

## Dielectric response of germanium clusters

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The dielectric response to an inhomogeneous electric field has been investigated for  $\text{Ge}_N$  ( $N=8-24$ ) clusters within a molecular beam experiment. The low temperature experiments give clear evidence of permanent electric dipole moments. These dipole moments mainly determine the response of the clusters to the electric field. An almost quantitative agreement between experimentally determined dipole moments and *ab initio* quantum theory could be achieved for  $\text{Ge}_8\text{-Ge}_{13}$ . At higher temperatures, an enhanced internal dynamics additionally influences the dielectric response of the germanium clusters.

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### I. INTRODUCTION

The dielectric properties of small isolated semiconductor clusters achieved much attention during the last decade.<sup>1,2</sup> This is a consequence of possible applications in a semiconductor based nanotechnology and is also due to the fundamental question of how the electronic structure of the clusters changes with cluster size.<sup>3,4</sup> Experiments concerning the dielectric properties of isolated semiconductor clusters are rare and only a few molecular beam experiments are reported for the case of  $\text{Si}_N$ ,  $\text{Ga}_N\text{As}_M$ , and  $\text{Ge}_N\text{Te}_M$ .<sup>5</sup> The theoretical investigations mainly focus on main group IV element clusters, and with an increasing number of theoretical work, distinct discrepancies between theory and experiments evolved,<sup>6,7</sup> e.g., the quantum chemical calculations predict only minor variations of about 10%–20% in the electronic polarizability per atom for different sizes and isomers of  $\text{Si}_N$ , whereas the experimental variations are an order of magnitude larger. Additionally, the proposed structures show permanent electric dipole moments, which are not found in experiment. Therefore, a satisfactory description of the dielectric properties of small semiconductor particles is still lacking.

It was already pointed out that the theoretically predicted permanent dipole moments might be responsible for the discrepancies between theory and experiment<sup>8</sup> because these permanent dipole moments could influence the obtained polarizabilities, even if the dipole moments are not directly observed in a molecular beam experiment.<sup>9–13</sup> For nearly rigid clusters, the permanent dipole moment is manifested not only in a possible broadening of the molecular beam but also in an adiabatic polarization of the cluster ensemble in the electric field, which leads to an additional deflection of the molecular beam.<sup>8,14</sup> Against that, vibrationally excited clusters display a Debye–Langevin-type behavior<sup>13,15,16</sup> because the thermally activated vibrational degrees of freedom take over the role of a heat bath and only a deflection of the molecular beam toward high field strength could be observed. Within both scenarios, the apparent polarizabilities could strongly depend on cluster size if the clusters exhibit permanent dipole moments, which vary with the cluster size.

It is the aim of this work to get a better understanding how the dielectric properties of semiconductor particles

change with size. For this purpose, we have investigated small germanium clusters and it will be demonstrated experimentally that small  $\text{Ge}_N$  clusters in the size range between  $N=8$  and 24 atoms exhibit permanent dipole moments. The permanent dipole moments could be directly detected from a broadening of the molecular beam for cold clusters. It will be shown that these permanent dipole moments strongly influence the observed polarizabilities. We will demonstrate that the measured molecular beam profiles could be quantitatively analyzed, giving a consistent picture of the size-dependent dielectric properties of semiconductor clusters, in good agreement with recent *ab initio* quantum chemical calculations.<sup>3,17,18</sup>

### II. EXPERIMENTAL METHODS

The dielectric properties of isolated particles have been measured by deflecting a highly collimated molecular beam in an inhomogeneous electric field. The molecular beam deflection method is sensitive to the derivative of the energy  $\epsilon$  with respect to the electric field  $E$ .<sup>19</sup> The deflection  $d_n$  of a single particle in a quantum state  $|n\rangle$  is given by

$$d_n = - \frac{A}{mv^2} \frac{\partial E}{\partial z} \frac{\partial \epsilon_n}{\partial E}. \quad (1)$$

