Surface Vibrations from Small Clusters to the Solid: He Atom Scattering from Ar_n

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In a crossed molecular beam arrangement helium atoms are scattered from argon clusters which are generated in the size range of $\bar{n} = 25$ to $\bar{n} = 4600$ by adiabatic expansion with conical nozzles. The inelastic energy transfer is detected by time-of-flight analysis of the scattered helium atoms with a resolution of better than 1 meV. The measured peak of the transferred energy is attributed to surface vibrations. It decreases as a function of the average cluster size and converges to the value of the surface phonons of solid argon.

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The knowledge of the vibrational frequency spectrum of a cluster is of crucial importance both for the structural and thermodynamic properties as well as for the dynamical behavior. This includes such quantities as the thermal free energy and the specific heat [1] which is important for melting and condensation processes and the excitation or deexcitation of the vibrational modes. The latter process is of special interest, since it is very sensitive to the transition of the cluster from the discrete spectrum of the vibrational modes of a moleculelike system to the lattice vibrations and the continuous phonon dispersion curves of the solid. Thus the bulk phonon density of solid Ar at 10 K which is based on the measurement of the dispersion relation shows a large peak at 8 meV with a sharp cutoff to larger values and a second one around 5 meV which are caused by the longitudinal and transverse vibrational modes, respectively [2]. In contrast, the calculated spectrum of Ar_{13} at 1.3 K exhibits a series of peaks around 3 meV and a single peak at 7.5 meV representing the motion of the surface atoms and the single central atom [3]. With increasing temperature the spectrum becomes continuous and changes, in addition, the character with the solidlike or liquidlike state of the cluster [4,5]. All other cluster sizes should lie in between these two limiting cases, whereby the overall size of the particles is reflected only in the relative amount of the intensities of the bulklike modes compared to the surface modes. Experiments to verify this behavior are not available.

The experimental methods which could be used for studying these vibrational modes include infrared and Raman spectroscopy for molecular-type systems and neutron, electron, and He atom scattering for probing bulk or surface phonons. While the former methods have essentially been applied only to very small molecular clusters, no such attempts have been reported for the systematic application of the latter methods. From all these techniques the scattering of He atoms appears to be the most general process to study the vibrational spectra of clusters, since this method is mainly sensitive to surface properties and obeys nearly no selection rules. In the last 10 years it has been developed into a very successful and vitally important technique for measuring surface phonons of the solid and for deriving a series of very interesting surface properties [6,7].

The helium scattering from clusters, however, differs from the reflection measurements from solid material in two aspects. First, there will be a pronounced dependence on the impact parameter and thus on the deflection angle and, second, the constraint of the conservation of the momentum parallel to the surface which simplifies the data analysis is not valid. Here we present the first systematic measurements of helium atom scattering from argon clusters Ar_n in the range from $\bar{n} = 25$ to 4600. The clusters are produced in an adiabatic expansion and represent an average value of a distribution. We concentrate on the vibrational excitation of these clusters which is detected by time-of-flight analysis of the scattered helium atom. A preliminary account of the fact that such processes can be measured appeared in Refs. [8,9].

The experiments have been carried out in a crossed molecular beam machine which is described in detail elsewhere [10]. A schematic view is shown in Fig. 1. Essentially it consists of a He supersonic nozzle beam collimated by the skimmer $S1$, an Ar_n cluster beam as target collimated by the skimmer $S2$, which intersect at an angle of 90°, and a detector D with an electron bombardment ionizer and a quadrupole mass filter operating under ultrahigh vacuum conditions. The angular dependence is

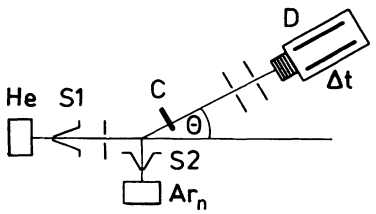

FIG. 1. Schematic view of the crossed molecular beam arrangement for conducting the double differential scattering experiments for He + Ar_n. $S1$ and $S2$ are skimmers, C is the chopper for time-of-flight analysis, and D is the detector, a mass filter with electron impact ionization.

