- [1] *P. Han and G. Bester* Physical Review B **85**, 041306(R) (2012).
- [2] *P. Han and G. Bester* Physical Review B **83**, 174304 (2011).