

Growth of tellurium clusters in presence of metal impurities

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Received 28 November 2000

Abstract. The growth of small tellurium clusters in helium and the influence of a metal impurity (dysprosium atoms) on the cluster size distribution are investigated in a double laser vaporization source. A model describing the role of the carrier gas as collision partner is presented, emphasizing the crucial influence of the gas pressure on cluster formation. Changes in cluster reactivity due to dysprosium addition are discussed in terms of ionic structures $\text{Dy}^{3+}(\text{Te}_N)^{3-}$ containing a radical electron.

PACS. 36.40.Jn Reactivity of clusters – 36.40.Qv Stability and fragmentation of clusters – 34.10.+x General theories and models of atomic and molecular collisions and interactions (including statistical theories, transition state, stochastic and trajectory models, etc.)

1 Introduction

Understanding of growth processes is a very complex and interesting topic in cluster science [1], which is investigated since many years. Detailed knowledge of mechanisms of cluster formation is crucial for the effective use of cluster sources. This is especially true for double vaporization sources, which allow generation of binary clusters of different compositions by mixing vapors of two elements together with helium as quenching gas. In such sources, product composition is very sensitive to source parameters. Two types of double vaporization sources are commonly available. One is the double oven source, where the elements are separately evaporated in two resistively heated crucibles [1]. This source has the advantage of producing relatively high cluster flux, but only elements with high vapor pressure at low temperatures can be used. A second source type is the double laser vaporization source, which was developed more recently [2,3] having the advantage, that almost all solid elements can be used as precursors. If we consider cluster growth in a mixture of vapors of two elements, one expects, that the presence of atoms or clusters of one element can influence the cluster growth of the other element. This influence is investigated in the present work by adding tellurium clusters and studying the effect on the cluster size distribution. The experimental conditions are chosen in such way, that Te_N clusters are doped with not more than one dysprosium atom each. Particular attention is paid to the role of the helium gas.

2 Experimental

In the pulsed double laser vaporization source, tellurium and dysprosium are vaporized separately, quenched by the

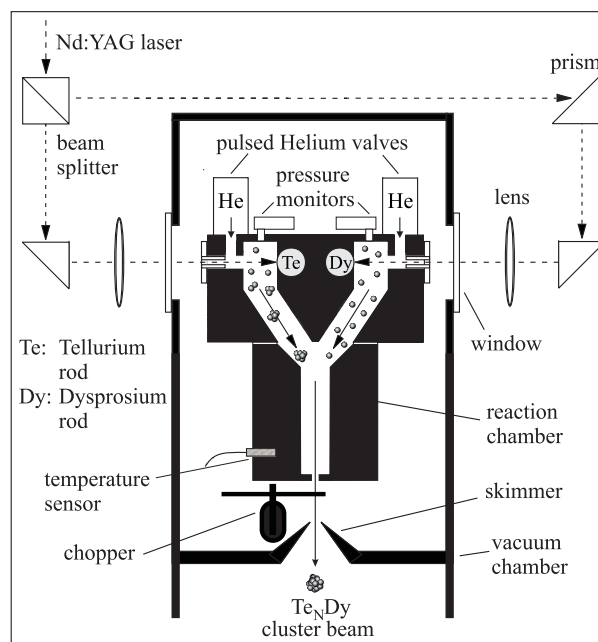


Fig. 1. Double laser vaporization source.

carrier gas, and mixed in the reaction chamber (Fig. 1). Due to the high sublimation enthalpy of bulk dysprosium [4], only low concentrations of dysprosium atoms are produced, while moderate vaporizing laser intensities are chosen. In this way, only Dy atoms are formed, but no condensation to Dy_N clusters is observed. In the reaction chamber, Te_N clusters and dysprosium atoms can undergo reactions. Product clusters leave through a nozzle in a molecular beam. The beam is skimmed and collimated to a width of $500 \mu\text{m}$. After a travel distance of 3.75 m, clusters are photoionized by means of collimated

