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Vibrational Spectrum, Caloric Curve, Low-Temperature Heat Capacity, and Debye Temperature of Sodium Clusters: The Na_{139}^+ Case

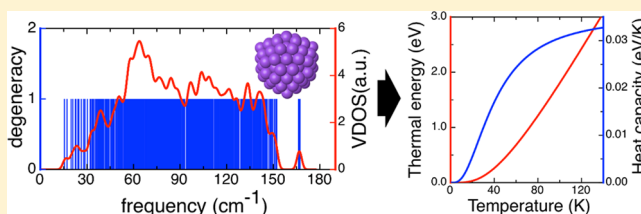
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W Web-Enhanced Feature S Supporting Information

ABSTRACT: The vibrational properties of atomic clusters are a fingerprint of their structures and can be used to investigate their thermodynamic behavior at low temperatures. In this work, we report a theoretical study, using density functional theory, on the vibrational spectrum and density of states (VDOS) of the cationic sodium cluster Na_{139}^+ . Our study focuses on the most stable isomer, which corresponds to a truncated icosahedron. This isomer displays an electronic density of states that is in good agreement with photoelectron spectroscopy data previously published. After validation of the sodium cluster structure, its vibrational frequency spectrum was obtained in the harmonic approximation through a diagonalization of the dynamical matrix. The calculated vibrational frequencies were used to evaluate the cluster caloric curve and heat capacity at low temperatures. An excellent agreement was obtained between the calculated caloric curve and experimental data recently reported down to 6 K. A fit to the bulk Debye model of the calculated and measured cluster thermal energy yields a large variation at low temperatures of the equivalent Debye temperature as compared with a weaker temperature dependence found in bulk materials. Moreover, a further analysis shows that the calculated heat capacity of the 139-atom cationic sodium cluster does not follow the bulk Debye T^3 law at very low temperatures, due to the discreteness of the cluster frequency spectrum, and to the finite value of its acoustic gap (lowest frequency value). These results, indicating a finite size effect on the cluster vibrational spectrum, reflect the difference in the VDOS between clusters and bulk, and confirm the limitation of the bulk Debye model (and Debye temperature) to describe the low-temperature thermal behavior of metal clusters in the size range of around 139 atoms. The calculated vibrational frequency spectrum also provides the temperature dependence of the total vibrational excitation for the 139-atom sodium clusters, indicating that at 6 K, $\sim 92\%$ of them are in their vibrational ground state.



INTRODUCTION

There is an increasing interest in the theoretical and experimental study of vibrational properties of clusters and nanoparticles since they are a signature of their structures and can be used to determine their mechanical and thermal behavior at low temperatures.^{1,2} Although it is not yet possible a direct measurement of the whole frequency spectrum of clusters and nanoparticles, their thermal behavior at low temperatures may provide indirect information on their vibrational properties.² For example in a recent experimental study, the low-temperature caloric curve of free 139-atom sodium cationic clusters was measured down to 6 K, showing a flattening behavior toward lower temperatures that indicated the freezing out of the cluster vibrational modes.² In addition, it was found that the best fit of the Na_{139}^+ measured caloric curve to the bulk Debye model yielded a Debye temperature of $\theta_D = 163.5 \pm 10$ K, which compares well to the Debye temperature of 158 K for bulk sodium.² Since no information on the vibrational frequencies of sodium clusters of that size was

available, this result was taken into account to suggest that the overall vibrational density of states (VDOS) of the Na_{139}^+ cluster must be similar to that of the bulk.² On the other hand, there had been several studies showing that the finite size of clusters and nanoparticles induces major differences in the VDOS as compared to bulk systems.^{2,3} Furthermore, a recent theoretical study on the vibrations of small gold clusters showed that their calculated VDOS differs dramatically from the function proposed by the Debye model.⁴ To clarify these controversial results, additional theoretical studies are necessary to investigate the relation between the vibrational properties and the low-temperature behavior of metal clusters and nanoparticles.

