Excitation, dynamics and dephasing in quantum dots

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Abstract.   This paper concerns the femtosecond dynamical relaxation of excited states in quantum dots or clusters. The clusters are typically polar, consisting of 150–200 atoms, and are of interest for potential photonic devices. Our work identifies certain novel effects, 'dynamic dilation' and 'ringing', associated with excited states of non-metallic dots of this size. Dynamic dilation occurs for dots at constant pressure, rather than constant volume. Dilation induces a modest but significant energy shift on a picosecond timescale, slower than the characteristic vibrational period of the configuration coordinate. The magnitude of the shift is clearly size dependent, tending to zero in the limit of a bulk system. This shift can be equivalent to dephasing, and may explain one component of dephasing already experimentally observed. Such dephasing may also affect the usefulness of dots in ultrafast optical switching. The second novel effect associated with the clusters is the relatively long-lived vibrational excitation of the dot leading to 'ringing'. This is strongly sensitive to the acoustic mismatch with the environment. Neither 'dynamic dilation' nor 'ringing' are especially sensitive to the composition of the dots, or to whether the excited states correspond closely to bulk excitons or to defect states, and hence need to be taken into account in the excitation of quantum dots.

1. Introduction: quantum dots and their dynamics under optical excitation

We discuss here some special and unexpected features of those quantum dots or clusters which comprise a few hundred atoms. Discussions of quantum dots [1] or clusters in this size range sometimes regard the dot as a bulk solid with confinement; many other approaches treat the dot as a large molecule. Both descriptions have merit; however, there are properties peculiar to systems of a few hundred ions (radii R of 1–2 nm). In particular, small changes in the volume of the dots can cause significant shifts in their electronic states. These dots are much smaller than the commonly discussed semiconductor dots of perhaps ten thousand atoms, which have a size appropriate for single-electron (Coulomb blockade) effects. The dots discussed in this paper might be incorporated in optical fibres or deposited on suitable substrates for optoelectronic applications.

1.1. Dot characterization

Even the best-characterized ensembles of dots of a few hundred atoms include a range of shapes and sizes. Sizes may be the same to within a few per cent of the average radius [2]. This is consistent with experiments showing that dot-to-dot variation of the optical excitation energy is of the order of 0.1 eV [3]. There are also shifts of the order of 0.1 eV associated with the external fields of charges on other dots or in the matrix in which the dots are embedded.

The dot shape will be very important for some phenomena. Both electric fields and strains will vary from one atomic site to another, depending on the precise structure and positions of the ions. In an ionic dot, the mere removal of a single ion can give a large change in internal electric fields: a proton charge at 1.4 nm (comparable with dot radii) gives a field of 10^7 V cm^{-1} if the dielectric constant is 10. Such electric fields will tend to separate electrons and holes, reducing luminescence efficiency. Clearly, charged defects, including surface and edge defects, will lead to diverse behaviour from one dot to another: average quantities and idealized geometries omit important features.

Nevertheless, other features are generic, and less sensitive to the details of the dot. There is a change in lattice parameter associated with the surface tension or stress of the dot [4]. There will be relatively large volume fluctuations in thermal equilibrium. For a dot of 200 atoms, the root mean square dilatational strain can be perhaps 0.5–1%, using equation 111.7 of [5]. Our main concern in this paper is to identify and analyse further such generic properties associated with the dynamical behaviour of dots following optical excitation. We shall identify new aspects of behaviour, 'dynamic dilation' and 'ringing', which are missing in standard descriptions. In addition, we shall show that dynamic dilation could affect the use of dots in optical components, not because the effect is especially large, but because of its timescale.

1.2. Timescales

Our interest is in the dynamic behaviour of dots, especially the motion of the ions after optical excitation. The timescales of interest here are those associated with the lattice vibrations of the dot. The first concerns how rapidly the excess vibrational energy induced by an optical transition will redistribute, either to other modes of the dot or its surroundings. The second timescale comes from the slower response arising from the timescale of the volume change of the dot upon excitation. We shall show that the dot size is in a range where this slower response may be important in applications. In effect, there is a shift in frequency of the zero-phonon line, varying from dot to dot. This spectral shift can appear as dephasing, i.e. spectral diffusion will result in dephasing.

