Photoabsorption spectroscopy on isolated Ga_NAs_M clusters

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Photoabsorption spectra of isolated Ga_NAs_M clusters ($N+M=4-80$) have been investigated in the range $\hbar\omega=1.7-6.4$ eV by measuring their absolute photodissociation and photoionization cross sections. The results are analyzed in terms of an effective optical band gap, and answer the question of how the well-known quantum-size effects in semiconductor colloids are transformed into the molecular spectra of small semiconductor clusters. [S0163-1829(96)07240-2]

There has been intensive research into the photoabsorption cross section $\sigma(\omega)$ of metal clusters in order to understand how the typical Mie resonances[1] of metal colloids transform into the molecular spectra of small clusters.[2] However, for semiconductor clusters only the relative spectra of small In_NP_M and Si_N clusters[3] have been investigated by Mandich and co-workers. Measurements on In_NP_M clusters have demonstrated that these clusters are optically transparent in the infrared region, and that the absorption increases for photon energies larger than a typical energy E_{bg} that seems to play a similar role for clusters as the band gap does in bulk semiconductors.

Similar results to those obtained for In_NP_M clusters were obtained in the present work for Ga_NAs_M clusters; however, we concentrated on the absolute values of the oscillator strength which allow us to determine an effective optical band-gap energy quantitatively, and its evolution with cluster size. This investigation was carried out with the purpose of contributing to the understanding of the behavior of optical properties observed for semiconductor quantum dots and colloids: the band gap of these particles increases continuously as their diameter D decreases. A typical example is the band gap of GaAs colloids,[4,5] which increases from $E_{bg}=1.5$ eV for $D=22$ nm ($N+M\approx 2\times 10^5$) to $E_{bg}=3.5$ eV for $D=3$ nm ($N+M\approx 600$). This effect is usually described by means of quantum particle models, where the electrons are represented by waves confined in a spherical box.[6] On the other hand, it is experimentally known that the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the diatomic GaAs molecule is only $E_{bg}\approx 3.0$ eV.[7] Hence two questions arise: (i) how the band gap evolves in the size range between $N+M=600$ and $N+M=2$, and (ii) how the formal divergence of the band gaps E_{bg} within the quantum particle model for $D\rightarrow 0$ can be avoided in order to connect the quantum-size effects of colloids to the molecular electronic structure of semiconductor molecules.

We have therefore experimentally investigated the size evolution of the optical-absorption spectra of Ga_NAs_M clusters. An effective optical band gap $E_{bg}(p)$ can be defined in order to quantify the onset of optical absorption in the vicinity of the band edge by

$$\int_0^{E_{bg}(p)} \sigma(\hbar\omega)\, d(\hbar\omega) = pF_e. \quad (1)$$

This formula determines the energy $E_{bg}(p)$, where the integral oscillator strength is increased to a certain fraction $p \ll 1$ of the complete, one-electron oscillator strength $F_e=1.1$ eV Å^2.[8]

The so-defined value of $E_{bg}(p)$is consistent in the limit $p\rightarrow 0$ with the conventional definition of the bulk band gap. However, an experimental determination is restricted to small, positive p values.

The cluster beam apparatus has been already described in detail elsewhere.[9] The clusters are produced by a pulsed-laser vaporization clusters source. The clusters leave the source through a nozzle at a temperature of 300 K, and a collimated molecular beam is formed. Size-selective cluster intensities are measured by ionizing the clusters with a second excimer laser ($\hbar\omega=7.89$ eV) and detecting the ionized clusters with a time-of-flight mass spectrometer. In the present experiment the clusters are excited on their way from the source to the detector by an excimer laser beam that intersects the cluster beam perpendicularly. Photoabsorption is followed by photodissociation,[10] and appears as a loss of intensity (depletion) of the excited clusters in their mass spectrum, similarly to the experiments described in Ref. 3. If the photon energy of the excitation laser reaches the ionization threshold, photoionization of Ga_NAs_M clusters provides an additional channel for light absorption.[11] Photoionization spectra are obtained recording directly the cluster cation signal, i.e., the second excimer laser is switched off. Simultaneously, the intensity of the excitation excimer laser beam is measured with a photometer (accuracy $\pm 20\%$).