In this work, we report a theoretical study of the vibrational frequency spectrum and VDOS of the Na_{139}^+ cluster using

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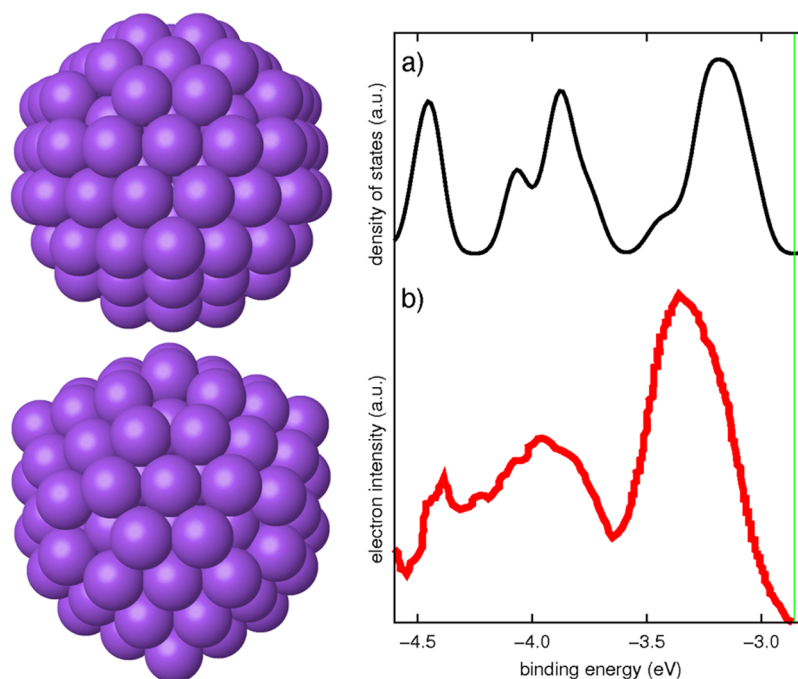


Figure 1. (Left) Lowest-energy (most stable) isomer of the Na₁₃₉⁺ cluster. The structures correspond to two different views of the truncated icosahedron. (Right) (a) Calculated electronic density of states of the most stable isomer of the Na₁₃₉⁺ cluster, obtained with a Gaussian broadening (0.07 eV) of the Kohn–Sham eigenvalues. The vertical line shows the calculated Fermi energy. (b) Photoelectron spectrum of the Na₁₃₉⁺ cluster taken from the measurements reported in ref 20. The experimental curve was shifted to lower energies to match the spectrum onset with the calculated Fermi energy.

density functional theory (DFT). The frequencies calculation was done for the most stable cluster isomer that was obtained using a global optimization procedure combining a genetic algorithm method and a semiempirical many-body potential, followed by a DFT local structural relaxation. A validation of the lowest-energy (most stable) cluster structure was done through a comparison of its calculated electronic density of states with the photoelectron spectrum of the Na₁₃₉⁺ cluster, previously measured. The calculated (discrete) frequency spectrum was utilized to obtain the *N*-atom cluster caloric curve and heat capacity at low temperatures, using a quantum mechanical description of the vibrational thermodynamics for a set of $3N - 6$ harmonic oscillators.^{4,5} These first-principles theoretical calculations are useful not only for a reliable interpretation of the available experimental data, but also to gain insights into the relation between the cluster vibrational and thermal properties at low temperatures, and for a detailed analysis of the validity of the bulk Debye model at the nanoscale. In fact, the theoretical caloric curve obtained using the calculated cluster frequency spectrum is in good agreement with the experimental data recently published.² Moreover, our results also show the failure of the bulk Debye model to fit the calculated low-temperature heat capacity of a 139-atom sodium cationic cluster, mainly due to the discreteness of the cluster frequency spectrum, as well as the finite value of its acoustic gap (lowest frequency value).

METHODOLOGIES

The most stable isomer of the Na₁₃₉⁺ cluster was obtained by following a similar procedure used by some of us for the structural optimization of gold,⁶ silver,⁷ and other metal clusters.⁸ In the first stage, a global optimization method, using genetic algorithms^{9,10} and a many-body Gupta