The deflection  $d_n$  depends on the mass  $m$  and velocity  $v$  of the particle, an apparatus function  $A$ , the gradient of the electric field  $\partial E / \partial z$ , and the Stark effect  $\partial \epsilon_n / \partial E$ . The apparatus function  $A$  depends on the geometry of the electrodes generating the inhomogeneous field and the distance between the electric field and the detection of the clusters.<sup>19–21</sup>

An overview of the apparatus used in the present investigation is reported in the literature.<sup>22</sup> Germanium clusters are produced by a pulsed laser vaporization source with helium buffer gas.<sup>23</sup> The helium-germanium cluster mixture is then expanded through a nozzle into a high vacuum apparatus, thereby producing a supersonic beam of  $\text{Ge}_N$  clusters. The nozzle has a length of 61 mm and a diameter of 2 mm. The leading 25 mm of the nozzle can be cooled with the help of a helium refrigerator down to 40 K, thereby reducing the

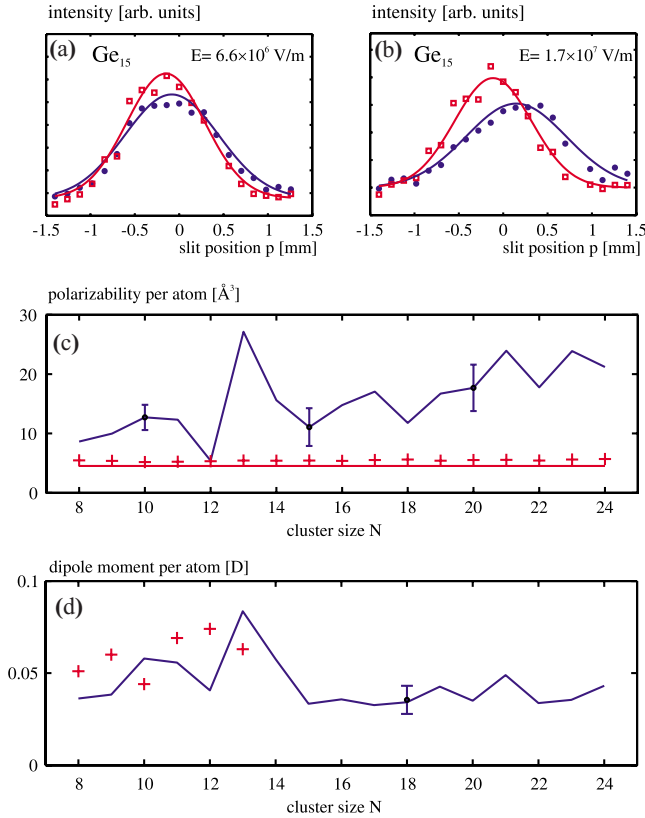


FIG. 1. (Color online) [(a) and (b)] Molecular beam profiles of  $\text{Ge}_{15}$  with (dots) and without deflection field (squares) at a nozzle temperature  $T_N$  of 45 K and two electric field strengths  $E$ . Both a broadening and a deflection of the beam profile are clearly visible. As a guide to the eye, Gaussian functions are fitted to the beam profiles. [(c) and (d)] Apparent size-dependent polarizabilities and dipole moments are extracted from the beam deflection and broadening at  $E=6.6 \times 10^6$  V/m and  $T_N=45$  K. The cluster-field interaction is described by using first order perturbation theory of spherical rigid rotors with a body-fixed dipole moment and an isotropic polarizability tensor. *Ab initio* quantum chemical results (+) for the dipole moments (Table I, see also Refs. 3, 17, and 18) and polarizabilities (Ref. 17) are shown for comparison with the experimental data. Also, the polarizability of a semiconducting sphere with bulk properties (red line) is given. The disagreement between the experimental and theoretically predicted dipole moments can be resolved if an asymmetric rotor model is used (Fig. 2).