For excitation energies lower than the ionization thresholds the experimentally determined depletion of the cluster signal is $x_{dis}=I/I_0$, where I and I_0 are the intensities of the cluster beam respectively in the presence or absence of the excitation laser. This depletion is theoretically related to the transition probability $w(a\rightarrow e)$ from an initial state $|a\rangle$ to a final state $|e\rangle$ of the cluster. Within the dipole approximation, and taking only single photon absorption into account, x_{dis} is given by[12]

$$x_{dis}=1-w(a\rightarrow e)=1-\frac{4\pi^2|W_{ea}|^2\,\delta(E_e-E_a)}{h}\Delta t, \quad (2)$$

wherein $W_{ea}=\langle e|\hat{W}|a\rangle$ is a transition matrix element of the perturbation operator $\hat{W}$, and Δt is the time period of the

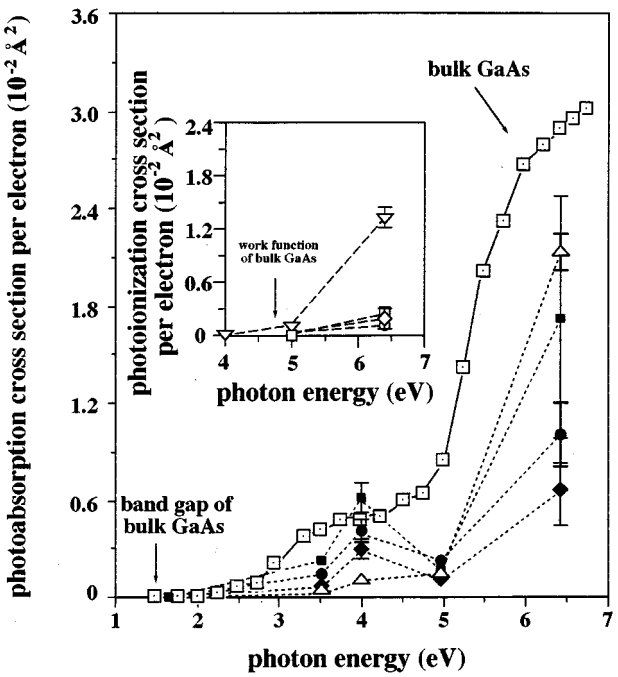

FIG. 1. Absolute photoabsorption and photoionization cross sections of Ga_NAs_M clusters. Photoabsorption cross sections per electron: $N+M=5$ (■), 6 (♦), 7 (●), 80 (△), and bulk (⊡). Photoionization cross sections per electron (inset): $N+M=5$ (□), 6 (◇), 7 (○), and 80 (▽). The accuracy of the absolute scale for the cross sections is about ±20%.

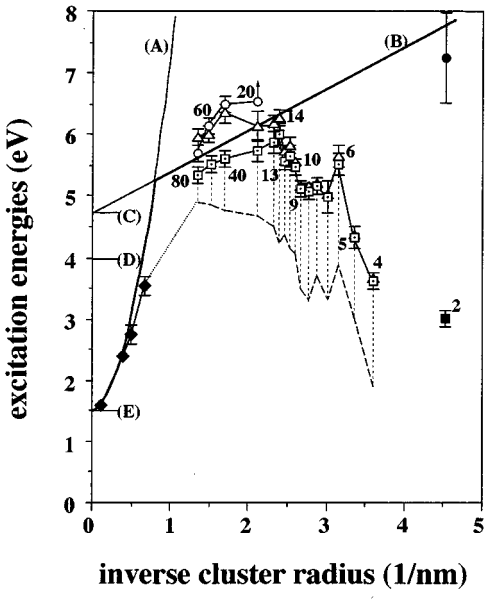

FIG. 2. Excitation energies of Ga_NAs_M clusters: Effective optical band gaps $E_{ip}(p=0.02)$ (⊡), effective photoionization gaps $E_{ip}(p=0.02)$ (○) and effective photodissociation gaps $E_{dis}(0.02)$ (△), photoabsorption band gaps $E_{bg}(p\approx 0)$ for GaAs colloids (♦), and photoabsorption and photoionization thresholds of diatomic GaAs (■ and ●). The quantum confinement model is represented by curve (*A*), the ionization thresholds $E_{ip}(p=0)$ within the dielectric sphere model by curve (*B*), the work function of bulk GaAs (Ref. 21) by curve (*C*), the effective optical band gap $E_{bg}(p=0.02)$ of bulk GaAs obtained by Mie theory by curve (*D*), and the bulk GaAs band gap $E_{bg}(p=0)$ (Ref. 6) by curve (*E*). The dashed line (− − −) corresponds to the estimated band gaps $E_{bg}(0)$ of the Ga_NAs_M clusters.