potential^{11–13} provides a set of candidate isomers. The structures of these isomers were further locally relaxed using DFT methodology. For the present calculation, we used the local density approximation (LDA) with the Ceperley–Alder (CA) correlation energy functional,¹⁴ a Troullier–Martins¹⁵ nonlocal pseudopotential (1 valence electron), and a double- ζ basis set. These approximations were implemented within the SIESTA code.¹⁶ The reliability of this level of theory was verified by comparing the calculated values of the equilibrium distance ($r_e = 2.96$ Å) and vibrational frequency ($\omega_e = 168$ cm^{−1}) of the sodium dimer Na₂, with the corresponding experimental values^{17,18} ($r_e = 3.079$ Å and $\omega_e = 159$ cm^{−1}). Additional tests to validate the DFT methodology used in this work were also performed by calculating structural and vibrational properties of the Na₄ and Na₈ clusters. Detailed information on these calculations can be found in the Supporting Information. In particular, it is shown that the calculated frequencies of the Na₄ and Na₈ clusters, using the DFT-LDA methodology described above, are in very good agreement with the available experimental data obtained by Raman spectroscopy measurements¹⁹ (see Supporting Information section for details of this comparison). The cluster structure optimization through DFT-LDA-CA also provides the Kohn–Sham eigenvalues of the most stable isomer, which can be used to generate the electronic density of states of the Na₁₃₉⁺ cluster. A comparison of this quantity with photoelectron spectroscopy measurements,²⁰ allowed the validation of the calculated cluster structure.²¹ The vibrational frequencies of the Na₁₃₉⁺ cluster were obtained, within the harmonic approximation, with the VIBRA utility of the SIESTA code,¹⁶ within the DFT-LDA-CA level of theory.

Once the $3N - 6$ vibrational frequencies are available, the caloric curve (temperature dependence of the cluster thermal

energy) and heat capacity were calculated from the quantum mechanical expressions for a set of $3N - 6$ harmonic oscillators:^{4,5}

$$E(T) = \sum_{j=1}^{3N-6} \frac{h\nu_j}{e^{h\nu_j/k_B T} - 1} \quad (1)$$

$$C(T) = \frac{\partial E}{\partial T} = k_B \sum_{j=1}^{3N-6} \frac{\left(\frac{h\nu_j}{k_B T}\right)^2 e^{h\nu_j/k_B T}}{(e^{h\nu_j/k_B T} - 1)^2} \quad (2)$$

RESULTS AND DISCUSSION

Cluster Structure and Electronic Density of States.

The search of the lowest-lying isomers for the Na_{139}^+ cluster was realized using the procedure described above. In the Supporting Information, we report the energy ordering, geometric structures, and the xyz Cartesian coordinates of the 6 lowest-energy isomers found in the structural optimization. The most stable (lowest-energy) isomer of the Na_{139}^+ cluster obtained from the present calculations corresponds to an incomplete icosahedron, which can be visualized as the 147-atom Mackay icosahedron with 8 missing vertex atoms. The second isomer in the energy ordering (0.244 eV higher in energy) has a similar structure as the ground state, but it displays a defect at the cluster surface inducing a local rearrangement of atoms. The next isomer (0.309 eV higher in energy) is also similar to the lowest-energy one, but it shows one atom popping out at a triangular facet. Higher energy isomers (with relative energy >1 eV), displaying larger structural distortions with respect to the most stable one, were also obtained during the structural optimization procedure (see Supporting Information for additional details on the lowest-lying isomers of the Na_{139}^+ cluster).

The most stable icosahedral structure is consistent with the structural patterns obtained from the comparison of theoretically calculated electronic density of states and photoelectron spectra of sodium anionic and cationic clusters with similar sizes.^{20,21} Figure 1 shows this comparison for the Na_{139}^+ cluster and the corresponding cluster structure. The level of agreement between theory and experiment is very good, and similar to that obtained for other cluster sizes whose structures have been assigned with this criterion.^{20,21} The truncated-icosahedron structure of the Na_{139}^+ cluster is, therefore, the best candidate for a vibrational analysis and a study of its thermal behavior at low temperatures.

Vibrational Properties. Figure 2a shows the vibrational spectrum and density of states of the Na_{139}^+ cluster. The calculated frequency spectrum is discrete, it has a finite acoustic gap (lowest frequency $\sim 15 \text{ cm}^{-1}$), and extends up to a maximum frequency of $\sim 167 \text{ cm}^{-1}$. These are characteristic features of the vibrational spectrum of metal clusters of similar sizes.^{22–26} The VDOS, generated with a Gaussian broadening (1.5 cm^{-1}) of each vibrational frequency, displays a line shape with the corresponding acoustic gap, an enhancement at low frequencies, and multiple peaks along the whole frequency range. It is notorious the presence of an isolated high frequency peak around $\sim 167 \text{ cm}^{-1}$, which mainly corresponds to vibrational motions of the inner icosahedral 13-atom core. An animation file displaying this highest frequency mode is available in the HTML version of this paper.