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measured by rotating the source assembly relative to the fixed detector position. The velocity of the scattered He atoms is measured by time-of-flight analysis using a pseudorandom chopper C with a flight path of 450 mm.

The helium atom beam is produced by the expansion of the gas under high stagnation pressure (typically 30 bars) through a small orifice (diameter 30 μm) into the vacuum. Most of the measurements were carried out at a temperature of $T_0 = 77$ K. With a speed ratio of $S = 90$, which is the flow velocity divided by the most probable thermal velocity, an internal temperature of lower than 0.1 K and a corresponding relative width of the velocity distribution of $\Delta v/v = 0.018$ are obtained. This leads at collision energies of about 27 meV to a resolution of better than 1 meV, since, because of the large mass difference, the spread in the cluster velocity does not influence the overall resolution.

The cluster beam is generated by expansion from stagnation pressures of 1.2 to 5.0 bars through different nozzles of conical shape [11] which vary in diameter (60 to 130 μm), length (1 to 12 mm), and opening angle (20° to 30°). It is interesting to note that the velocity analysis of the Ar beam which contains a fraction of large clusters gave two contributions: a faster one around 615 m/s, which is attributed to the remaining Ar monomers, and a slower one around 500 m/s, which is attributed to the clusters and their fragments including the monomer mass. The contribution of the remaining monomers gradually decreases with the production of larger clusters.

The beam contains only a distribution of cluster sizes, the average value of which can be shifted to the desired size range by varying the different shape parameters of the nozzle and the stagnation pressure. The key parameter which relates the corresponding average cluster sizes $\bar{n}$ to the stagnation pressure p_0, the source temperature T_0, and the nozzle diameter d is given by $\Gamma^* = 1646 p_0 d^{0.85} T_0^{2.2875}$ [12]. The numbers refer to Ar if the units are mbar, μm, and K, respectively. For conical nozzles the relation $d = 0.737 d^*/\tan\alpha$ is used where d^* is the nozzle throat diameter and 2α the opening angle. The relation between $\bar{n}$ and Γ^* is taken from independent measurements of the diffraction oscillations in He + Ar_n scattering experiments which are carried out in the same apparatus under similar experimental conditions [13]. For sizes up to $\bar{n} \leq 400$ we obtain $\bar{n} = 38.4(\Gamma^*/1000)^{1.64}$. The results are in good agreement with previous [14,15] and recent [16] mass spectrometer data, but deviate from those determined by electron diffraction [17].

The information on the vibrational excitation is obtained from time-of-flight (TOF) spectra taken at different laboratory deflection angles. Measurements were carried out at collision energies between 25.0 and 28.0 meV for a range of averaged cluster sizes from $\bar{n} = 25$ to 4600 and different center-of-mass scattering angles from $\Theta = 5°$ to 100°. A typical example for $\bar{n} = 77$ at 5° and 25° is shown in Fig. 2. From the measured primary and target beam velocities, the velocities of elastically scattered

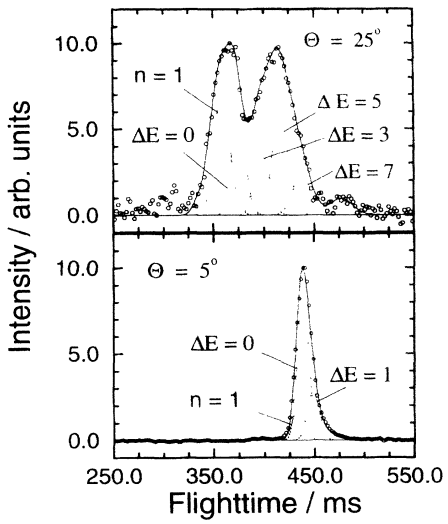

FIG. 2. Measured time-of-flight spectra for the average cluster size $\bar{n} = 77$ and two different deflection angles. The monomer contribution $n = 1$ and the energy transfer ΔE of the cluster in meV are indicated.

