On the internal energy of sputtered clusters

A Wucher\textsuperscript{1,3}, C Staudt\textsuperscript{1}, S Neukermans\textsuperscript{2}, E Janssens\textsuperscript{2}, F Vanhoutte\textsuperscript{2}, E Vandeweert\textsuperscript{2}, R E Silverans\textsuperscript{2} and P Lievens\textsuperscript{2}

\textsuperscript{1} Fachbereich Physik, Universität Duisburg-Essen, D-47048 Duisburg, Germany
\textsuperscript{2} Laboratorium voor Vaste-Stoffysica en Magnetisme, K U Leuven, Celestijnenlaan 200d—bus 2414, B-3001 Leuven, Belgium
E-mail: andreas.wucher@uni-due.de

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\textbf{Abstract.} We have used laser ionization and time-of-flight mass spectrometry to investigate the internal excitation of neutral clusters that were generated by sputtering from a solid indium surface under bombardment with 15 keV Xe\textsuperscript{+} ions. More specifically, single photon ionization of the clusters is accomplished by a tunable, frequency doubled laser and the photoionization efficiency (PIE) curves are collected with the photon energy varied around the ionization energy in a range between 4.2–6 eV. The results are compared with the PIE curves of supposedly cold indium clusters which were produced by a supersonic nozzle expansion using a laser vaporization source and investigated under otherwise similar conditions. As a result, the sputtered clusters show a distinctive broadening and shift of the PIE curve in the threshold region, thus illustrating the influence of the sputtering process in increasing the internal energy of the ejected clusters. The experimental PIE curves are interpreted in terms of a simple model using the internal temperature and ionization energy of the cluster as fit parameters. Depending on the cluster size, temperatures between 3850 and about 1000 K are found for sputtered In\textsubscript{n} clusters.

\textsuperscript{3} Author to whom any correspondence should be addressed.
1. Introduction

If a solid is bombarded with energetic particles, a cascade of mostly elastic collisions is generated within a surface-near region and material is transformed from the surface into the gas phase. It has long been known that this process, which is generally termed ‘sputtering’, produces not only atoms but also molecular species that leave the surface in a bound state. In the case of a pure elemental solid, these molecular species manifest as homonuclear clusters which may contain up to a hundred and more atoms. How such entities can survive the relatively violent collisional processes governing the sputter emission and still remain intact is an intriguing question. Various theoretical models of molecule and cluster formation during sputtering have appeared in the literature extending from simple statistical descriptions [1]–[7] to time consuming molecular dynamics (MD) computer simulations [8]–[15]. Some of the predictions of these models have been checked by experiments determining, e.g. the flux and the kinetic energy distributions of sputtered clusters [9], [16]–[22]. A general prediction of all models is that sputtered clusters should carry a high internal (vibrational and rotational) excitation, the spectrum of which can be predicted and should hence be indicative of the molecule formation mechanism. In order to gain further insight into the fundamental processes leading to cluster emission in sputtering, it is therefore of great interest to study the internal energy distribution of sputtered clusters experimentally. For a diatomic molecule, this is a relatively straightforward task since the ro-vibrational excitation remains largely unchanged on the microsecond timescale of a typical experimental detection scheme. Clusters containing more than two atoms, on the other hand, can be metastable on much shorter timescales if their internal energy exceeds the dissociation threshold, thus leading to unimolecular fragmentation processes occurring either prior to or even during experimental detection. A theoretical interpretation of the data must therefore certainly include these processes in order to relate measured excitation spectra to the sputter emission process itself.

Due to the generally large number of populated ro-vibrational states, the experimental detection of the internal energy of sputtered clusters is difficult. For the case of diatomic species, either emission spectroscopy or laser spectrometric tools have been successfully applied in some cases in order to determine ro-vibrational population distributions and temperatures. For a number of diatomic molecules emitted from silicon containing various impurities [23] and from several elements bombarded with N\textsubscript{2}\textsuperscript{+} ions [24, 25], extremely broad rotational
population distributions with pronounced non-Boltzmann character were reported. Using laser-induced fluorescence, de Jonge et al. [26]–[29] investigated S₂ dimers sputtered from elementary sulphur and CS₂ targets and found a quasi-thermal vibrational population distribution showing a vibrational temperature of 1500 K, whereas the rotational population was again found to be strongly non-thermal. For alkali metal dimers, Fayet et al. [30] employed resonant multiphoton ionization techniques and interpreted their results by assuming thermal population distributions to deduce internal temperatures between 1000 and 1500 K. It should be noted at this point, that all systems mentioned so far represent rather special cases in view of the sputtering mechanisms involved and, hence, the results cannot be regarded as typical for a purely collisional sputtering process. Employing the same technique, we therefore investigated sputtered Ag₂ dimers and found much higher vibrational and rotational temperatures of 3500 and 7000 K, respectively [31]. Both the magnitude and the ordering of these values could be reproduced by MD simulations of the sputtering process [14] and must therefore be regarded as typical for dimer emission from the metallic surfaces.

For clusters containing more than two atoms, practically no direct data on internal energy distributions exist in the literature. This is mostly due to the fact that the density of ro-vibrational states becomes so high that usual emission or laser spectroscopy is no longer applicable. Using a somewhat indirect approach, the unimolecular fragmentation of sputtered ionic species has been investigated by several groups [32]–[40]. These results clearly manifest the existence of sputtered clusters with internal energies larger than their dissociation threshold. Due to the experimental method employed, such data could be exclusively collected for charged species leaving the surface. Secondary ions, however, cannot generally be regarded as representative for sputtered fluxes, since their probability of being ionized in the sputtering process is a complicated, not well-understood quantity, which may—besides many other parameters—in principle depend on the internal energy as well. Moreover, the majority of sputtered species is in most cases neutral. It is therefore highly desirable to obtain direct information on the internal energy of sputtered neutral clusters, since these data can then be compared to theoretical models and may therefore be of great value in order to understand the complex cluster formation process in sputtering.