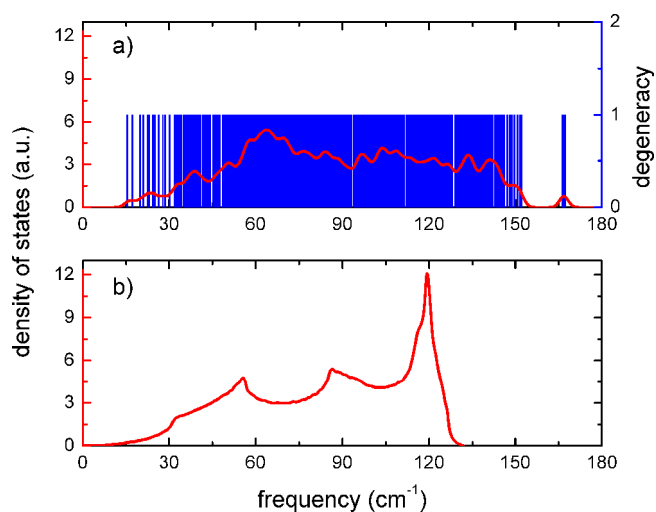


Figure 2. (a) Vibrational frequency spectrum (blue lines) and density of states (red line) of the Na_{139}^+ cluster. The VDOS line shape was generated using a 1.5 cm^{-1} Gaussian broadening. (b) Vibrational density of states of bulk sodium taken from ref 27. The vertical scale was chosen to have the same total number of vibrational modes as in the case of the Na_{139}^+ cluster.

One interesting question is how different the VDOS of the Na_{139}^+ cluster is from that one of bulk sodium. Figure 2b shows the frequency distribution for bulk sodium obtained from neutron scattering measurements.^{27–29} It displays an overall similar behavior at low frequencies, but a quite different line shape in the high frequency region, as compared with the VDOS of the Na_{139}^+ cluster shown in Figure 2a. A more careful comparison between both VDOS shown in Figure 2 shows that some differences still exist in the low frequency region. These are related with a nonzero acoustic gap and an enhancement of vibrational modes in the frequency range of $15\text{--}25 \text{ cm}^{-1}$ displayed by the Na_{139}^+ VDOS, which are due to the finite size effect. In the following section, it is shown that these distinct features in the VDOS generate different thermal properties for the Na_{139}^+ cluster at low temperatures, as compared with the corresponding bulk thermal behavior.

Thermal Properties. The calculated frequency spectrum can be utilized to evaluate the caloric curve and heat capacity of the Na_{139}^+ cluster using eqs 1 and 2. Figure 3 displays these quantities as a function of temperature, together with the experimental measurements of the caloric curve reported in ref 2. The excellent agreement between the calculated and experimental caloric curves is remarkable, and not only indicates the reliability of the theoretical methodology used in this work, but also illustrates the importance and necessity of using the whole vibrational frequency spectrum to appropriately describe the low temperature behavior of thermal properties of metal clusters. Figure 3 also displays the temperature dependence of the heat capacity. It shows the expected increasing behavior with temperature of the heat capacity of a finite set of harmonic oscillators at low temperatures, also indicating the usefulness of the vibrational frequency spectrum to calculate thermal properties of metal clusters.

Once the low temperature dependence of the thermal energy (caloric curve) and heat capacity were obtained, in order to gain more insight, the appropriateness of the bulk Debye model to describe these results was tested, as proposed in ref 2. For