1.3. Dynamics of optical excitation

When analysing the dynamical behaviour of dots, there is a crucial distinction to be made between the normal modes of a harmonic system and reaction coordinates, such as the configuration coordinate of standard optical transition studies. The normal modes are dynamically independent; their relationship to individual ionic displacements includes the boundary conditions, like the free surface: there can be no question of 'scattering' of these modes by the surface. In typical dots these modes are obviously not plane waves, nor do they have a continuous spectrum. It is these modes which are used in constructing vibronic states of the dot. The configuration coordinate is rarely a normal mode (except, perhaps, for small molecules) but is a combination of modes which is optimized to give the best single coordinate for some purpose, usually to represent the electron–lattice coupling for some state or some transition [6]. This has several consequences. One is that a configuration coordinate will usually consist of a mixture of modes of different frequencies. After some rapid event, these components will get out of step, and this is one class of dephasing. Another consequence is that, if the dot shape relaxes after excitation (so as to relieve surface shear stresses) the precise mix of modes in a configuration coordinate will change.

2. Dephasing: characteristic times and energies

Dephasing is important as it might limit ultrafast coherent control of the formation or destruction of excited states. Clearly, inelastic scattering between different vibronic states of the dot causes decoherence. As Leggett observed, 'the part of the system–environment interaction which tends to destroy quantum coherence is just the part which causes dissipation in the classical motion' [7]. It is plausible that elastic scattering, which redistributes energy over degenerate vibrational modes, will also lead to loss of coherence. However, certain other proposed mechanisms should have no effect. In particular, 'scatter of phonons from the dot surface' [8] cannot be a mechanism for dephasing. As noted above, the phonons describe the excitation of normal modes, the dynamically independent combinations of ionic displacements, which already include the surface.

Experimentally, three-pulse photon echo experiments yield dephasing times in CdSe dots from 85 fs in a 21.2 Å dot up to 270 fs in a 40.5 Å sample [8]. Similarly, in InP a dephasing time of 280 fs was observed for a 29 Å sample [9]. The resulting dephasing times or, more strictly, the homogeneous linewidths, obtained by Mittleman *et al* [8] for an ensemble of CdSe nanocrystals are summarized in their figure 11. Their discussion distinguishes several contributions, the most important of which, at 15 K, is the so-called elastic part ($\propto 1/R$) where R is the dot radius. This is described as scatter of phonons from the surface. We do not believe that this is the right description: this scatter should have no effect on the homogeneous width. Our analysis offers another explanation, namely dynamic dilatation, which also predicts a $1/R$ dependence of the dephasing.

Another group of important experiments is the work of Empedocles *et al* [3] which describes two main classes of experiment, the most important being single-dot luminescence, as opposed to fluorescence line narrowing. The samples that they used were single-domain wurtzite CdSe dots (slightly prolate along the *c*-axis; diameters of 3.9, 4.5, 5.0 nm) and dots coated with ZnS. This coating seems to have solely beneficial effects, although the large lattice mismatch of about 10% raises questions. Some of the results of Empedocles *et al* are unique to studies of individual dots, such as the observation that dots can flicker on and off. The evidence suggests that dots are being photoionized. There can be optically induced charge transfer between dot and matrix, as well as within the dot. Probably there is charge transfer within the matrix as well. This electrostatic part (shift due to random charges outside the dot) is quite large, since there is spectral diffusion. Lines can shift to red or blue by perhaps 0.01 eV on the one-minute timescale of the measurements (read from their figure 4; see also their figure 3). The extent of the shift and the linewidth both increase with power. The idea proposed is that there are changing electric fields as charges move in the surrounding matrix. These effects are plausible, but lie outside the range of phenomena that we discuss here. The most important observations of Empedocles in the light of the work presented here is that, again, the linewidth broadenings are of the right order of magnitude to be explained by the effect of volume expansion. It is interesting that the more constrained 'capped' dots have narrower luminescence linewidths. All of the experiments referred to here are carried out at low temperature of less than 15 K, so thermal contributions to volume fluctuations are small.

3. Model dots

Our simulations are of model dots, which retain the critical features of actual dots, but which are simpler, so generic features are easier to identify and interpret. Our aim is to aid interpretation of experiments and to provide a guide for future, more realistic, simulations.