For clusters produced in a supersonic expansion, Röthlisberger et al published an experimental method [41] to measure the internal temperature of sodium clusters by interpretation of their photoionization efficiency (PIE) curves in the threshold region. The basic idea behind this method is that a ro-vibrationally excited cluster will exhibit a modified ionization energy that is in principle reduced by up to the amount of its internal excitation energy. For the case of sputtered clusters, first hints pointing in that direction were observed for Ag₄ and Ag₆ emitted from an ion-bombarded silver surface [31]. In contrast to similar experiments performed on a supersonic silver cluster beam [42], single photon ionization of these species could be observed in the sputtering experiment using a photon energy significantly below the published ionization energy. In the present work, we utilize this subthreshold photoionization process by measuring the PIE curves of sputtered neutral clusters and adopt the technique of [41] to determine their internal temperature. As a target material for this study, we have selected indium instead of silver since (i) rare gas ion bombardment of this material produces neutral Inₙ clusters in comparable amounts to silver, and (ii) the ionization energies of these clusters are easily accessible with frequency doubled tunable laser radiation. For reference, the PIE data measured on sputtered clusters are compared with those measured for supposedly cold indium clusters produced in a supersonic expansion.
Figure 1. Scheme of the experimental setup used in the present investigation. The laser vaporization source (located at Leuven) is used for the generation of a supersonic indium cluster beam, whereas the sputter source (located at Essen) is used to generate the same clusters by sputtering.

The experimental conditions were chosen such as to produce as large a number of sputtered clusters containing as many atoms as possible. Previous experiments have shown that the relative abundance of clusters among the flux of sputtered material increases with increasing sputter yield and becomes largest for heavy projectiles impinging with large kinetic impact energy [43]. Therefore, the experiments were performed using Xe⁺ ions of 15 keV (the highest kinetic energy available with the equipment used) bombarding a clean, polycrystalline indium surface. Under these conditions, indium clusters containing more than 200 atoms have been detected in the sputtered flux [44], but the cluster formation process is still dominated by collisional sputtering. On the other hand, computer simulations predict that the average internal energy of sputtered clusters does not strongly depend on the bombarding conditions [14], so that the results obtained here should be representative for the cluster formation process occurring under collisional sputtering conditions.

2. Experimental

The experiment was performed in a collaboration between two laboratories using two different setups as sketched in figure 1. In one part, we measured the PIE curves of clusters produced in a supersonic nozzle expansion. The corresponding setup has been described in detail elsewhere [45]–[49]. In short, indium is evaporated into a helium gas pulse (pulse length ≈ 120 µs, backing pressure ≈ 8 bar) by ablation using the second harmonic of a Nd : YAG laser. After thermalization and initiation of cluster production, the clusters are cooled down in a
supersonic adiabatic expansion through a conical nozzle (diameter 1.5 mm) into the vacuum. The neutral clusters produced in this way are ionized by a tunable optical parametric oscillator laser system (Spectra-Physics MOPO 730 with an additional crystal for frequency doubling) and mass separated in a reflectron-type time-of-flight mass spectrometer. Under the expansion conditions employed, neutral In\(_n\) clusters could be detected containing up to more than 100 atoms with a bimodal size distribution showing maxima at \(n \sim 30\) and 110, respectively [50]. The PIE curves were measured by tuning the laser wavelength in 1 nm steps and recording the mass spectrum as a function of the photon energy of the ionization laser in the range of 4.6 to 6 eV. Long term fluctuations in the cluster production process were taken into account by normalization to a reference spectrum sequentially taken with an ArF excimer laser (Lambda Physik Compex 102) operated at a fixed wavelength of 193 nm.

In the second setup, which has also been described in great detail elsewhere [51, 52], the neutral clusters are produced by bombarding a polycrystalline indium target under ultrahigh vacuum conditions with a pulsed 15 keV Xe\(^+\) ion beam of about 500 nA (continuous current) impinging under 45\(^\circ\) with respect to the surface normal. The sputtered neutral particles produced during the primary ion pulse are ionized by a laser beam guided parallel to the surface at a distance of about 1 mm. A primary ion pulse length of 2 \(\mu\)s was chosen which is long enough to produce an ion signal that is equivalent to continuous bombardment and, hence, ensures that sputtered particles of all relevant emission velocities can interact with the laser. As in setup one, the photoionized species are detected in a reflectron-type time-of-flight mass spectrometer. Photoionization was accomplished either with a frequency doubled dye laser (Lambda Physik LPD 3002) or with an ArF excimer laser (Lambda Physik LPX120i), respectively. Under the bombarding conditions employed, sputtered neutral indium clusters are detected in a size range up to \(n > 100\) with a monotonically decaying size distribution [44, 50]. Again, the PIE curves are measured by tuning the dye laser wavelength in 1 nm steps and recording the mass spectrum as a function of the photon-energy in the range of 4.2 to 6 eV. The ArF excimer laser ionization was employed to generate a reference spectrum which is needed in order to allow a quantitative comparison of the PIE data obtained for sputtered and supersonic beam clusters in the two different experiments. To reach a high dynamic range of about six orders of magnitude, two different detection modes are employed. Small clusters with high abundance are detected in an analog mode with reduced microchannel plate (MCP) gain voltage by directly digitizing the output of the MCP detector, whereas large clusters with low abundance are detected in a single ion counting mode using the full MCP gain. For further details of the procedures employed to collect data with both setups, the reader is referred to the above mentioned publications.

During all experiments, the pulse energy of the employed ionization lasers was carefully monitored using a calibrated photodiode. Moreover, all laser beams were expanded to a diameter of several millimetres and geometrically apertured at the entrance to the vacuum chamber. This procedure ensures that the beam cross section in the ionization region and, hence, the effective ionization volume is the same for both the tunable and the fixed frequency reference laser. In connection with the measured beam cross section, the pulse energy density of the different lasers was determined relative to each other and later used for signal normalization as explained below. In addition, the laser intensity was kept sufficiently low to ensure that saturation of the photoionization process was avoided and all measured signals depended strictly linearly on the laser fluence, as is characteristic of a single photon absorption process. All measured signals were then normalized to the respective ionization laser fluence, thus delivering a quantity which in the following will be called ‘PIE’. It is important to note that this quantity is proportional to
the photoionization cross section integrated over the spectral profile of the laser beam. Since the single photon ionization process employed here is quasi-non resonant, the cross section will to a good approximation be constant across the spectral laser profile. In spite of the largely different spectral widths of the tunable laser (∼0.4 cm⁻¹) and the ArF excimer laser (∼180 cm⁻¹), the ratio between the normalized signals measured with both lasers therefore directly represents the ratio between the photoionization cross sections at the two respective center wavelengths.