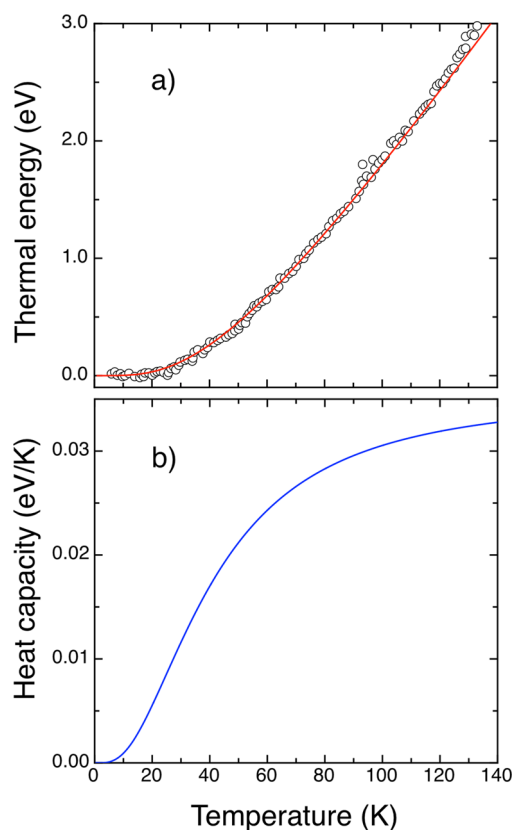


Figure 3. (a) Caloric curve and (b) heat capacity of the Na_{139}^+ cluster. The red and blue lines correspond to the theoretical results using eqs 1 and 2, respectively. The open circles are experimental data taken from ref 2.

this purpose, we fit the theoretical results shown in Figure 3 to the thermal energy and heat capacity expressions provided by the bulk Debye model, scaled to the number of degrees of freedom of the cluster:^{2,30}

$$E^D(T, \theta_D) = 3(3N - 6)k_B T \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx \quad (3)$$

$$C^D(T, \theta_D) = 3(3N - 6)k_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (4)$$

The best fit of the calculated thermal energy and heat capacity to eqs 3 and 4 over the whole temperature range (up to 140 K) yields values for the Debye temperature θ_D of 164 and 165 K, respectively. These fitted values are in good agreement with that one obtained in ref 2 ($\theta_D = 163.5 \pm 10$ K), fitting the experimental data of the caloric curve. Interestingly, they compare well with the bulk Debye temperature of bulk sodium (158 K).³¹ In fact, the very similar values of the Debye temperatures obtained for the Na_{139}^+ cluster and bulk sodium deserved special attention in ref 2, leading to the suggestion that the cluster VDOS must be similar to that of the bulk.² Since we have already shown, through a first-principles calculation, how different the VDOS of the Na_{139}^+ cluster is from that one of the bulk sodium, one additional objective of the present work is to clarify what is the meaning of the Debye temperature for a cluster and, even more important, to test the

validity of the bulk Debye model to describe the thermal behavior of clusters with a finite number of atoms.

To elucidate the meaning of the Debye temperature values obtained by a fitting of the Na_{139}^+ cluster thermal energy and heat capacity over a range of temperatures up to ~ 140 K, further considerations need to be taken into account. Since the bulk Debye model is based on an oversimplification of the real VDOS, it should not be expected that a single value of the Debye temperature θ_D , which fits the heat capacity at a certain temperature, will be the optimum value for the whole temperature range. However, for any pair of measurements of the heat capacity and temperature, it is possible to calculate the *equivalent* Debye temperature, and for a series of such measurements the temperature dependence of $\theta_D(T)$ can be obtained.³² In fact, bulk solids always show some variations in θ_D with temperature, although for most metals this variation is small.³³ An interesting task in the context of the present work would be to investigate what is the variation of $\theta_D(T)$ for the Na_{139}^+ cluster.

By implementing the corresponding fitting procedure, we have calculated $\theta_D(T)$ using both the theoretical and experimental data displayed in Figure 3a. The variation with temperature of the fitted values for θ_D is displayed in Figure 4.

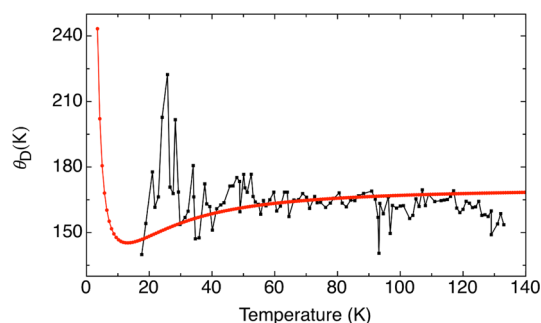


Figure 4. Temperature dependence of the Debye temperature for the Na_{139}^+ cluster using the data displayed in Figure 3a. The red curve was obtained using the theoretical values of the thermal energy. The black squares were obtained using the experimental data of the thermal energy reported in ref 2.