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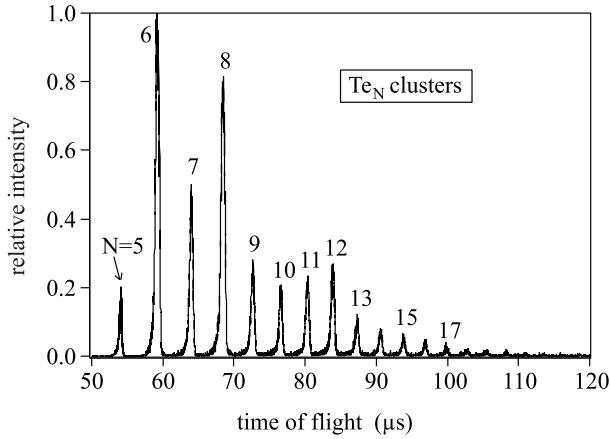


Fig. 2. Mass spectrum of pure tellurium clusters.

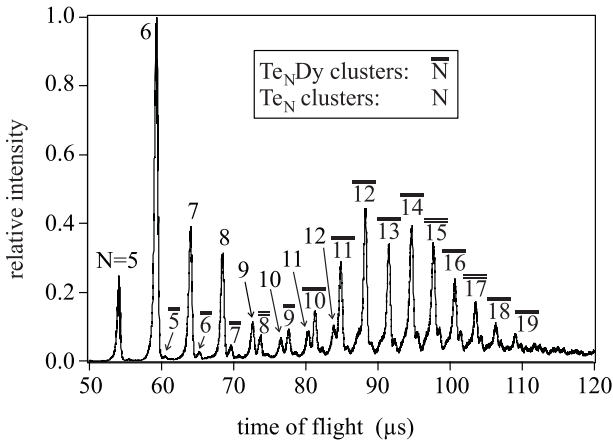


Fig. 3. Mass spectrum of Te_N and Te_NDy clusters.

excimer laser light ($h\nu = 7.9$ eV) and analyzed by time-of-flight mass spectrometry. Experimental details have already been described in [3]. Differing from [3], the reaction chamber (Fig. 1) has a modified design (inner diameter 6 mm, length 30 mm) and is kept at room temperature ($T = 300$ K). A chopper located at the source nozzle allows for determination of the dwell time of clusters in the reaction chamber. The helium pressure in the cluster source is measured with a commercial pressure sensor [6].

3 Results

Pure tellurium clusters Te_N of varying sizes are generated, if the laser at the dysprosium rod is blocked and only tellurium is vaporized (Fig. 2). In contrast, if only dysprosium is vaporized, no Dy_N clusters are observed as mentioned in the previous section. Vaporization of both tellurium and dysprosium results in a mixture of Te_N and Te_NDy clusters (Fig. 3), indicating that an addition reaction $\text{Te}_N + \text{Dy} \rightarrow \text{Te}_N\text{Dy}$ is taking place in the reaction chamber. It is obvious from Fig. 3, that by proper choice of experimental conditions, doping of Te_N clusters with just one dysprosium atom each is feasible. Additionally, the envelope of the size distribution of Te_NDy (Fig. 3)

is shifted to higher masses compared with size distribution of Te_N (Fig. 2). That means, presence of dysprosium atoms during growth of Te_N promotes formation of large clusters. Since this cannot be explained by a simple dysprosium addition, certain consecutive reactions, leading to formation of larger clusters, must be assumed.

To understand these observations, we take into account the time scale of the reactions and the concentrations of involved species. Reaction time is restricted by the dwell time of particles in the reaction chamber. Its mean value, measured using the chopper, is approximately 1.0 milliseconds. The cluster concentrations in the reaction chamber can most easily be estimated by means of a deposition experiment. Long-time operation (5 hours) of the cluster source with a small glass rod placed into the reaction chamber leads to an increase in the rod mass due to deposited clusters. From this mass increase, the cluster concentration in the reaction chamber can be estimated [7]. For Te_N clusters with an assumed mean cluster size of $N = 10$, we get a concentration of 10^{14} clusters/ cm^3 . The concentration of dysprosium atoms is much smaller than 10^{15} atoms/ cm^3 (upper limit). For the helium atoms in the reaction chamber, concentration is calculated from the peak pressure of the helium pulses in the source, which is 10 mbar at 300 K corresponding to 2.4×10^{17} helium atoms per cm^3 .