The most comprehensive data are for dots of cadmium chalcogenides, such as CdS, sometimes capped by another chalcogenide. The chalcogenides are polar systems, but significant covalency is implied by their fourfold coordination and relatively open structure. Such systems can present problems in molecular dynamics, and artificial instabilities are not easy to avoid. However, none of the phenomena which we discuss actually depend on the ionic/covalent mix, nor on the coordination. We have therefore used NaCl dots of diameters between 14 Å and 25 Å as model systems, choosing NaCl largely because there are validated and stable interatomic potentials.

The NaCl dots are realistic in certain important respects:

(i) they include long-range Coulomb forces;
(ii) there is phonon dispersion, which includes the discreteness and confinement of the modes;
(iii) there is a free surface (we can, of course, attach the dot to a substrate, or embed it, when appropriate); and
(iv) we can vary dots by removing atoms or substituting atoms in ways which are simple to model.

The NaCl model is unrealistic in other respects. NaCl is not CdS, and we shall not be able to identify any CdS-specific features, such as surface reconstructions and their dependence on excitation. Even for NaCl, we shall oversimplify some of the consequences of the electron–phonon interaction. In real NaCl, for instance, the exciton self-traps. We constrain our model so that self-trapping does not occur, since self-trapping does not occur in CdS. We also make simple assumptions about the nature of the excited states. These assumptions are entirely conventional and standard. We shall be able to avoid the unrealistic elements in planned developments to use self-consistent molecular dynamics. The calculations presented here use the DL_POLY code† to carry out molecular dynamics on classical ground- and excited-state potential energy surfaces.

Table 1. Born–Huggins–Meyer parameters for NaCl, following [10].

	A (eV)	B (Å^{-1})	C (eV Å^{-6})	D (eV Å^{-8})
Na–Na	0.9113×10^{10}	13.8122	3.10	1.60
Na–Cl	0.5862×10^{4}	3.7850	21.79	20.76
Cl–Cl	0.3361×10^{4}	2.8058	193.92	269.12

3.1. The model for the dot in its ground state

We have simulated cubic clusters of NaCl, concentrating on dots consisting of $6 \times 6 \times 6$, $8 \times 8 \times 8$ or $10 \times 10 \times 10$ ions, with approximate diameters 14.0 Å , 19.6 Å and 25.2 Å. The parameters for the short-range potential were those from the shell model of Sangster and Atwood [10] (see table 1), slightly modified to eliminate the shells, and with an ionic charge of 1.00 rather than 0.97. For our potential, the elastic constants were $c_{11} = 6.72 \times 10^{10}$ N m^{-2} and $c_{12} = 2.00 \times 10^{10}$ N m^{-2}; the dielectric constants were $\epsilon_0 = 3.58$ and $\epsilon_\infty = 1.00$ calculated using PLUTO [11]. The elastic constants are

slightly larger than the experimental values of 5.72×10^{10} N m^{-2} and 1.1×10^{10} N m^{-2} respectively, and the dielectric constants are smaller than the experimental values of 5.45 and 2.35 respectively. The velocity of sound in the crystal, $v = \sqrt{c_{11}/\rho}$, is 5.52×10^3 m s^{-1}.

3.2. Modelling the excitation process

Again, our simple model includes the essential features of the excited state, but avoids some features which are not generic. For example, at this stage we do not need to know the details of how surface or edge defects polarize excitons within the dot, but we do need to know how exciton creation affects the ionic motions.

We have considered two types of excited state. Both lead to sudden changes in the forces acting on the ions. The first type of excited state, referred to hereafter as *Coulombic*, mimics the NaCl exciton created in absorption [12]. This involves the transfer of one electron from a central Cl ion to its six nearest Na neighbours. The redistribution of charge leads to changes in forces directly on all of the ions, although the closest are most affected. As noted, we do not let the exciton self-trap during the motion. Nor, for simplicity, do we allow the charge to transfer between ions during the ionic motion, although this will be incorporated in planned calculations exploiting molecular dynamics with quantum chemistry. The second type of excited state, referred to hereafter as *non-Coulombic*, mimics the intra-site excitation of an impurity, in which the excited state of the impurity ion has short-range force constants different from those in its ground state. This we did by reducing the exponential decay of the Buckingham potential between a central Cl ion and its nearest neighbours. The direct change in force is only on these ions. The magnitude of the change in force was chosen to be of the same order as the exciton-like excitation. The forces are relatively small since we are interested in the effect of excitation upon the zero-phonon line.