3. Results and discussion

The ultimate goal of this work is to determine the internal temperature of sputtered clusters and interpret the results in terms of published theory on cluster formation in sputtering. In approaching that goal, we will in a first subsection present the PIE curves measured for the sputtered indium clusters and compare them with similar curves that have been obtained on a supposedly cold supersonic indium cluster beam. The results will reveal distinct differences that qualitatively demonstrate the larger internal excitation of sputtered clusters. In order to interpret the measured data in a more quantitative manner, we then try to describe the shape of the PIE curve in a parametrized form that is based on a simple model taken from the literature. The result will, in a third subsection, then be employed to fit the measured data on the basis of the model parameters, i.e. the cluster ionization energy and temperature. The resulting temperatures will in the last subsection be discussed in terms of theoretical model descriptions of the sputtering and subsequent unimolecular fragmentation processes.

3.1. PIE spectra

Figure 2 shows the PIE of neutral sputtered and supersonic beam Inₙ clusters measured as a function of the photon energy of the ionizing laser. Again, we note that the laser intensity was kept sufficiently low to eliminate all multiphoton absorption processes. As outlined in section 2, the data therefore represent the photon energy dependence of the cross sections for single photon ionization of the clusters at the respective laser wavelength. For each cluster size n, two curves are shown that correspond to clusters generated by sputtering and in a supersonic beam, respectively. In both cases, the data have been normalized to the PIE measured with the ArF reference laser at a photon energy of 6.4 eV. It should be noted that this normalization procedure results in a somewhat arbitrary relative scaling of the two curves, which implicitly assumes the ionization cross section of sputtered and supersonic clusters to be the same at the reference wavelength of 193 nm (hv = 6.4 eV).

The most important observation in figure 2 concerns the apparent difference between the PIE curves of sputtered and supersonic beam clusters. More specifically, it is clearly visible that the ionization cross sections of sputtered clusters rise faster at low photon energies than those of the supersonic beam clusters, thus leading to an apparent red-shift of the PIE curve. It is important to note that this qualitative result is not influenced by the exact scaling of the two curves depicted in each plot. Since the ionization cross section of sputtered clusters at the reference photon energy of 6.4 eV is likely to be larger than that of clusters produced in the supersonic beam, the curve for sputtered clusters must—if anything—be scaled upwards with respect to that of supersonic beam clusters, thereby even enhancing the apparent difference between the two curves. Since the ionization and detection schemes employed in both experiments are virtually identical, this difference must be due to the different cluster production
Figure 2. PIE curves, i.e. measured photoion signal normalized to the laser pulse energy density versus wavelength of the ionization laser, of neutral In$_n$ clusters that are (i) sputtered from a polycrystalline indium target under bombardment with 15 keV Xe$^+$ ions or (ii) generated in a supersonic indium cluster beam.
processes. In the laser vaporization cluster source used to generate the supersonic beam, the particles are cooled down in an adiabatic expansion into the vacuum, and the produced clusters are therefore expected to be relatively cold. The apparent difference observed in figure 2 clearly shows that clusters produced by sputtering are hot, i.e. contain a significantly larger amount of internal excitation energy than those produced in the supersonic expansion. Moreover, at least part of this internal energy is available for photoionization, thus leading to an apparent lowering of the photoionization threshold. From the observed shift of the PIE curves, we can therefore deduce lower limits to the difference in the average internal energy contained in clusters produced by the two methods. Unfortunately, particularly the PIE curves determined for small supersonic beam clusters show only little variation in the wavelength range explored. In order to estimate the energy shift, we therefore interpolate between these data and the reference point at $h\nu = 6.4$ eV, which due to the employed normalization procedure also corresponds to a virtual data point at a relative PIE value of 1.0 (cf section 2). The resulting energy shift is listed as $\Delta E_{\text{exp}}$ in table 1 and varies between zero and 0.5 eV with an average value of about 0.35 eV. It must be interpreted as that part of the average internal energy of sputtered clusters which is available for photoionization and, hence, manifests a lower limit to the total average internal energy contained in the sputtered clusters.

3.2. Theoretical model

In order to model the PIE in the threshold region, we will closely follow the procedure described by Röthlisberger et al [41], which in turn is based on a treatment published by Guyon and Berkowitz [53]. In principle, the PIE is the convolute of transition probabilities between various electronic and ro-vibrational states of the neutral cluster and the cluster ion, respectively. Any internal excitation energy that is present in the cluster will modify the population distribution of neutral vibrational and rotational states and therefore alter the PIE that is measured at a specific photon energy. To model the PIE curve in the threshold region, we have to make a number of simplifying assumptions:

Firstly, we disregard dissociative ionization processes and restrict ourselves to direct ionization. This assumption seems reasonable since we discuss only the near threshold region where ionization induced fragmentation can be expected to be negligible. To a first approximation, we also neglect possible effects of autoionization, even though autoionizing states near the threshold can in principle interfere with the threshold determination.