monomers and clusters are known. They are used together with the measured velocity distributions and angular divergencies of the two intersecting beams to calculate in a Monte Carlo procedure the experimental resolution of the apparatus [18]. Based on the resulting distribution functions, the measured time-of-flight spectra are fitted by the possible elastic and inelastic transitions. The overall result is given by the solid lines in the figures and some of the single contributions, the dotted lines, are marked by the corresponding energy transfer ΔE in meV.

The monomer scattering, which is always elastic in the investigated energy range, is indicated by $n = 1$ and comes first in the time-of-flight spectrum. It can be distinguished from the elastic cluster scattering, indicated by $\Delta E = 0$, since the velocities of the latter one are slower. Then the possible inelastic contributions appear with increasing energy loss. The results for $\Theta = 5°$ clearly demonstrate that the cross section is dominated by elastic cluster scattering. These nearly grazing collisions with large impact parameters do not excite the cluster. The situation changes drastically for the measurement at $\Theta = 25°$. Now the monomer and the elastic cluster scattering are clearly separated from the inelastic part with a most probable energy transfer of about $\Delta E = 5$ meV and the largest detectable energy transfer which does not exceed $\Delta E = 8$ meV, the value which has also been observed for bulk phonons. These results are essentially confirmed by measurements at other angles. In general, the energy transfer increases with increasing deflection angle. Up to deflection angles of 12°, however, the energy transfer remains small. In the angular range between 15° and 40° the spectra are similar to the one taken at 25° as far as the general shape, with a maximum and a cutoff of the intensity at 8 meV, is concerned. The results observed

for deflection angles from 70° to 100° exhibit energy transfers which exceed 10 meV, probably an indication of multiphonon excitation. Thus we consider in the further course of this work mainly results out of the middle angular range in which the coupling is large enough to excite the vibrations completely but small enough to restrict it to one phonon processes.

An example for the dependence of the spectra from the cluster size is shown in Fig. 3. Here the spectra taken at 18.75° for the average clusters $\bar{n} = 77$ and $\bar{n} = 354$ are displayed. Again the monomer and the elastic cluster scattering are clearly separated from the inelastic part, the intensity of which increases with increasing cluster size. The most important result is that the maximum in the distribution decreases from $\Delta E = 4$ meV at $\bar{n} = 77$ to $\Delta E = 3$ meV at $\bar{n} = 354$. This general trend is also observed for a number of other cluster sizes investigated. We summarize the experimental results as follows: (1) The vibrational energy transfer exhibits a maximum at ΔE values between 2 and 5 meV and goes to zero at very small ΔE and at $\Delta E = 9$ meV. (2) The maximum value shifts slightly to smaller ΔE with increasing cluster size.

How do these experimental findings compare with what is known about the density of vibrational states of clusters or particles of finite size from calculations? The general shape of the measured excitation probability, a maximum at energy transfers between 2 and 5 meV and a cutoff value around 8 meV, has been predicted in a number of calculations. The methods include molecular dynamics (MD) simulations from which the frequency spectrum is obtained by the Fourier transform of the velocity autocorrelation function [9,19–21]. Other calculations are based on the collective motion of elastic vibrations of the solid [22,23] which manifests itself in the excitation of spheroidal or torsional surface modes. The results of all these calculations treating clusters in the range from $n = 13$ to 14 000 or finite layers and nearly spherical blobs [19] can be summarized as follows. In addition to the peaks which already appear for the bulk material at 5 and 8 meV, two further peaks are recognized at smaller frequencies at about 2–3 meV and at about 1.2 meV. They are attributed to surface modes with amplitudes normal to the surface and edge atoms, respectively. The overall size of the particles is reflected only in the relative amount of the intensities of the different modes to each other. Bulklike modes are less probable than surface modes in particles with a large surface-to-volume ratio and vice versa. The comparison with the measured distributions indicates that the best qualitative agreement occurs with the excitation of vibrational surface modes. The effect that no intensities appear in the experimental results at very low energy transfers which correspond to soft vibrational modes says that the investigated clusters are solidlike.