4. Volume changes upon excitation in a continuum model

The excitation of the cluster results in a change in volume of the system as the cluster relaxes to the equilibrium volume in response to the new electron–ion forces. However, due to the channels for dissipating the excitation energy being limited, the cluster in fact oscillates about an average value, the corresponding static volume change. The static change in volume of a solid due to the introduction of a defect is a much-studied problem [13–15] and can be estimated in terms of the defect forces acting on the ions.

The change in volume in a harmonic system is determined by the Betti reciprocity theorem [16] which asserts that if a set of forces $\boldsymbol{f}'$ lead to displacements $\boldsymbol{x}'$ and a set $\boldsymbol{f}''$ lead to displacements $\boldsymbol{x}''$, then $\boldsymbol{f}'' \cdot \boldsymbol{x}' = \boldsymbol{f}' \cdot \boldsymbol{x}''$, i.e. the work done is independent of the order of the application of the forces. In this case, $\boldsymbol{f}''$ corresponds to the external hydrostatic pressure. Because $\boldsymbol{f}''$ is normal to the surface at each point and uniform over the surface, $\boldsymbol{f}'' \cdot \boldsymbol{x}'$ is proportional to the volume change induced by the defect, or in this case excitation forces. Carrying through this analysis, one arrives at the following expression for the volume change is terms of the virial of the defect forces corresponding to the excitation:

$$\Delta V = \sum_{i,j} \sum_{k} \sum_{l} s_{ijkk} F_i(R_l) R_{jl} \tag{1}$$

where the forces $F(R_l)$ correspond to the force due to the defect on the ions in their unrelaxed positions. From this expression it can be seen that for a localized defect which does not exert significant forces upon the cluster surface, ΔV should be independent of the cluster size.

In our case the excitation corresponds to the effective introduction of a defect into the relaxed cluster and the corresponding volume change, ΔV, can be calculated. The most important feature is the lack of dependence of ΔV on cluster size. Thus, for dots, just as for crystals, we expect a volume change on excitation of order one atomic volume, this being typical of observed values. This has an important corollary: if the volume change ΔV is independent of the total volume, then the strain $\Delta V/V$ varies inversely with the dot volume V. For a ΔV of one atomic volume, a dot of 200 ions would have a $\Delta V/V$ of perhaps 0.005, i.e., 0.5%. This can be significant. This hydrostatic strain is significantly less important for the larger quantum dots considered for single-electron devices; for them (with typically 10 000 atoms), $\Delta V/V$ would be only 0.01%.

There is a second corollary from the relatively large strain associated with excitation. Deformation potentials give the shifts under stress of energy gaps, exciton energies, or band energies, with typical values of a few eV. Assume that, for a dot, there is a deformation potential of 5 eV, in the middle of the ranges known. The energy change from a hydrostatic strain of 0.5% (a band-edge shift or an exciton energy shift) will be 2.5×10^{-2} eV. This shift should be compared with the width of the narrowest peaks seen for individual dots (10^{-4} eV [3]), the typical spacings between the (discrete) vibrational mode energies (10^{-4} eV), with the homogeneous linewidths seen in three-pulse–echo experiments (10^{-2} eV [8]) and with typical laser linewidths. There is thus an energy shift associated with the dilation, and this is comparable with or larger than other key energies.

To summarize, the volume change to relieve surface shear leads to a small but significant shift in transition energy. This shift is largest for very small dots, since it is the strain that matters, not the volume change. This is a shift of the zero-phonon line (and distinct from the usual optical shifts, such as the Stokes shift). For typical deformation potentials and volume changes, the shift would be few meV. Since ΔV is approximately fixed, $\Delta V/V$ will vary inversely as V, and one expects the shift to vary inversely as R^{-3}. For bulk solids, the dilatational strain from a single excitation is negligible, and has observable effects only in special situations such as for donors in silicon [17] or when the appropriate radius R is the distance between defects.

5. Dynamics and dilatation

The volume change in a finite elastic solid has two parts [18]. One part is a uniform dilation, independent of position in the dot. The other part is linked to the displacements of the nearby atoms which fall off at large distances as r/r^3. These short-range displacements dominate the configuration coordinate. However, it is displacements of surface atoms which give a volume change, and it is these which have a slower relaxation. At a free surface, tractions must vanish [19], and the time-dependent dynamics of the tractions is critical.