Secondly, we assume the density of states in the threshold region to be so high that every absorption of a photon which produces an energetic state located above the ionization threshold corresponds to a resonant neutral cluster to ion transition. Metal clusters are expected to have soft modes with vibrational frequencies slowly decreasing from the dimer to the bulk. We therefore assume the main contribution to ionization from thermally populated states to result from vibration. If we view the ionization threshold as composed of Rydberg series continuously converging to ionic states, we can assume adiabaticity and the validity of the Franck–Condon approximation. The contribution of a specific transition to the total ionization efficiency is then proportional to the corresponding Franck–Condon factor. Following [41, 53], we assume modest changes of the ground state geometry between the neutral and ionized clusters, thus resulting in a transition envelope with a range of participating transitions having nearly equal Franck–Condon factors. The threshold variation of the PIE curve can thus be considered as a series of step functions shifted by the average vibrational quantum energy. As discussed in detail in [53], this
Table 1. Effective number of ionization active oscillators $s_{\text{eff}}$, internal temperature $T$ and ionization energy $E_I$ which have been determined as best fit parameters from a non linear least squares fit of equations (4) and (5) to the experimental PIE curve of sputtered In$_n$ clusters. $\Delta E_{\text{mod}}$: modeled shift between PIE curves of cold and sputtered clusters calculated on the basis of the temperature $T$ and the effective number $s_{\text{eff}}$ of ionization active vibrational degrees of freedom; $\Delta E_{\text{exp}}$: measured shift; $E_{\text{int}}$: total internal excitation energy calculated on the basis of the temperature $T$ and the total number $s = 3n - 6$ of vibrational degrees of freedom.

| $n$ | $s_{\text{eff}}$ | $T$ (K) | $E_I$ (eV) | $\Delta E_{\text{mod}}$ | $\Delta E_{\text{exp}}$ | $E_{\text{int}}$ (eV) |
|-----|-----------------|----------|-----------|--------------------------|--------------------------|---------------------|
| 3   | 3               | 2236     | 5.93      | 0.58                     | 0.52                     | 0.58                |
| 4   | 6               | 1057     | 5.90      | 0.55                     | 0.44                     | 0.55                |
| 5   | 4               | 1093     | 5.94      | 0.38                     | 0.30                     | 0.85                |
| 6   | 3               | 1204     | 5.95      | 0.31                     | 0.22                     | 1.25                |
| 7   | 1               | 1308     | 5.67      | 0.11                     | 0.10                     | 1.69                |
| 8   | 3               | 1064     | 5.93      | 0.28                     | 0.12                     | 1.65                |
| 9   | 4               | 981      | 5.92      | 0.34                     | 0.20                     | 1.78                |
| 10  | 3               | 1075     | 5.90      | 0.28                     | 0.20                     | 2.22                |
| 11  | 3               | 1159     | 5.96      | 0.30                     | 0.28                     | 2.70                |
| 12  | 4               | 1077     | 5.98      | 0.37                     | 0.30                     | 2.79                |
| 13  | 3               | 1224     | 5.94      | 0.31                     | 0.24                     | 3.48                |
| 14  | 3               | 1296     | 5.92      | 0.34                     | 0.25                     | 4.02                |
| 15  | 4               | 1015     | 5.8       | 0.35                     | 0.24                     | 3.41                |
| 16  | 4               | 975      | 5.92      | 0.34                     | 0.36                     | 3.53                |
| 17  | 3               | 1135     | 5.88      | 0.29                     | 0.24                     | 4.40                |
| 18  | 8               | 747      | 5.90      | 0.52                     | 0.44                     | 3.09                |
| 19  | 6               | 894      | 5.83      | 0.46                     | 0.44                     | 3.93                |
| 20  | 6               | 876      | 5.80      | 0.45                     | 0.40                     | 4.08                |
| 21  | 6               | 897      | 5.80      | 0.46                     | 0.40                     | 4.41                |
| 22  | 5               | 1024     | 5.80      | 0.44                     | 0.44                     | 5.30                |
| 23  | 6               | 996      | 5.86      | 0.52                     | 0.32                     | 5.41                |
| 24  | 6               | 990      | 5.80      | 0.51                     | 0.42                     | 5.63                |
| 25  | 7               | 765      | 5.68      | 0.46                     | 0.48                     | 4.55                |
| 26  | 6               | 881      | 5.69      | 0.46                     | 0.40                     | 5.47                |
| 27  | 5               | 1039     | 5.75      | 0.45                     | 0.38                     | 6.72                |
| 28  | 15              | 542      | 5.75      | 0.70                     | 0.40                     | 3.64                |
| 29  | 6               | 921      | 5.70      | 0.48                     | 0.36                     | 6.43                |
| 30  | 7               | 872      | 5.70      | 0.53                     | 0.24                     | 6.31                |
| 31  | 10              | 686      | 5.70      | 0.59                     | 0.40                     | 5.14                |
| 32  | 6               | 808      | 5.60      | 0.42                     | 0.33                     | 6.27                |
| 33  | 6               | 927      | 5.65      | 0.48                     | 0.20                     | 7.43                |
| 34  | 6               | 829      | 5.60      | 0.43                     | 0.25                     | 6.86                |
leads to an approximately linear variation of the 0 K PIE curve that can be parametrized in the form

$$\text{PIE}^0(E) = \begin{cases} a(E - E_1), & \text{for } E \geq E_1, \\ 0, & \text{for } E < E_1, \end{cases}$$

(1)

where $E_1$ denotes the threshold energy to form a ground state ion.

Thirdly, the influence of internal excitation on the measured PIE curve is treated by assuming that every absorption of a photon leads to the production of an ion, provided the sum of the internal excitation energy $E_{\text{int}}$ of the initial state and the photon energy $E_{\nu}$ equals or exceeds the ionization energy. Moreover, we assume the Franck–Condon factor for all relevant transitions to be roughly the same. The fact that not all possible vibrational modes may be ionization active is taken into account by defining an effective number of oscillators as described below. In this approximation, the PIE curve of a hot cluster containing an internal excitation energy distribution $\Phi(E_{\text{int}})$ is given by [41, 53]

$$\text{PIE}(E_{\nu}) = \int_{E_{\text{min}}}^{\infty} \text{PIE}^0(E_{\text{int}} + E_{\nu}) \Phi(E_{\text{int}}) dE_{\text{int}}$$

(2)

with

$$E_{\text{min}} = \begin{cases} E_1 - E_{\nu}, & \text{for } E_{\nu} \leq E_1, \\ 0, & \text{for } E_{\nu} > E_1. \end{cases}$$

Given the shape of $\text{PIE}^0$ is known, it should therefore in principle be possible to determine the internal energy distribution from a deconvolution of the measured PIE curve. Our first attempt to interpret the data presented in figure 2 was pointed in that direction by assuming the PIE curves measured for supersonic clusters to closely resemble the 0 K behavior. Unfortunately, particularly the data acquired on the supersonic cluster beam are far too noisy for standard deconvolution methods. Moreover, this procedure cannot account for the fact that part of the internal energy may not be available for photoionization. As will be shown below, this is an important restriction which may significantly falsify the results.