kinetic energy of the clusters in the molecular beam but also cooling the internal degrees of freedom of the clusters. In the present work, experiments with nozzle temperatures of 45 and 150 K have been performed. After passing two collimators, the molecular beam reaches the inhomogeneous electric field.<sup>24</sup> About 1200 mm downstream of the deflection unit, the clusters are ionized with an excimer laser (7.89 eV) after they have passed a slit having a width of 400  $\mu\text{m}$ . The position  $p$  of the slit can be varied with an accuracy of 2  $\mu\text{m}$ . Ionized clusters are then detected by a time-of-flight mass spectrometer. Examples of molecular beam profiles with and without passing an inhomogeneous electric field are shown in Figs. 1(a) and 1(b) for the case of  $\text{Ge}_{15}$ . Both a deflection and broadening of the beam profiles is clearly visible.

### III. RESULTS AND DISCUSSION

In order to analyze the measured beam profiles, one has to consider that the experimentally observed beam deflection of a specific cluster size  $\text{Ge}_N$  is the weighted average  $\langle \dots \rangle$  over all deflections  $d_n$  of the populated quantum states  $|n\rangle$ , which are present in the molecular beam experiment. Therefore, the measured beam profiles depend on molecular properties, as the permanent electric dipole moment and the electric polarizability, as well as the thermal distribution, approximately characterized by a rotational and vibrational temperature  $T_{\text{rot}}$  and  $T_{\text{vib}}$ .

To analyze the electric field induced beam deflection, a model for the Stark effect  $\partial \epsilon_n / \partial E$  has to be assumed. In the approach taken by Schäfer *et al.*,<sup>5</sup> the clusters are treated as spherical rigid rotors with a rotational energy far exceeding the interaction energy of the particle with the electric field. Hence, the Stark effect can be described by first order perturbation theory (FOPT). In this model, the net deflection  $d = \langle d_n \rangle$  of the molecular beam solely depends on the isotropic polarizability of the particle, whereas the dipole moment leads to a broadening,  $b = \sqrt{\langle (d_n - d)^2 \rangle}$ . In order to extract  $d$  and  $b$  from the beam profiles, Gaussians are adapted to the measured data points. The values of  $d$  are obtained from the shift of the maxima of the Gaussians without and with electric field, and  $b$  from the square root of the difference of the variances. The polarizabilities and dipole moments per atom  $\alpha/N$  and  $\mu/N$  obtained from such an approach are shown for  $\text{Ge}_N$  clusters for a nozzle temperature of 45 K and an electric field strength of  $6.6 \times 10^6$  V/m in Figs. 1(c) and 1(d).

The polarizability per atom for a small semiconducting sphere with the density and dielectric constant of bulk  $\alpha$ -Ge (Refs. 25 and 26) is also shown in Fig. 1(c). Again, as in the studies on  $\text{Si}_N$ ,  $\text{Ga}_N\text{As}_M$ , and  $\text{Ge}_N\text{Te}_M$ ,<sup>5</sup> the variation of  $\alpha$  with cluster size also far exceeds what is expected from quantum chemical calculations. Contrary to the previous investigations, we observe significant permanent dipole moments for most cluster sizes. Therefore, we can check if the adiabatic polarization mechanism proposed by Schnell *et al.*<sup>8</sup> is capable of explaining the discrepancy between theoretical and experimental results for the polarizability of  $\text{Ge}_N$  clusters.