The energy shift from the volume change on excitation is modest. One might assume that it would be unobservable, since there will also be shifts associated with other mechanisms. Why should the modest shift from the volume change following excitation be important? The answer depends on timescales. The shift is of interest because of its dynamics, which we have studied using molecular dynamics.

For optical transitions, there are several natural timescales. First, there is a fast timescale, typically tens of femtoseconds, the characteristic time being $\tau_L = 2\pi/\omega$, the vibration period for the configuration coordinate. Secondly, there is a timescale τ_S associated with the optical lifetime. This is of order nanoseconds for allowed optical transitions, but can be as short as picoseconds when induced (stimulated) transitions are used in optical switching. Thirdly, in the case of the cluster there is an intermediate timescale, τ_V, associated with the change

in the dot volume (measured by the normal outward motion of the external surface of the dot) as it adjusts to constant-pressure and zero-surface tractions. This characteristic time will be of the order of the dot radius divided by the velocity of sound in the material. The velocity of sound is itself of the order of the interatomic spacing divided by the period of the highest-frequency acoustic modes. Both of these simple descriptions and our computer modelling agree that τ_V will be a few hundred femtoseconds for dots of a few hundred atoms. Thus we expect that $\tau_V \sim \tau_L(R/a)$. This characteristic time is proportional to the dot radius, R. Clearly, for small molecules with $R \sim a$, τ_V will be of the same order as molecular vibrations so the standard picture of molecular spectra will hold. For bulk solids the timescale is also irrelevant because the energy shift would be vanishingly small. Only for quantum dots and perhaps large molecules such as photosynthetic molecules [20] will the dynamical shift be important.

The fact that τ_V is greater than τ_L means that, for the dots that we consider, the zero-phonon line in absorption will involve the motion of near neighbours on the timescale τ_L, and the lattice dynamics is essentially that appropriate to constant volume. Slower relaxations with timescale τ_V will lead to a slightly delayed shift in the zero-phonon-line energy, as described. Even for a zero-phonon line, there will be changes on this τ_V-timescale which shift the emission relative to the corresponding absorption. This shift would be interpreted as dephasing in some photonics applications, in particular in ultrafast switching on a timescale of the optical lifetime of the excited state.
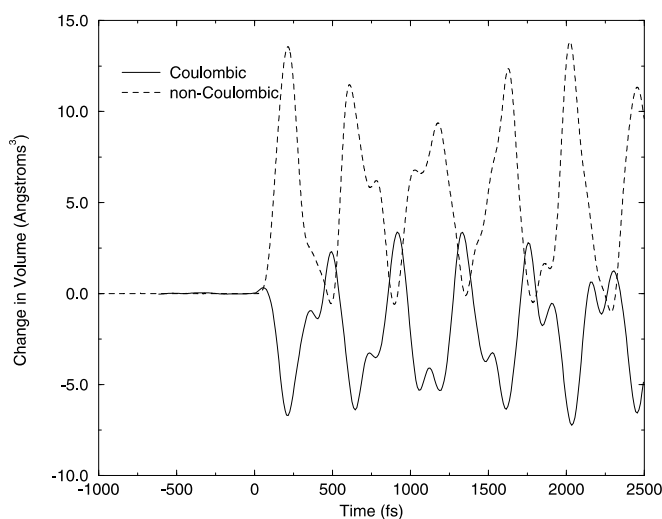

Figure 1. The effect of excitation (at $t = 0$ fs) upon the volume of a 216-ion NaCl cluster: (i) undamped oscillation of the volume ('ringing') about a smaller average upon Coulombic excitation, (ii) undamped oscillation of the volume about a greater average upon non-Coulombic excitation. The period of oscillation corresponds to the breathing mode of the cluster.

The dynamic relaxation can be usefully described in a thought experiment. Suppose that external forces are applied to the outermost atoms of the dot, so that the average positions of these outer atoms do not move following excitation. The zero-phonon line will be precisely that for constant volume. Now, instead, suppose that the external forces relax slowly to zero after excitation, with a time constant τ_V. The energy of the lowest vibronic state will fall on this timescale. This is the dynamical shift. When τ_V/τ_L is reasonably large, the fast vibrational motion will be distinct from the slower relaxation. This corresponds to

the condition just described when the dot dimension is significantly larger than one lattice spacing. In reality, the slower relaxation is not due to imaginary external forces but arises because the vibrations take a finite time to reach the surface [21].