This information is very illustrative since it indicates that indeed the *equivalent* Debye temperature of the sodium cluster is temperature-dependent, and that its overall variation is similar to the one displayed by bulk materials, characterized by a dip at low temperatures and a stabilization with increasing temperature.³⁴ It should be noted that this behavior was obtained using both the theoretical and experimental data of the thermal energy. Also, it is notorious that the two curves asymptotically approach to a constant value when the temperature increases. On the other hand, Figure 4 also shows a quite distinct feature in $\theta_D(T)$ for the sodium cluster indicating a stronger variation at very low temperatures (< 15 K), as compared with the corresponding variation in bulk sodium.^{27–29} In fact, Figure 4 shows fitted values for θ_D decreasing from ~ 250 to ~ 140 K in a range of 3–10 K, whereas for bulk metals, this variation is much weaker.^{27–29} This distinct variation in $\theta_D(T)$ at very low temperatures between clusters and bulk might be considered as a size effect in the thermal properties of clusters, however, additional calculations for larger cluster sizes and nanoparticles would be necessary to confirm its existence.

Although the *equivalent* Debye temperature $\theta_D(T)$ might be more adequate than the constant fitted value θ_D to describe the

thermal properties of the Na_{139}^+ cluster, it would be insightful to investigate the appropriateness of using the bulk Debye model for clusters with a finite number of atoms. One interesting test is to check its validity at very low temperatures, where it would be expected that the cluster heat capacity follows the Debye T^3 law.^{4,30} For this purpose, the deviations from the T^3 law can be better appreciated by plotting the variation of C/T with T^2 . Figure 5 displays this variation

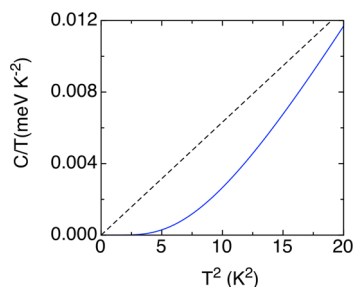


Figure 5. Variation of C/T vs T^2 for very low temperatures (up to ~ 4.5 K). The blue line corresponds to the calculated heat capacity of the Na_{139}^+ cluster using its vibrational frequency spectrum. The dashed black line represents the Debye T^3 law using the Debye temperature (163.5 K) obtained in ref 2.

calculated from eq 2 using the cluster vibrational spectrum in the range of temperatures up to ~ 4.5 K. For comparison, Figure 5 also shows the straight line representing the Debye T^3 law, whose slope corresponds to the Debye temperature of the Na_{139}^+ cluster obtained in ref 2 (163.5 K). Over this range of temperatures, it is evident that the exact cluster heat capacity (calculated from eq 2) does not follow the T^3 law, but decays faster with decreasing temperature. In fact, it decays according to: $(h\nu_1/k_B T)^2 \exp(-h\nu_1/k_B T)$, depending on the value of the cluster acoustic gap (lowest vibrational frequency) ν_1 .⁵ The clear deviation from the T^3 law at very low temperatures shown in Figure 5 confirms the failure of the bulk Debye model to describe the thermal properties of metal clusters with ~ 139 atoms, as had been previously discussed for smaller gold clusters.⁴ A further analysis of these results indicates that the cluster acoustic gap value is the main factor that determines the deviation from the bulk Debye T^3 law: the larger this value is, the larger obtained deviation. Since it is known that the acoustic gap value decreases for larger cluster sizes,¹ they would show a smaller deviation from the bulk Debye T^3 law. Nevertheless, additional calculations are required to investigate the transition to the bulk behavior.