perturbation. The transition probability $w(a\rightarrow e)$ determines the absolute photodissociation cross section σ_{dis} for a number of photons φ per unit area and per excitation laser pulse: $\sigma_{dis}=w_{dis}(a\rightarrow e)/\varphi$. In the case when photoionization has to be taken into account, the photoionization cross sections σ_{ion} are analogously calculated from $x_{ion}=I_{ion}/I_0$, where I_{ion} is the intensity of cluster cations. The total photoabsorption cross section σ_{abs} is then given by $\sigma_{abs}=\sigma_{dis}+\sigma_{ion}$.

We have determined the absolute absorption cross section σ_{abs} by measuring the number of photons φ per unit area and per excitation laser pulse, the depletion ratio x_{dis} and/or the ionization ratio x_{ion}. The finite overlap existing between the depletion laser and the molecular beam[2] has been thereby taken into account.

From this procedure we obtain the absolute photodissociation, photoionization, and total photoabsorption cross sections of Ga_NAs_M clusters ($N+M=4-80$) in the photon energy range $\hbar\omega=1.7$–6.4 eV for several fixed excimer laser wavelengths ($\lambda=193$, 248, 308, 348, and 713 nm).

Figure 1 shows the results for several Ga_NAs_M clusters in comparison with the bulk absorption spectrum, which is calculated from the bulk dielectric functions using the Mie theory.[13,14] There is a significant increase of the total absorption cross section to high photon energies for all Ga_NAs_M clusters. Moreover, a cross-section minimum is observed at 5.0 eV for the smaller clusters, though this minimum vanishes when the clusters become larger.

Within our experimental setup, we are not able to observe absorption of light for photon energies lower than 1.7 eV, i.e., infrared absorption due to, e.g., vibrational excitations or weakly bond electrons.

We have shown in a recent paper[15] that small Ga_NAs_M clusters with an odd number of atoms ($N+M=5,7,\ldots$) have significantly larger static polarizabilities than those clusters with an even number of atoms ($N+M=6,8,\ldots$). This result has been explained by a simple model taking into account the existence of additional donorlike or acceptorlike electrons for the odd $N+M$ clusters. The experimental photoabsorption and photoionization[16] spectra exhibit characteristic features that can be related to the measured polarizabilities. For example, the absolute values of the absorption cross sections of the clusters with odd $N+M=5,7$ (■ and ● in Fig. 1) are larger than the values of $N+M=6$ (▲ in Fig. 1) over our experimental energy range (1.7–6.4 eV). Nevertheless, only 20% of the expected full one-electron oscillator strength due to the additional defectlike electron can be found in this energy range. The missing transitions contributing to the oscillator strength must be located at energies above 6.4 eV, because the oscillator strength is expected to be very weak for transition energies below 1.7 eV.[17] Within the last assumption we are able to estimate the resonance energies according to Mie's dipole excitation theory applied to small Ga_NAs_M clusters ($N+M=4-15$). This is done by fitting the parameters of a two-Drude-oscillator-model polarizability $\alpha_D(\omega)$ (Ref. 18) by using the measured static polarizability $\alpha(0)$ and the photoabsorption cross section $\sigma(\omega)$ which is related to the dynamic polarizability $\alpha(\omega)$ by $\sigma(\omega)\propto\mathrm{Im}\{\alpha(\omega)\}/\omega$. This calculation additionally requires tak-

TABLE I. Shifts of the Mie dipole resonance excitation energies for small Ga_NAs_M clusters ($N+M=4-15$) from the bulk value $\hbar\omega_0=9.0$ eV.