In experiment, the dots rest on a surface, or are embedded in another medium with different elastic properties. There will be an interface-related stresses which will modify V, and affect the non-hydrostatic strains. These stresses can also have spectroscopic consequences, but these are less easy to estimate in a simple general way. We have modelled some representative cases. Perhaps the most important consequence of the substrate or embedding medium is in its role in taking up energy from a dot. For example, distributing 5 eV over 200 atoms corresponds to a 300 K rise in temperature.

6. Results of molecular dynamics

Our simulations (see figure 1) show clearly the change in volume of the dot upon excitation and the accompanying excitation of low-frequency acoustic modes. We have estimated the volume change upon excitation as a function of time by calculating the normal displacement of the ions from the average surface for the ground state. In our simulations we also know the effective forces corresponding to the excitation, and so we have compared our dynamical result with the calculation of the static equilibrium volume change using the virial (section 6.1). Although the static change provides a scale for comparison, the neglect of anharmonic terms and defect forces acting directly upon the surface hinders quantitative prediction, as is well known from previous work [14, 15].

Upon excitation, the clusters relax and vibrate about new equilibrium positions. In our simulation the dots are initially at zero temperature. The excitation activates breathing-mode oscillations of the cluster, with a period of between 450 and 600 fs, the period increasing with the diameter of the cluster. There are three important aspects of the dynamic dilation: firstly, the effect on the energy of the electronic state, secondly the time taken for the system to reach the new mean volume and thirdly the relaxation of the dot. We have calculated the deformation potential corresponding to the excitation and hence have obtained the change in energy of the electronic state. The time taken for the system to respond to the excitation is relevant for switching properties of the dot, and we find in agreement with the previous discussion that the time is of the order of the breathing-mode period. We find that the clusters continue to oscillate in the excited state due to the possibilities for dissipation of vibrational energy in an isolated dot being limited.

6.1. Static volume change

Excitation of the dot results in a change in dot volume. The dynamics can be examined both in terms of the overall volume change of the dot, and also from the changes in volume of cubes of increasing size surrounding the ion excited. The change in volume $\Delta V(t)$ at each time-step was calculated by averaging over the normal displacements of the ions of the appropriate surface. We also obtained the total change in volume from a time average of $\Delta V(t)$. We have compared the average change in volume with the change according to the virial—see table 2.

The virial calculation involves the ionic positions and the change in forces on excitation. As discussed, we considered two model excitations. For the Coulombic case (charge transferred from a central Cl^- to its six nearest Na^+), we calculated the change in forces due to these changed charges on other ions of the unrelaxed cluster. For the non-Coulombic

Table 2. The change in volume of the clusters: virial versus measured.

Cluster	ΔV_{meas} (Å^3)	ΔV_{virial} (Å^3)
C 216	−2.12	−6.53
C 512	−2.28	−6.40
C 1000	−2.70	−6.35
NC 216	5.26	10.27
NC 512	5.77	10.15
NC 1000	6.70	10.09

excitation, the forces arise from the change in short-range potential between the nearest-neighbour Na$^+$ ions and the central Cl$^-$ ion.

The magnitude of the volume change predicted by the virial is roughly double that observed in the molecular dynamics simulations and indicates the problems recognized in previous work [14, 15]. In particular, as for bulk ionic solids, it is necessary to include correction terms to account for anharmonicity and relaxation effects to obtain agreement between static and dynamic estimates. Nevertheless the change in volume of the cluster is roughly independent of cluster size, as predicted by the virial.

6.2. Dynamic dilation

The dynamical dilation leads to a change in energy for the electronic transition. This is the case even for what would be a normal zero phonon. However, this is a time-dependent shift, since the lattice takes a finite time to reach the new volume. We have measured the deformation potential D of the dot by measuring the dependence of the energy gap between excited and ground states as a function of dilation. We obtained for our model system a

Table 3. The change in electronic energy due to dilation.

Cluster	ΔV_{meas} (Å^3)	Percentage change	ΔE_{gap} (meV)
C 216	−2.12	0.08	0.66
C 512	−2.28	0.03	0.25
C 1000	−2.70	0.02	0.16
NC 216	5.26	0.20	−1.6
NC 512	5.77	0.08	−0.66
NC 1000	6.70	0.04	−0.25

Table 4. Change in volume of clusters compared with thermal fluctuations.