Within the adiabatic polarization mechanism, the total polarizability of a rigid symmetric rotor is divided into two parts: one resulting from a pure electronic polarizability  $\alpha_e$  and one due to the permanent dipole moment,

$$\alpha = \alpha_e + z(\kappa) \frac{\mu^2}{k_b T_{\text{rot}}}. \quad (2)$$

The parameter  $z(\kappa)$  depends on the structure of the clusters and ranges from  $(-\frac{1}{3} + \frac{\pi}{6})$  to  $\frac{1}{3}$ . The rotational temperature  $T_{\text{rot}}$  is, in general, not known from experiment but can be deduced, as shown below, to be  $3 \pm 2$  K at a nozzle temperature  $T_N=45$  K in the case of  $\text{Ge}_{10}$  by analyzing the asymmetric broadening of the molecular beam deflection profile. Assuming that all cluster sizes have the same rotational temperature, we can estimate the dipole contribution to  $\alpha$  within the adiabatic polarization model.  $\text{Ge}_{23}$ , e.g., shows an effective polarizability of 25  $\text{\AA}^3$ . Taking the apparent dipole mo-

TABLE I. Dipole moments  $\mu$  and moments of inertia  $I$  of  $\text{Ge}_8$ - $\text{Ge}_{13}$ , which were used in the MD simulation. The putative global minimum  $\text{Ge}_{12,a}$  (Ref. 31) does not reproduce the beam deflection profile, whereas the isomer  $\text{Ge}_{12,b}$  proposed by Wang and Han (Ref. 18) fits the experimental data. All values are given in the principal axis system.

	$ \mu $ (D)	$\mu_a$ (D)	$\mu_b$ (D)	$\mu_c$ (D)	$I_a$ ( $10^{-44}$ kg m $^2$ )	$I_b$ ( $10^{-44}$ kg m $^2$ )	$I_c$ ( $10^{-44}$ kg m $^2$ )
$\text{Ge}_8$	0.41	0.25	0	0.32	2.64	3.51	4.06
$\text{Ge}_9$	0.48	0.20	0	0.44	3.52	4.54	4.58
$\text{Ge}_{10}$	0.44	0.44	0	0	4.78	4.95	4.95
$\text{Ge}_{11}$	0.76	0.70	0.28	0	5.06	6.60	6.94
$\text{Ge}_{12,a}$	0.04	0	0.04	0	4.15	8.10	8.25
$\text{Ge}_{12,b}$	0.89	0	0.73	0.52	5.76	7.79	8.73
$\text{Ge}_{13}$	0.82	0.71	0	0.41	6.58	9.30	10.30

ment of 0.92 D from FOPT and a rotational temperature of  $T_{\text{rot}}=3$  K into account, the contribution of the permanent dipole moment to the polarizability is 17.2–30.2  $\text{\AA}^3$  depending on the parameter  $z(\kappa)$ . This clearly demonstrates that for all investigated cluster sizes, the permanent dipole moments not only give a significant contribution to the measured polarizability but also dominate the deflection of the molecular beam. That the dipole moments per atom of  $\text{Ge}_N$  clusters with  $N > 15$  are at a first glance independent of clusters size nicely explains why the polarizabilities per atom linearly increase with the cluster size. The presence of permanent dipole moment, which increases with the cluster size, was already known for colloidal semiconductor nanoparticles<sup>27</sup> but is now also observed for isolated semiconductor clusters. If this is related to the elongated structures of  $\text{Ge}_N$  cluster cations, as demonstrated by ion mobility measurements,<sup>28</sup> it needs a deeper quantum chemical investigation. The estimation of the induced dipole moments of smaller  $\text{Ge}_N$  clusters indicates so far that the pure electronic contributions  $\alpha_e$  to the polarizabilities could be close to the values predicted from quantum chemical calculations<sup>17,18</sup> even if the measured apparent polarizabilities are much larger.

Comparing the values of the electric dipole moments obtained from the analysis of the beam profiles on the basis of first order perturbation theory to the quantum chemical investigations based on density functional theory<sup>17,18</sup> shows that the experimentally determined dipole moments are on the same order of magnitude but significant differences exist, e.g., for  $\text{Ge}_9$  or  $\text{Ge}_{12}$ . From an experimental point of view, this finding can be the result of two reasons. On the one hand, most of the clusters are predicted to be asymmetric rotors, which could have an influence on the measured beam profiles.<sup>11</sup> On the other hand, the assumption of rigid rotors could be problematic. In order to study the influence of the asymmetry, we have implemented a classical molecular dynamics (MD) simulation, as described by Dugourd *et al.*<sup>29</sup> for  $\text{Ge}_N$  ( $N=8-13$ ). The classical treatment is justified because even with rotational temperatures of a few Kelvins, the values of the angular momentum quantum numbers are already larger than 10. The moments of inertia as well as the magnitude and direction of the dipole moments of the different cluster sizes (Table I) are obtained by taking the putative