Cluster size $N+M$	4	5	6	7	8	9	10	11	12	13	14	15
Shift of the Mie dipole resonance energies (eV)	0.4	3.0 ±0.5	0.5 ±0.7	3.6 ±0.6	2.4 ±1.2	3.1 ±0.2	-0.4 ±3.5	2.7 ±1.5	0.5 ±3.1	2.3 ±0.9	-0.4 ±2.1	0.6 ±1.3

ing into account the so-called sum rule for the oscillator strength.[8] The first oscillator describes the peak at $\hbar\omega=4.0$ eV in Fig. 1, and the second the Mie resonance that is expected to occur at $\hbar\omega_{\text{cluster}}>\hbar\omega=6.4$ eV in the vicinity of the bulk surface-plasmon energy $\hbar\omega_0=9.0$ eV.[19] The calculated energy shifts $\Delta E=\hbar\omega_0-\hbar\omega_{\text{cluster}}$ are shown in Table I. The table shows how the defectlike electrons systematically influence the appearance of the spectra. The values of the dipole resonance energies of the clusters containing odd numbers of atoms are shifted toward lower excitation energies by about 1.5–2.5 eV against the bulk value. This result relates the strong variations of the static polarizabilities more to the variation of the dipole resonance excitation energies, rather than to a distinct defectlike electronic state on which we have speculated in our previous paper.[15]

Another important result shown in Fig. 1 is the reduction of the total absorption cross sections of larger Ga_NAs_M clusters with $N+M=80$ ($\triangle$ in Fig. 1) in comparison to the cross sections of the bulk or that of smaller clusters. This means that the effective optical band gaps strongly increase for these larger clusters. However, the photoionization cross sections of large Ga_NAs_M clusters ($\triangledown$ in the inset of Fig. 1) are much larger than those of the smaller clusters. Figure 2 shows the size dependence of the effective photodissociation gaps $E_{\text{dis}}(p=0.02)$ ($\triangle$), the effective photoionization gaps $E_{\text{ip}}(p=0.02)$ ($\bigcirc$), and the effective optical band gaps $E_{\text{bg}}(p=0.02)$ ($\boxdot$) of the Ga_NAs_M cluster. The value of $p=0.02$ is suitable in order to describe the essential physical effects in the measured spectra. However, we can give an idea of the limit $E_{\text{bg}}(0)$. These values are also shown in Fig. 2 ($---$). They have been roughly estimated by extrapolating $E_{\text{bg}}(p)$ for $p\rightarrow0$, using the experimental values $p=0.02$ and 0.01. Some measurements of the photoabsorption band gaps of GaAs colloids $E_{\text{bg}}(p\approx0)$ ($\blacklozenge$),[3,4] and the photoabsorption and photoionization thresholds of the diatomic GaAs molecule ($\bullet$ and $\blacksquare$),[7] are additionally included in this figure.

The effective optical band gaps $E_{\text{bg}}(0.02)$ of the large Ga_NAs_M clusters seem to follow the trend of the GaAs colloids, and are still increasing from $N+M=80$ to $N+M=14$ [$N+M=80\rightarrow14$: $E_{\text{bg}}(p=0.02)=5.3\rightarrow6.0$ eV]. Then $E_{\text{bg}}(0.02)$ starts to decrease gradually for the smaller Ga_NAs_M clusters to $N+M=4$, and its value comes close to the HOMO-LUMO gap of the diatomic GaAs molecule. The size evolution of the effective dissociation gaps $E_{\text{dis}}(0.02)$ of the smaller Ga_NAs_M clusters is similar to the one of the effective band gaps, whereas the $E_{\text{dis}}(0.02)$ values are nearly constant ($E_{\text{dis}}\approx6.2$ eV) for the larger cluster ($N+M>14$). However, the effective ionization gaps $E_{\text{ip}}(0.02)$ of the larger Ga_NAs_M clusters decrease from $N+M=20$ to $N+M=80$ [$N+M=20\rightarrow80$: $E_{\text{ip}}(0.02)=6.4\rightarrow5.7$ eV], showing therefore an opposite behavior to $E_{\text{dis}}(0.02)$.