Cluster	ΔV_{meas} (Å^3)	Percentage change	ΔV_{therm} at 27 K
C 216	−2.12	0.08	0.06
C 512	−2.28	0.03	0.04
C 1000	−2.70	0.02	0.03
NC 216	5.26	0.20	0.06
NC 512	5.77	0.08	0.04
NC 1000	6.70	0.04	0.03

value of -3.5 eV for the Coulombic exciton-like excitation, which agrees respectably with the experimentally measured value of -2.5 eV for NaCl [22]. The corresponding shifts in the transition energy (see table 3), namely 0.6 to -1.6 meV for the clusters investigated, are in agreement with the estimates in section 4. For the clusters examined here, this shift is too small to be resolved directly in our molecular dynamics.

Because the dilation is not large, thermal fluctuations of the volume will rapidly broaden the transition as temperature increases. Table 4 contains the expected percentage volume fluctuation [5] for the dots, from which it can be seen that even at low temperatures there will be a significant thermal contribution to the linewidth.
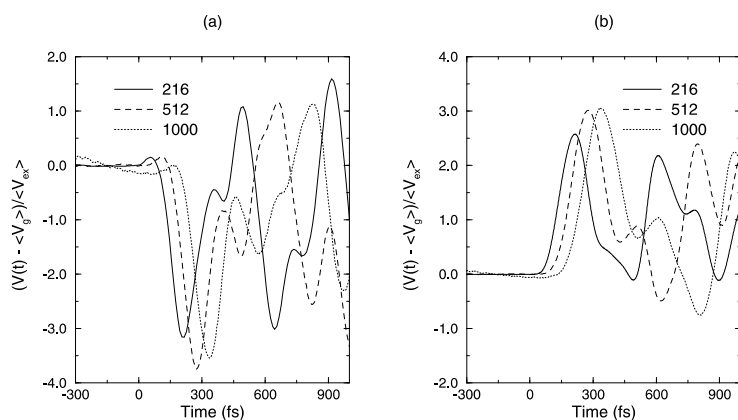

Figure 2. The dependence of the delay in volume increase after excitation at $t = 0$ fs upon cluster size for (a) Coulombic excitation and (b) non-Coulombic excitation. To aid comparison between the 216-, 512- and 1000-ion NaCl clusters, the vertical axis indicates the relative change in volume (the difference between the volume and the average ground-state volume/average excited-state volume).
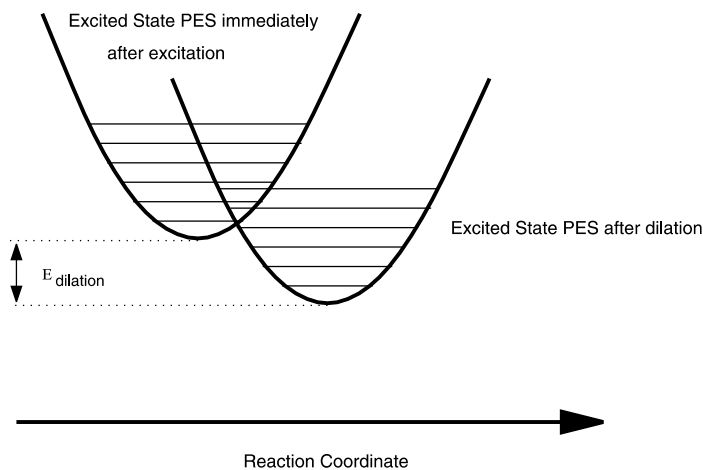

Figure 3. A diagrammatic representation of the effect of dilation upon the effective-reaction-coordinate potential energy surface after excitation, indicating the origin of the shift in the zero-phonon line.