In order to extract quantitative information about the internal energy distribution, we therefore model the measured PIE curve by assuming thermal equilibrium within the vibrational modes of a sputtered cluster along with a continuous, classical density of vibrational states with a quantum energy $\hbar \omega_{\text{vib}}$ much smaller than the mean thermal energy $kT$. As a first approximation, the internal energy distribution of a cluster containing $n$ atoms can then be approximated by a Boltzmann distribution of $s = 3n - 6$ harmonic oscillators. For a dimer ($n = 2$), we have $s = 1$, and the convolution in equation (2) leads to a purely exponential dependence in the pre-threshold region and a parallel shift by $kT$ in the post-threshold region. The semilogarithmic plot of the measured PIE curve therefore reveals the internal temperature as well as the ionization energy as the first break from the linear dependence as proposed by Watanabe [54].

For polyatomic clusters, an expression for the density of vibrational states is needed. Employing the semiclassical density expression for a distribution of $s$ harmonic oscillators as given in [53], one finds

$$\Phi(E_{\text{int}}) = A(E_{\text{int}} + \alpha E_{\nu})^{s-1} \exp(-E_{\text{int}}/kT)$$

(3)
with

\[
A = \left[ (kT)^s (s-1)! \sum_{i=0}^{s-1} \frac{(\alpha E_z / kT)^i}{i!} \right]^{-1}
\]

and \( E_z \) being the total zero point energy of all oscillators. Inserting this expression into the convolution (2) together with (1) yields the PIE curve in the post-threshold \((E_v \geq E_1)\) region as a linear function

\[
\text{PIE}(E_v) = a \left\{ kT \left( s - \frac{U_0 \sum_{i=0}^{s-2} U_i^j / i!}{\sum_{i=0}^{s-1} U_i^j / i!} \right) + E_v - E_1 \right\}
\]

and for the pre-threshold \((E_v \leq E_1)\) region

\[
\text{PIE}(E_v) = akT \exp \left( \frac{E_v - E_1}{kT} \right) \cdot \left( \frac{s \sum_{i=0}^{s-1} U_i^j / i! - U_1 \sum_{i=0}^{s-2} U_i^j / i!}{\sum_{i=0}^{s-1} U_i^j / i!} \right),
\]

with

\[
U_0 = \alpha E_z / kT, \quad U_1 = (E_1 - E_v + \alpha E_z) / kT,
\]

\( E_z \) denoting the total zero point energy summed over all \( s \) oscillators and \( \alpha \) being an empirical correction factor for the partition function. Compared to the diatomic case, the pre-threshold dependence is no longer a pure exponential but contains a pre-exponential polynome of degree \((s - 1)\).

3.3. Comparison with measured PIE curves

In the following, we will employ equations (4) and (5) to model the photoionization threshold of indium clusters \(\text{In}_n\) \((n = 2–35)\) assuming thermal equilibrium in the vibrational degrees of freedom, a number of \( s \) ionization-active harmonic oscillators with a typical average vibrational quantum energy of 0.005 eV \((70 \text{ cm}^{-1})\) and \( \alpha = 1 \) [41]. Although these parameters appear to be somewhat arbitrarily chosen, we note that the results described below do not strongly depend on the exact values. As a first approximation, the harmonic oscillator model is used even though the clusters are expected to have soft and, hence, strongly anharmonic modes. The influence of rotation is neglected, i.e. it is assumed that the rotational excitation energy is not available for direct photoionization. This assumption is supported by the selection rule allowing rotational quantum numbers to change by only \( \pm 1 \) during a photon-induced molecular transition [55, 56], thus rendering the allowed change of rotational energy upon ionization very small.

For the case of diatomic clusters, where \( s = 1 \), the interpretation of the experimental data is relatively straightforward. According to equations (4) and (5), one expects a pure exponential dependence in the pre-threshold region which should turn linear at photon energies above the ionization threshold. Figure 3 shows a semi-logarithmic plot of the experimental PIE curve measured for sputtered \(\text{In}_2\) dimers. In the photon energy range between 4.9 and 5.4 eV, a straight line corresponding to an exponential behavior can be fitted to the data, the slope of which...
is given by $1/kT$ and converted to an internal temperature of $T = 3850 \pm 100 \text{ K}$ [50]. This result compares well with other experimental data on the internal excitation of sputtered dimers (cf section 1) and provides another piece of evidence that at least the diatomic molecular species generated by sputtering are internally hot. Note that the exponential slope tends to become larger at larger energy deficit (4.6–4.9 eV photon energy), indicating that internal excitation energies above 0.5 eV are non-thermally populated. In the region between 5.5 and 6.0 eV, a linear dependence can be fitted to the data which is indicated by the dashed line in figure 3. The break between both curves occurs at a photon energy of approximately 5.4 eV. According to the assignment suggested by Watanabe [54]—and also seen from equations (4) and (5)—this energy should correspond to the ionization energy of the cluster. It should be noted that the ionization energy of neutral In$_2$ deduced here is below the value of $5.8 \pm 0.25$ eV which has been determined by Rayane et al [57] using electron impact ionization. Inspection of our PIE curve measured for cold In$_2$ generated in the supersonic beam, on the other hand, clearly reveals a measurable signal at photon energies down to about 5.5 eV. In fact, a linear extrapolation onto the baseline yields an ionization energy of $5.5 \pm 0.1$ eV, the error bar being due to a relatively large statistical noise induced by the very low abundance of dimers in the cluster beam. In this case, the linear extrapolation method (applied to cold dimers) and the Watanabe assignment (applied to hot dimers!) therefore yield approximately the same ionization energy values, which in view of the large internal excitation of the sputtered species seems to be a

**Figure 3.** PIE curve measured for sputtered In$_2$ dimers plotted semi-log (upper panel) and linear (lower panel). The solid and dashed lines represent the theoretical dependence in the pre- and post-threshold region according to equations (4) and (5).
very good agreement. The cause of the relatively large deviation from the electron impact data of [57] still remains to be determined. It may in principle be due to the fact that the electron impact experiment likely detects the vertical ionization energy which may be significantly larger than the adiabatic ionization energy that is generally believed to be determined by the linear extrapolation method.