global minima structures reported in the literature<sup>17,18,30,31</sup> and locally reoptimizing them by using the B3LYP density functional<sup>32</sup> and the SBKJC basis set<sup>33</sup> with the corresponding pseudopotential as implemented in GAMESS.<sup>34</sup>

The resulting molecular beam deflection profiles at an electric field strength of  $6.6 \times 10^6$  V/m and a rotational temperature of 3 K are displayed in Fig. 2. It can be nicely seen

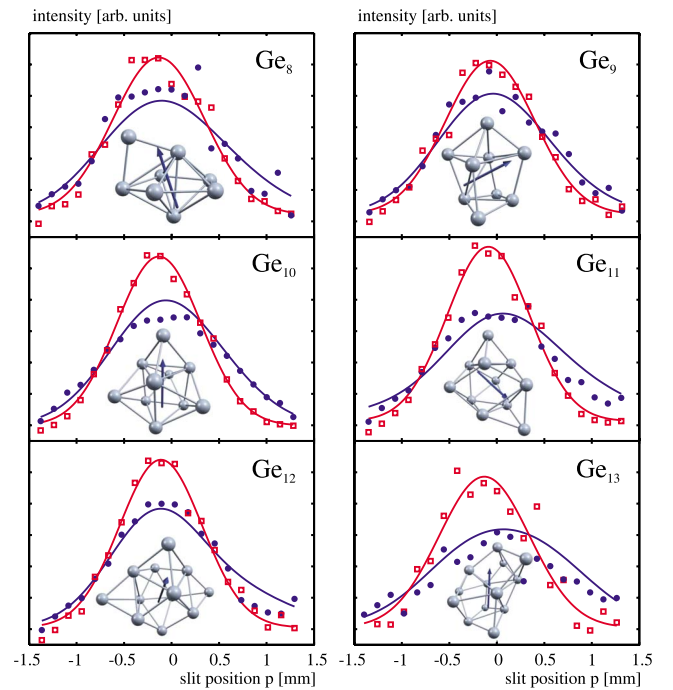


FIG. 2. (Color online) Molecular beam deflection profiles of  $\text{Ge}_8$ - $\text{Ge}_{13}$  at a nozzle temperature  $T_N=45$  K and an applied deflection field  $E=6.6 \times 10^6$  V/m are shown. As a guide to the eye, the undeflected molecular beam profiles (squares) are approximated by Gaussians (solid, red line). The deflected beam profiles (dots) are well described by a molecular dynamics simulation (Ref. 29) (solid, blue line), which treats the clusters as rigid rotors. The moments of inertia and dipole moments are taken from an *ab initio* calculation (Table I). A size-independent polarizability per atom of 5  $\text{\AA}^3$  and a rotational temperature  $T_{\text{rot}}$  of 3 K were assumed but the results do not depend sensitively on these actual values.

that the variation in the experimentally observed broadening is almost quantitatively reproduced by the simulated profiles for  $\text{Ge}_8\text{-Ge}_{11}$  and  $\text{Ge}_{13}$  taking the putative global minima structures. In the case of  $\text{Ge}_{12}$ , the structure proposed by Bulusu *et al.*<sup>31</sup> has an almost vanishing dipole moment of 0.04 D resulting in no observable beam broadening, which is contrary to the experimental profile, whereas the structure reported by Wang and Han,<sup>18</sup> which is 0.28 eV higher in energy at our level of theory, gives a good description of the experimental data. The MD simulations clearly demonstrate the influence of the molecular symmetry on the observed beam profiles, i.e., a part of the dipole moments of the asymmetric rotors becomes averaged out due to the rotational motion of the clusters, thereby resulting in reduced values for the electric dipole moments obtained with FOPT.