The vibrational frequency spectrum can also be used to calculate the temperature dependence of the cluster vibrational ground state occupancy $f(T)$. This quantity would be useful in studies of high-resolution spectroscopy of molecules and clusters.² It can be calculated as the probability of occupying the cluster vibrational ground state using the canonical partition function of a system of $3N - 6$ independent quantum oscillators with different frequencies ν_i ,^{30,32} leading to the following expression:

$$f(T) = \prod_{i=1}^{3N-6} [1 - e^{-h\nu_i/k_B T}] \quad (5)$$

Figure 6 indicates the percentage of clusters that are in the vibrational ground state as a function of temperature. For example, at 6 K, the lowest temperature reached in the

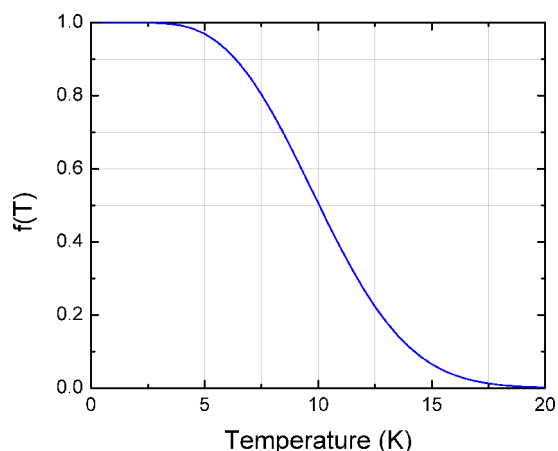


Figure 6. Temperature dependence of the vibrational ground state occupancy of the Na_{139}^+ cluster calculated with eq 5.

experiments described in ref 2, $\sim 92\%$ of the Na_{139}^+ clusters are in their vibrational ground state. This value is in good agreement with the estimated one reported in ref 2 using an approximated VDOS for the sodium clusters. A further analysis of the vibrational ground state occupancy as a function of temperature indicates that it also depends on the cluster acoustic gap value. In the present case, Figure 6 also shows that the complete freezing out of the vibrational modes of the 139-atom sodium clusters up to ~ 3 K, is a consequence of the finite value ($\sim 15 \text{ cm}^{-1}$) of its acoustic gap.

SUMMARY

The vibrational frequency spectrum and VDOS of the Na_{139}^+ cluster have been calculated from first principles methods based on the DFT-LDA level of theory. The calculation was done for an isomer with a truncated icosahedron structure, which has an electronic DOS in good agreement with photoelectron spectroscopy measurements performed on this cluster size. In this work, it was shown that the sodium cluster frequency spectrum, which differs from the bulk sodium frequency distribution, can be used to calculate thermal properties like the caloric curve and heat capacity. The calculated caloric curve was found to be in very good agreement with the experimental data recently reported. This agreement confirms the reliability of the theoretical methodology used in this work, and indicates the importance of the availability of the whole vibrational frequency spectrum to appropriately describe the low temperature behavior of thermal properties of metal clusters.

The calculated thermal energy and heat capacity were also used to explore the validity of the bulk Debye model in a cluster with a finite number of atoms. It was found that the calculated cluster thermal properties can be fitted to the corresponding bulk Debye expressions by introducing an *equivalent* (temperature dependent) Debye temperature $\theta_D(T)$, which has a similar overall behavior to that one seen for bulk metals, but showing a much stronger variation at very low temperatures. A further analysis shows that the calculated heat capacity of the Na_{139}^+ cluster does not follow the bulk Debye T^3 law at very low temperatures (< 5 K), due to the discreteness of the cluster frequency spectrum, and to the finite value of its acoustic gap. These features, reflecting the difference in the VDOS between clusters and bulk, indicate the existence of a finite size effect on the cluster vibrational spectrum and corroborate the failure of the bulk Debye model (and Debye temperature) to describe

the low-temperature thermal behavior of metal clusters in the size range around 139 atoms. The calculated vibrational frequency spectrum, particularly the acoustic gap value, also provides the temperature dependence of the total vibrational excitation for the sodium clusters, indicating that at 6 K, $\sim 92\%$ of them are in their vibrational ground state.

In this work, it has been shown how the finite size effect present in the vibrational frequency spectrum of a 139-atom sodium cluster is responsible for the differences in thermal properties compared with the bulk behavior. Further calculations for larger clusters and nanoparticles are necessary to study the size evolution of such thermal properties toward the bulk limit.

■ ASSOCIATED CONTENT

● Supporting Information

DFT test calculations for Na_2 , Na_4 , and Na_8 clusters; structure and energetics of the lowest-lying isomers of the Na_{139}^+ cluster, and their relaxed xyz Cartesian coordinates are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

● Web-Enhanced Feature

An animation file displaying the highest frequency mode is available in the HTML version of this paper.

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Notes

The authors declare no competing financial interest.

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