For polyatomic clusters with \( n \geq 3 \), the interpretation of the data is more complicated. In principle, we use the functional dependence of equations (4) and (5) to model the measured PIE curve by means of a non linear least squares fitting procedure, treating the PIE\(^0\)-slope \( a \), the internal cluster temperature \( T \) and the ionization energy \( E_1 \) as fitting parameters. Since the value of \( a \) basically serves as a scaling factor between calculated and measured signals, the only free adjustable parameters are \( T \) and \( E_1 \). In doing so, we note that the resulting fits yield in many cases unrealistically high ionization energies and fail to describe the PIE curve at photon energies far below the ionization threshold. A typical example is shown in figure 4(a), which depicts a semilogarithmic plot of the experimental PIE data determined for sputtered In\(_{13}\) along with three different model curves that represent best fits of equations (4) and (5) under different constraints. If, on one hand, the number of ionization-active harmonic oscillators is assumed to be equal to the total number \( s = 3n - 6 \) of vibrational degrees of freedom, i.e. \( s = 33 \) with \( n = 13 \), the model curve (dotted line in figure 4(a)) underestimates the PIE at low photon energies below 5.5 eV. At the same time, the fitted ionization energy of 6.95 eV is unrealistically high, as seen from the comparison with the PIE curve determined for cold, supersonic clusters depicted in figure 2. The only way to remove the deviation at low photon energies, while keeping the fit in the region of larger photon energies comparatively good, is by reducing the number of ionization active harmonic oscillators assumed in the simulation to an effective number \( s_{\text{eff}} \leq s \). Therefore, we conducted a series of fits where \( s_{\text{eff}} \) was set to all possible values allowed for a specific cluster size \( n \) and inserted into equations (4) and (5) instead of \( s \). The best fits obtained with both the temperature \( T \) and the ionization energy \( E_1 \) allowed to run freely are shown in figure 4(a) for \( s_{\text{eff}} = 3 \) and \( s_{\text{eff}} = 1 \).

For the case of \( n = 13 \), the best approximation of the experimental data (solid line in figure 4) is achieved for \( s_{\text{eff}} = 3 \), where the fitting procedure yields an ionization energy of 5.97 eV that compares reasonably well with the shape of the PIE curve measured for supersonic clusters. At the same time, the fitted value of the internal temperature is significantly increased from 487 K (at \( s_{\text{eff}} = s \)) to 1291 K (at \( s_{\text{eff}} = 3 \)), thus leading to a much better description of the low energy part of the experimental data. If \( s_{\text{eff}} \) is reduced further, the fitted curve tends to overestimate the PIE at low photon energies, as is shown for \( s_{\text{eff}} = 1 \) in figure 4(a) (dashed line, \( E_1 = 5.81 \) eV, \( T = 2131 \) K).

The same behavior is consistently observed for all clusters with \( n \geq 7 \). This observation indicates that only a small fraction of the total vibrational energy contained in a larger sputtered cluster is available for photoionization. While this finding may at first glance appear surprising, it can be rationalized by assuming that the clusters generated by sputtering are internally excited to such high energies that they rapidly fluctuate between different isomeric structures and therefore appear to be in a quasi-liquid state. MD computer simulations of the cluster formation process in sputtering indeed point in that direction. By following the internal dynamics of a cluster subsequent to its formation/emission from the surface, such simulations clearly show that none of the sputtered clusters containing more than three atoms can be assigned a specific geometric structure. Figure 5 illustrates this situation by depicting a schematic potential diagram of a cluster as a function of some generic isomerization parameter. At low internal temperatures,
Figure 4. Comparison of measured and modeled PIE curve of sputtered neutral In\textsubscript{13} clusters. Dots: experimental data; lines: least squares fit of equations (4) and (5) with fixed values of $s_{\text{eff}}$ as indicated using (a) variable $a$, $T$ and $E_I$ and (b) fixed $E_I = 5.4$ eV and variable $a$, $T$.

the constituent atoms vibrate around a fixed geometric configuration which corresponds to the equilibrium ground state of the cluster. As soon as the internal energy becomes sufficiently high to populate metastable states corresponding to different isomeric structures, the cluster will begin to fluctuate between different isomers, until at even higher internal energies these fluctuations become so rapid that the internal structure is completely broken. In this situation, much of the internal energy has been used up for melting the cluster, and the vibrational states correspond to those of a liquid drop, i.e. an ensemble of $n$ atoms moving in a confining potential well. In order to utilize the entire internal energy for photoionization, a transition has to be induced between such a high lying vibrational state of the (liquid) neutral cluster and a low lying vibrational state of the corresponding (solid) cluster ion. According to the Franck–Condon principle, such a transition requires all atoms of the neutral cluster to reside by coincidence in their relative positions corresponding to the ground state configuration of the ion. It is clear that such a coincidence is highly unlikely, thus rendering the Franck–Condon factor for such a transition practically zero. The same argument is valid for all vibrational ionic states below the melting energy of the cluster ion, thus leading to the fact that a liquid neutral cluster can effectively ionize only to form a liquid cluster ion as well. As a consequence, only a small fraction of the internal energy originally contained in the neutral cluster is actually available for photoionization, and the assumption of a restricted $s_{\text{eff}}$ appears reasonable. In fact, this notion

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Figure 5. Schematic potential diagram of a cluster versus a generic isomerization coordinate. The local minima correspond to the ground state cluster configuration and metastable isomers.

is strongly supported by ab initio calculations by Akola et al, who determined the PIE curves of various Naₙ [58] and Alₙ [59] clusters as a function of temperature. From the temperature-dependent shift of the PIE curves calculated in this work, one deduces values of $s_{\text{eff}} \sim 2, 4$ and 6 instead of $s = 18, 36$ and 114 for Na₈, Na₁₄ and Na₄₀, respectively.