The measured trend that the maximum of the surface vibrations slightly decreases with increasing cluster size is predicted in the model calculations of Ref. [23]. For Ar_n clusters in the range of $n = 13$ to $n = 55$ this effect is attributed to the spheroidal mode of the breathing vibration in the dense sphere model. Their eigenvectors k are related to the phonon velocity c and the frequency ω by $\omega = kc$ and this frequency is approximated by $\omega = \pi c/R_c$ where R_c is the cluster radius. In order to test this behavior experimentally, we have analyzed the vibrational excitation for cluster sizes from $\bar{n} = 25$ to $\bar{n} = 4600$ at the deflection angle of 30°. The maximum of the excitation function is therefore plotted versus the inverse cluster radius $R_c = R_0 n^{1/3}$ which is proportional to $n^{-1/3}$ in Fig. 4. The result is a straight line which converges to the calculated surface phonons of bulk fcc argon [24,25]. The best agreement is obtained with the lowest energy mode, the well known Rayleigh mode, of the (001) surface at $\Delta E = 1.87$ meV. It is another nice example of the cluster

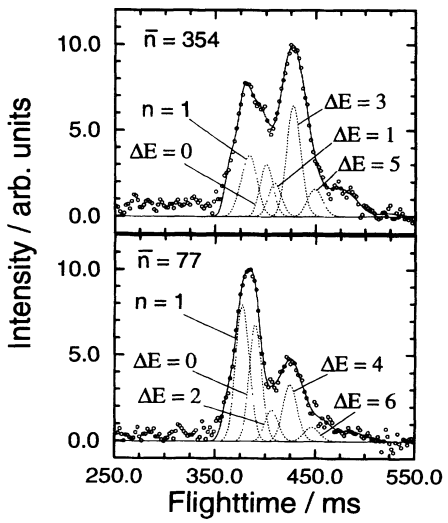

FIG. 3. Measured time-of-flight spectra for two different average cluster sizes $\bar{n}$ at the deflection angle 18.75°. The monomer contribution $n = 1$ and the energy transfer ΔE of the cluster in meV are indicated.

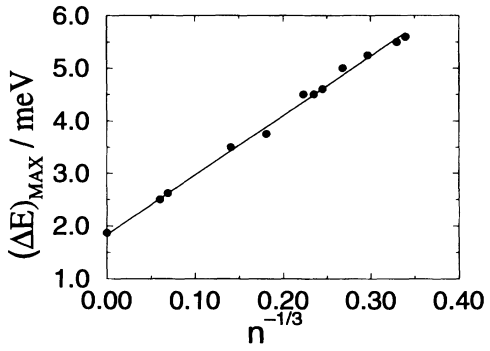

FIG. 4. The cluster size dependence of the maximum of the vibrational energy transfer measured at a deflection angle of 30°. The points cover the range from $\bar{n} = 25$ to $\bar{n} = 4600$. They converge to the calculated lowest energy mode of the (001) surface phonons of bulk Ar.

size effect which has been quantified recently by Jortner [26] for a series of other cluster properties. Thus we conclude that the measured vibrational excitation spectra represent essentially the surface vibrations of the outer atoms over the whole size range investigated.

These first results on the measurement of the vibrational frequency spectrum of free clusters by He atom scattering look, in spite of using only a distribution of cluster sizes as target, very promising and open a new class of experimental possibilities. The great advantage of this technique is the general applicability to any kind of system and any kind of vibrational spectrum. Together with calculation on the underlying dynamics this method should develop into an effective tool for investigating cluster properties.

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