4 Discussion

4.1 Mechanism of addition of single dysprosium atoms to Te_N clusters

First, we want to derive a detailed model of the addition of single dysprosium atoms to tellurium clusters. If a reaction of a dysprosium atom with a Te_N cluster occurs, a certain reaction energy is released. Its magnitude can be estimated by the bond energy of a TeDy molecule, which is $E_{\text{TeDy}} = 2.4$ eV [5, a]. Because of this large heat of reaction, the product is a hot intermediate Te_NDy^* , which can rapidly undergo fragmentation unless cool-down by collisions with helium atoms of the surrounding carrier gas occurs. The lifetime τ of hot clusters Te_NDy^* can be calculated using RRKM theory [8,9] in combination with a thermodynamic description of the clusters as particles of a certain vibrational temperature T_{vib} . This is done on two assumptions. Before addition of dysprosium, Te_N clusters are in thermal equilibrium with the reaction chamber, *i.e.* $T_{\text{vib}} = 300$ K. This is justified by the high collision frequencies of clusters with helium atoms, as shown below. Secondly, the reaction energy is equally distributed over all vibrational degrees of freedom of the product cluster Te_NDy^* , leading to an increased vibrational temperature T_{vib}^* , which can be estimated in the following way. The mean energy E_v of a vibrational mode of a harmonic oscillator is given by

$$E_v = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \quad (1)$$

where ν is the frequency of the mode. For small tellurium clusters, ν is of the order of 100 cm^{-1} [10]. After dysprosium addition, the intermediate Te_NDy^* has a vibrational energy of

$$E_v^* \approx E_v + \frac{2.4 \text{ eV}}{(3(N+1) - 6)} \quad (2)$$

from which we can calculate T_{vib}^* . This equation is valid in the high temperature limit only ($kT \gg h\nu$), however in our case it serves as rough estimation ($kT \approx h\nu$). Using RRKM theory [8,9], we can calculate the rate constant k_c of decay of a Te_NDy^* cluster, which is the inverse lifetime $\tau = 1/k_c$ of this cluster.

$$k_c = \frac{kT_{\text{vib}}^*}{h} \left(1 - e^{-\frac{h\nu}{kT_{\text{vib}}^*}} \right) e^{-\frac{E_0}{kT_{\text{vib}}^*}} \quad (3)$$

where $E_0 \approx E_{\text{TeDy}} = 2.4 \text{ eV}$ is used as approximate dissociation energy of Te_NDy^* , k is the Boltzmann constant, and h is Planck's constant. The calculated lifetimes vary from 10^{-8} to 10^5 s depending on cluster size (Table 1). However, in the molecular beam apparatus, clusters need some milliseconds to pass from the cluster source to the mass spectrometer, as known from velocity measurements using the chopper. Consequently, hot Te_NDy^* with less than 13 atoms cannot be observed, since at temperatures T_{vib}^* they have lifetimes shorter than several milliseconds and would therefore be depleted from the beam by fragmentation. Nevertheless, small clusters Te_NDy are observed in the mass spectra. Hence, there must be a mechanism for cooling down the hot intermediates, leading to a longer lifetime. This can be achieved by collisions with other species. Generally, there are two possible pathways for the cool-down process:

- (a) Cooling by collisions with He atoms of the carrier gas.
- (b) Cooling by collisions with other clusters.

At first glance, path (a) should be the most important, but to validate the picture, the other possibility is considered, too. To decide which path is relevant, collision numbers are calculated using the kinetic theory of gases. The Te_NDy clusters are regarded as close packed hard spheres (space-filling 74%) having radii of

$$r_{\text{cluster}} = \sqrt[3]{\frac{1}{0.74} (N r_{\text{Te}}^3 + r_{\text{Dy}}^3)} \quad (4)$$

with $r_{\text{Te}} = 143 \text{ pm}$, $r_{\text{Dy}} = 175 \text{ pm}$ [11]. Bimolecular collision frequencies z are calculated by

$$z = \pi (r_A + r_B)^2 [N] \sqrt{\frac{8kT}{\pi\mu}} \quad (5)$$

where r_A and r_B are the radii of the colliding species (for helium we use the van-der-Waals radius $r = 140 \text{ pm}$ [11]), $[N]$ is the number density, and μ is the reduced mass.