The absorption of the larger Ga_NAs_M clusters ($N+M\geqslant15$) is dominated by their large effective photodissociation gaps, which reflect pure absorption without ionization effects. These enhanced $E_{\text{dis}}(0.02)$ gap values can be understood as a result of quantum confinement effects, i.e., the pure photoabsorption spectra shift to the blue as it is observed for semiconductor GaAs colloids. The calculation of the band gaps for colloids[6] within the quantum confinement model is also shown in Fig. 2 [curve (A)]. It is obvious from the figure that this simple model overestimates the values of the photoabsorption band gaps, especially for the smaller GaAs colloids. The effective optical band gaps of the Ga_NAs_M clusters with $N+M=14-80$ ($\boxdot$ in Fig. 2) are 1.3–2.0 eV larger than those corresponding to the effective optical band gap of bulk GaAs $E_{\text{bg}}^{\text{bulk}}(0.02)$ obtained by Mie theory. This shift $\Delta E^{\text{cluster}}=E_{\text{bg}}^{\text{cluster}}(0.02)-E_{\text{bg}}^{\text{bulk}}(0.02)$ is comparable to the shift $\Delta E^{\text{colloid}}=E_{\text{bg}}^{\text{colloid}}(0)-E_{\text{bg}}^{\text{bulk}}(0)$ observed for the GaAs colloids. However, $\Delta E^{\text{cluster}}$ is much smaller than expected from the quantum confinement model for this cluster size range.

These deviations from the quantum confinement model can be related to the efficient photoionization of large Ga_NAs_M clusters. The $E_{\text{ip}}(0.02)$ gaps of the Ga_NAs_M clusters with $N+M=20-80$ are about the same as the effective dissociation gaps. This is theoretically confirmed by curve (B) in Fig. 2. This curve represents the theoretical ionization thresholds $E_{\text{ip}}(p=0)$ of a dielectric sphere, calculated by classical electrostatics[20] using the bulk dielectric constant and the bulk work function in the calculation. These theoretical $E_{\text{ip}}(0)$ values give an upper limit for the quantum confinement energies for cluster sizes smaller than $N+M=100-200$, and can be understood considering a finite potential depth $V\approx-E_{\text{ip}}$ in the quantum confinement model.

This idea is confirmed by our experiments for the larger clusters ($N+M=14-80$). The measured effective photoionization gaps are indeed close to the calculated $E_{\text{ip}}(0)$ values obtained from the electrostatic model. The increase of these effective band gaps $E_{\text{bg}}(0.02)$ from $N+M=80$ to $N+M=14$ is also due to the increase of the experimental $E_{\text{ip}}(0.02)$ values. This gives further support to the idea that the effective optical band gaps are strongly influenced by photoionized effects for $N+M<200$.

The absorption behavior of the Ga_NAs_M cluster with $N+M\leqslant15$ is dominated by the decrease of the effective photodissociation gaps and by their molecular electronic structure, i.e., the defectlike electrons give rise to even/odd oscillations in the decreasing effective band gaps. It is clear that this effect cannot be understood within the quantum confinement model. Hence there seems to be a qualitative change in the electronic structure of the Ga_NAs_M clusters with $N+M<14$. The reason for the decrease of the effective optical band gaps is the fact that $E_{\text{dis}}(0.02)$ becomes smaller.

This effect makes the $E_{bg}(p=0.02)$ values for $N+M\,4-5$ to be close to that of the diatomic GaAs molecule (3–4 eV). These small clusters have a molecular electronic structure. This means that the transition between the bulklike clusters and the molecularlike clusters takes place at a cluster size of around $N+M\approx 14$. Ga_NAs_M clusters with more than 14 atoms behave surprisingly simple, like small bulklike nanocrystallites. Their photoabsorption behavior can be understood with the bulk dielectric constant, including photoionization and quantum confinement effects. The understanding of this crossover from bulklike to molecular behavior seems to be a challenge for theoretical investigations.

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[10] We have measured the photodepletion cross sections at 4.0 eV for two nozzle temperatures (38 and 300 K). Within our experimental resolution, the cross sections are not affected by the internal temperature of the Ga_NAs_M clusters. This result gives evidence of a direct photofragmentation process after the initial photoabsorption (see also Refs. 2 and 3).

[11] We have also investigated the photoluminescence as another alternative channel after the initial photoabsorption. The photoluminescence quantum yield has been measured using a photomultiplier with dielectric filters in combination with the determination of the absolute number of Ga_NAs_M clusters in the molecular beam. The sensitivity of this setup has been calibrated by diluted dye laser solutions. This quantum yield is very weak for Ga_NAs_M clusters ($\leqslant$3% for 1.5–1.8 eV, $\leqslant$2% for 1.8–2.2 eV, $\leqslant$1% for 2.1–2.4 eV, and $\leqslant$0.8% for 2.5–3.1 eV for excitation at 5.0 eV).

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