As a consequence of the above discussion, we conclude that it is not sensible to allow the ionization energy $E_1$ to vary freely. Instead, we chose to select this parameter for consistency with the PIE curve measured for supersonic clusters and then keep it fixed during the fitting procedure. For the example of In₁₃, this is illustrated in figure 7, which depicts the respective PIE data along with different linear approximations. In order to extract information about the ionization energy, three different straight line fits were applied to the measured data. Firstly, the baseline is fitted in the energy range from 4.5 to 5.5 eV and extrapolated towards higher photon energies. Secondly, a fit is applied in the threshold energy range where the PIE starts to deviate from the baseline, i.e. between 5.5 and 6.0 eV. At first glance, it appears tempting to use the crossing point of this line with the baseline to determine an ionization energy of 5.48 eV for In₁₃. However, it is clearly seen that there is another abrupt increase of the PIE for energies larger than 5.9 eV. Applying a straight line fit in this region, one finds a larger value of 5.94 eV. At the same time, the slope of the straight line is comparable with that observed for the sputtered clusters, a finding which is consistent with the prediction of equation (4). Therefore, the value of 5.94 eV was assumed to correspond to the actual ionization energy of In₁₃ and used in the fitting procedure described above. We interpret the ‘tail’ of the PIE curve displayed in figure 7 toward lower photon energies as an indication that the clusters entrained in the supersonic beam are not completely cold and contain a residual internal energy in qualitatively the same way as the sputtered clusters with, however, much lower temperature. This notion agrees with the temperature measurement of Röthlisberger et al for Naₙ clusters formed in a supersonic beam [41]. Alternatively, the presence of different isomers in the rapidly quenched supersonic beam may also lead to a distribution of multiple ionization thresholds.

Using a fixed ionization energy of 5.94 eV, the PIE curve of sputtered In₁₃ was refitted for different values of $s_{\text{eff}}$ using $a$ and $T$ as freely running fitting parameters. The results are presented in figure 4(b), which shows the best fit curves along with the corresponding temperature values. These fits, which are now consistent with the PIE data measured for ‘cold’ clusters, even more clearly demonstrate that only $s_{\text{eff}} = 3$ or $s_{\text{eff}} = 4$ provide a reasonable
description of the experimental data in terms of the photoionization model described above, with the fit being slightly better for $s_{\text{eff}} = 3$, thus rendering an internal temperature of 1000–1200 K for sputtered In$_{13}$. The model PIE curves of other sputtered clusters that represent the best fits obtained in the same way are shown along with the respective measured data in figure 6.

Figure 6. Model PIE curves that represent the best fit of equations (4) and (5) to the measured data for different cluster sizes.
It is seen that in all cases a relatively good fit of the experimentally determined PIE data can be found. The ionization energy values used in the fitting procedure and the resulting internal temperatures are listed in table 1. It is seen that only for the smallest clusters (In$_3$ and In$_4$) all possible vibrational degrees of freedom appear to be ionization active. For all larger clusters, the value of $s_{\text{eff}}$ appears to gradually increase with increasing cluster size, ranging from $s_{\text{eff}} = 3–4$ at $5 \leq n \leq 15$ to $s_{\text{eff}} = 6–7$ at $n > 30$, with only a few exceptions which may in principle arise from experimental errors. Note, however, that the low value of $s_{\text{eff}} = 1$ for In$_7$ is well in accordance with the fact that here the PIE curves of sputtered and supersonic clusters are almost the same. For clusters larger than $n = 25$, the determination of $s_{\text{eff}}$ becomes more and more ambiguous, so that the exceptionally large values obtained for In$_{28}$ and In$_{31}$ may not be significant.

Using the internal temperature depicted in table 1, it is now possible to model the observed shift between the PIE curves of sputtered and beam clusters as

$$\Delta E_{\text{mod}} = s_{\text{eff}}kT.$$  \hspace{1cm} (6)

The resulting values are also listed in table 1. Comparison with the experimental data reveals an astonishingly good agreement between experiment and model. Since the modeled curve shift is calculated relative to the assumed 0 K PIE curve, this agreement corroborates the notion of the supersonic beam clusters being rather cold. Even more, it supports the relative scaling of the PIE curves measured for sputtered and supersonic clusters in figure 2 along with the underlying assumptions discussed in section 3.1. In view of the discussion of figure 7, however, it still appears problematic to deduce ionization energies from a simple linear threshold extrapolation of PIE curves measured for the supersonic clusters.

### 3.4. Internal energies

The temperature of the sputtered clusters as determined from the fitting procedure described in section 3.3 is plotted as a function of cluster size in figure 8. Interestingly, the sputtered
Figure 8. Internal temperature of sputtered clusters versus cluster size as obtained from fitting equations to the measured PIE data. \( s_{\text{eff}} \): number of ionization active vibrational degrees of freedom; \( s \): total number of vibrational degrees of freedom.

Dimers appear to be ‘hottest’, with the temperature falling rapidly with increasing cluster size up to about \( n = 6 \). For larger clusters, on the other hand, the emission temperature appears to become constant at values around 1000 K, with the apparent structure between \( n = 4 \) and 26 being within the range of uncertainty induced by the approximate nature and many assumptions entering the data treatment. For comparison, the data extracted from fits assuming all vibrational degrees of freedom to be ionization active are included as open symbols. These values, which must be regarded as lower boundaries of the actual temperature, are found to decrease further and even drop below room temperature for cluster sizes \( n > 15 \).