The most important feature of the dilation, as expected from the analytical model, is that expansion of the outer surfaces of the dots is not instantaneous. The dots take between 100 fs and 250 fs to expand to their new average volume (see figure 2). As expected, this corresponds to approximately a quarter of the breathing-mode period of 450 to 600 fs†. The predicted time dependence of the volume expansion is readily seen: there is a process with characteristic time $\tau_V \sim R$. Hence, following absorption of the resonant energy E at time $t = 0$, there is a slower relaxation (characteristic time τ_V), leading to a lower resonance energy E' for the emission process (see figure 3). For processes which involve stimulated absorption and emission in rapid succession, even for transitions between well-defined vibronic states, the dot will behave as if there is a loss of coherence for times $t > \tau_V$.
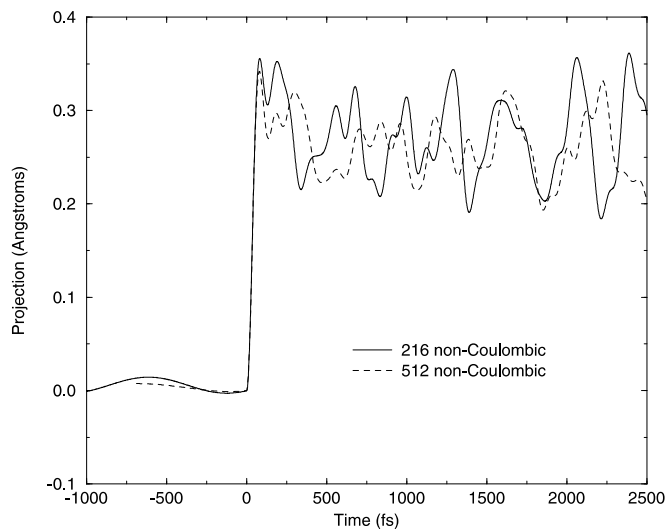

Figure 4. The projection of the ionic motion along the reaction coordinate versus time for 216- and 512-ion clusters upon non-Coulombic excitation at $t = 0$ fs. The reaction coordinate is the direction of the displacement of the ions between the ground state and the relaxed excited state.

We can also monitor the effective reaction coordinate as a function of time. The reaction coordinate is determined as the direction of the displacement of the ions between the average ground-state configuration and the relaxed excited-state configuration. Figure 4 illustrates the projection of the ionic displacements along the reaction coordinate for the non-Coulombic 216- and 512-atom clusters, from which it can be seen that the motion has a number of frequency components, the shortest having a period of order 100 fs which is considerably less than that of the volume oscillations.

7. Conclusions

We have used both analytical and molecular dynamics methods to understand some of the relaxation processes in dots of a few hundred atoms, following excitation. The two approaches agree in key features, and especially as regards the generic features which are likely to hold for the quantum dots of interest in optoelectronics.

† The periods are slightly longer for dots of the given sizes than would be expected from a calculation using the velocity of sound given in section 3.1. This is because v was obtained for the perfect, unrelaxed cluster.

Following excitation of a dot of a few hundred atoms, there are both rapid and slower vibronic relaxation processes. The rapid optical absorption process corresponds to the zero-phonon line for which the nuclear motions are essentially vibrations at constant volume. These fast processes follow a slower dynamical dilatation adiabatically. This slower process may be complicated, but dilation is probably a major component.

The slower dynamic dilation process will appear to give dephasing in certain types of optical experiment. Is this behaviour seen? Apparently, yes it is. The behaviour, with its observed R^{-1}-dependence, appears to match the so-called elastic processes [3, 8] of dephasing. The explanations given in the original papers refer to phonon collisions with surfaces [8]. As noted above, this cannot be right as it stands, since any discussion of optical lineshapes should be based on the normal modes in the initial and final states, and not on the plane waves used as a conceptual tool. The surface is already built into the harmonic normal modes, and they cannot cause scattering between the properly defined normal modes. However, dephasing through the shift from volume relaxation (dynamic dilatation) does have the right R-dependence. It also seems to have the right implied picosecond timescale: for dot radii of about ten nearest-neighbour distances, a time of about 1 ps should be typical. This lies between the values 0.1 ps reported by Mittleman *et al* [8] and 10 ps reported by Empedocles *et al* [3].

For very small dots of the sort discussed, the low-frequency normal modes are discrete, and do not form a continuum. The process of establishing thermal equilibrium can be quite slow. Further, the root mean square volume fluctuations for a dot of this size will be quite large. The vibrational energy generated on electronic excitation will lead to 'ringing' in which there are relatively persistent, approximately periodic, volume fluctuations. These fluctuations will be influenced by the 'capping' of clusters (e.g. a layer of ZnS outside the basic CdS dot). The benefits of capping may be dynamical, as well as electronic and we plan to study this further in separate work.

In principle, our ideas could be checked in a molecular beam experiment. To our knowledge, this has not been done.

Acknowledgments

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