The molecular dynamics approach described above can also be used to deduce the rotational temperature. If higher electric fields are used and the interaction energy with the field becomes comparable to the rotational energy of the particle, the dipole starts to align in the field, which leads to an asymmetric broadening of the beam, which depends on the rotational temperature. This effect is shown in Fig. 3(a) for the molecular beam deflection of the symmetric rotor<sup>35</sup>  $\text{Ge}_{10}$  at an electric field strength of  $1 \times 10^7$  V/m. A rotational temperature of  $T_{\text{rot}} = (3 \pm 2)$  K describes the experimental deflection best.

The influence of the internal dynamics becomes visible if one increases the nozzle temperature to 150 K. This is shown for  $\text{Ge}_{10}$  in Fig. 3(b). The broadening of the molecular beam profile at  $T_N = 150$  K is strongly reduced compared to the one observed at 45 K. This results in a smaller apparent permanent dipole moment if first order perturbation theory is used for the analysis of the beam profiles. Since the low temperature data could be nicely explained with the help of molecular dynamics simulations that result in a dipole moment, which is in agreement with the density functional calculation, the strong reduction in the beam broadening indicates that the molecular structure is no longer rigid, i.e., one has to take into account the fact that the clusters are flexible.<sup>13</sup> Therefore, the obtained values of the dipole moments in the high temperature regime are a lower limit for the true dipole moments and the experimentally determined dipole moments are smaller than the theoretically predicted ones. Extrapolating these results to room temperature data, it

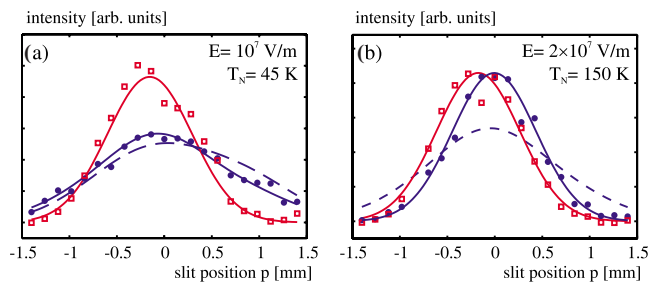


FIG. 3. (Color online) Molecular beam profiles of  $\text{Ge}_{10}$  with (dots) and without (squares) deflection field  $E$  at two nozzle temperatures  $T_N$  are shown. (a) At  $T_N = 45$  K, the beam deflection can be simulated as a symmetric rigid rotor with a permanent dipole moment  $\mu = 0.44$  D and a rotational temperature between 5 K (solid, blue line) and 2 K (broken, blue line).  $T_{\text{rot}}$  is therefore estimated to be  $3 \pm 2$  K. (b) At  $T_N = 150$  K, the simulation as a symmetric rigid rotor (broken, blue line,  $T_{\text{rot}} = 5$  K) fails. Instead of a field induced beam broadening, only a net deflection is observed. However, the apparent polarizability of  $7.0 \pm 0.7 \text{ \AA}^3$  is still enlarged compared to the expected electronic polarizability.

is clear that even if a broadening of the beam profiles could not be observed, the masked permanent dipole moments can strongly influence the dielectric response, which could lead to the reported discrepancy between experiments and theory.<sup>5-7</sup>

In conclusion, we have experimentally proven that small isolated semiconductor clusters possess permanent electric dipole moments and have analyzed their contribution to the apparent polarizability. The analysis of the measured beam profiles in the context of first order perturbation theory together with a classical MD simulation demonstrates the importance of molecular asymmetry, which results in an almost quantitative agreement between the experimentally determined dipole moments and first quantum chemical calculations in the case of the low temperature experiments.

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