Assuming, as a first-order approximation, a specific heat of \( (3n - 6)k \) for a cluster containing \( n \) atoms, the temperatures can be converted into the average internal energy contained in a sputtered cluster. The resulting values are listed in the last column of table 1 and plotted against the cluster size in figure 9. Again, the lower limits determined under the assumption of an unrestricted \( s_{\text{eff}} \) are included for comparison. It is seen that the average internal energy appears to be roughly constant up to \( n = 6 \) and then rises approximately linearly with increasing \( n \). Fitting a straight line to the entire data set displayed in figure 9, one finds a relation

\[
E_{\text{int}}(n) \sim (0.22n - 0.05) \text{ eV}.
\] (7)

A similar linear behavior has been predicted for sputtered Ag\(_n\) clusters by means of MD computer simulations [14] with, however, a slope which is about a factor of 5 larger than that measured here.

The difference between the internal energies predicted by MD and measured here is easy to understand. The MD simulation refers to ‘nascent’ sputtered clusters which are identified immediately after they leave the ion bombarded surface. With the average internal energy being of the order of 1.5 eV per constituent atom [14], these clusters are highly unstable and will therefore fragment on a very short (picosecond) timescale [34, 35, 60]. A cluster containing an internal excitation energy \( E_{\text{int}} \) larger than the (cluster size-dependent) dissociation threshold...
Figure 9. Average internal energy of sputtered clusters versus cluster size as obtained from the data of figure 8. $s_{\text{eff}}$: number of ionization active vibrational degrees of freedom; $s$: total number of vibrational degrees of freedom. The shaded area depicts the range of possibly observable values limited by unimolecular fragmentation (see text). Solid line: linear fit according to equation (7); Dashed and dotted lines: maximum possible internal energy calculated by equation (9) using either the sublimation energy of solid indium or the binding energy of the In$_2$ dimer as limiting values of the cluster dissociation threshold $D_n$.

$D_n$ may undergo unimolecular fragmentation reactions and thereby lose internal energy prior to photoionization and detection. In the present experiment, the sputtered neutral clusters are detected at timescales of typically microseconds after their formation and emission at the surface. Therefore, only the residual internal energy that may be left after such an evaporative cooling process can be detected here.

A quantitative interpretation of the measured internal excitation energies requires a theoretical description of the fragmentation rates involved. Among the various models connecting fragmentation rates and internal energies, we—for the sake of simplicity—employ the classical Rice–Ramsberger–Kassel–expression [61]

$$k_n(E_{\text{int}}) = v g \left(1 - \frac{D_n}{E_{\text{int}}}\right)^{s-1},$$

(8)

describing the fragmentation rate of clusters consisting of $n$ atoms and containing an internal excitation energy $E_{\text{int}}$. In equation (8), the parameter $v$ denotes a typical vibrational frequency ($10^{12} - 10^{13}$ Hz), $s = 3n - 6$ is the number of vibrational degrees of freedom of the cluster, and $g$ is a degeneracy factor which is usually taken equal to the number of cluster atoms [61]. As a result, the maximum internal energy that can be left in a cluster of $n$ atoms detected at time $t$ after its generation is given by

$$E_{\text{int}}^{\text{max}}(n) = \frac{D_n}{1 - (vnt)^{(1/s)}}.$$

(9)
Using equation (9) with an estimated average flight time of one microsecond and $\nu \approx 3 \times 10^{12}$ Hz (the measured dimer vibrational frequency [62]) we can estimate a maximum residual internal energy of $\text{In}_n$ clusters depending on their dissociation threshold $D_n$. In principle, $D_n$ must lie somewhere between the binding energy of $\text{In}_2$ in its ground electronic state (1.0 eV [62]) and the sublimation energy of solid indium (2.5 eV [63]), with the former and latter representing the limits for small and large $n$, respectively. Plotting equation (9) with both values (dotted and dashed lines in figure 9) therefore results in a range of possibly observable excitation energies which is indicated by the shaded area in figure 9. It is seen that the measured average internal energies closely represent the maximum possible values detectable in the experiment, thus demonstrating that the internal temperature distribution displayed in figure 8 must be largely determined by evaporative cooling. As a consequence, the internal excitation energies and temperatures determined here must be regarded as lower limits to the nascent excitation of sputtered clusters immediately after their generation at the surface. Even with this limitation, the results clearly reveal that sputtered clusters must be hot, i.e. much hotter than the same clusters produced in a supersonic beam. In this respect, the data represent the first direct experimental evidence for this fact, which has long been predicted by sputtering theory.

4. Conclusions

Using the ‘PIE-thermometer’ approach, it is possible to obtain information regarding the internal excitation of sputtered clusters in very much the same way as for clusters contained in a supersonic beam. By measuring the PIE curve of the same clusters formed either by sputtering or in a supersonic expansion, we show direct evidence that the sputter generated clusters are internally ‘hot’, i.e. strongly vibrationally excited. Using a simple theoretical model, the measured data can be used to derive quantitative information on the internal temperature of the sputtered clusters. We find, however, that the model only fits the experiment in a reasonable way if the number of ionization active vibrational degrees of freedom is significantly restricted. Apparently, only a small fraction of the total internal excitation energy contained in a sputtered cluster is effective to lower its ionization threshold, a finding which becomes understandable if isomerization and melting of the clusters are taken into account. From the model fits, we deduce internal temperatures of the detected clusters which are highest ($\sim 4000$ K) for sputtered dimers, drop rapidly with increasing cluster size for $n \leq 6$ and become roughly constant around 1000 K for larger clusters ($n \geq 7$).

Utilizing standard fragmentation rate theory, it is found that the observed average internal energy of the sputtered clusters roughly corresponds to the maximum possible value expected from unimolecular fragmentation and the (microsecond) timescale on which the particles are detected. Therefore, the measured internal cluster temperatures are strongly influenced by evaporative cooling, and the initial temperature of the sputtered clusters immediately after their formation and emission from the surface must be even larger. Comparison of the data presented here with MD computer simulations suggests that the original internal temperature of these ‘nascent’ clusters must be by roughly a factor 5 above that measured here. As a consequence, we postulate that sputtered $\text{In}_n$ clusters exhibit an original internal temperature of the order of $4-5 \times 10^3$ K, which is largely independent of cluster size. This finding suggests that the large majority of sputtered clusters (and, in particular, all larger ones) are formed at relatively late stages of a collisional spike which is induced by the projectile impact. Again, this notion is in good agreement with MD simulations of the cluster emission process.
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