The collision number of hot Te_NDy^* with other tellurium clusters within the lifetime of the Te_NDy^* is very small (less than 17 for largest observed cluster Te_{24}Dy and even less than one for clusters smaller than Te_{10}Dy).

Table 1. Properties of Te_NDy^* clusters: hard sphere radii, collision frequencies with He atoms, lifetimes, and collision numbers with He atoms within the Te_NDy^* lifetime.

cluster	cluster radius (pm)	collision frequency (s^{-1})	lifetime of Te_NDy^* (s)	coll. number within lifetime
Te_5Dy	300	1.86×10^8	1.40×10^{-8}	2.60
Te_6Dy	314	1.98×10^8	1.38×10^{-7}	2.73×10^1
Te_7Dy	327	2.09×10^8	1.21×10^{-6}	2.52×10^2
Te_8Dy	339	2.20×10^8	9.39×10^{-6}	2.06×10^3
Te_9Dy	350	2.30×10^8	6.58×10^{-5}	1.61×10^4
Te_{10}Dy	361	2.40×10^8	4.18×10^{-4}	1.01×10^5
Te_{11}Dy	371	2.49×10^8	2.43×10^{-3}	$2.5 \times 10^{5(a)}$
Te_{12}Dy	380	2.59×10^8	1.30×10^{-2}	$2.6 \times 10^{5(a)}$
Te_{13}Dy	389	2.68×10^8	6.41×10^{-2}	$2.7 \times 10^{5(a)}$
Te_{14}Dy	397	2.76×10^8	2.95×10^{-1}	$2.8 \times 10^{5(a)}$
Te_{15}Dy	406	2.85×10^8	1.27	$2.8 \times 10^{5(a)}$
Te_{16}Dy	414	2.93×10^8	5.12	$2.9 \times 10^{5(a)}$
Te_{17}Dy	421	3.01×10^8	1.95×10^1	$3.0 \times 10^{5(a)}$
Te_{18}Dy	428	3.09×10^8	7.00×10^1	$3.1 \times 10^{5(a)}$
Te_{19}Dy	436	3.17×10^8	2.39×10^2	$3.2 \times 10^{5(a)}$
Te_{20}Dy	443	3.24×10^8	7.79×10^2	$3.2 \times 10^{5(a)}$
Te_{21}Dy	449	3.32×10^8	2.42×10^3	$3.3 \times 10^{5(a)}$
Te_{22}Dy	456	3.38×10^8	7.21×10^3	$3.4 \times 10^{5(a)}$
Te_{23}Dy	462	3.46×10^8	2.06×10^4	$3.5 \times 10^{5(a)}$
Te_{24}Dy	468	3.53×10^8	5.66×10^4	$3.5 \times 10^{5(a)}$
Te_{25}Dy	474	3.60×10^8	1.50×10^5	$5.6 \times 10^{5(a)}$

(a) If the lifetime of Te_NDy^* exceeds the dwell time in the reaction chamber (1.0 ms), the collision number with helium atoms is restricted correspondingly ($\approx 10^5$ collisions within the dwell time).

Hence cluster-cluster collisions (b) cannot explain the observed size distribution. However, collision numbers of hot Te_NDy^* with helium atoms within its lifetime can be quite large as shown in Table 1. According to the conservation of linear momentum, the maximum energy transfer for a single collision of a Te_NDy^* with one helium atom is approximately equal the kinetic energy of helium, which is 0.039 eV at 300 K. Consequently, at least 62 collisions are necessary to transfer the whole reaction energy of approximately 2.4 eV. This requirement is fulfilled for almost all clusters. Only the collision numbers calculated for the two smallest observed clusters, Te_5Dy and Te_6Dy , are less than 62. However, these model-based numbers are lower limits and can in fact be somewhat larger. Hence, the mechanism of dysprosium addition can be explained assuming the formation of intermediates Te_NDy^* , whose reaction energy is removed by collisions with helium atoms. This model emphasizes the crucial role of the carrier gas. The helium pressure in the cluster source is not allowed to be much less than it was during our experiments, since otherwise no small Te_NDy clusters can be formed.

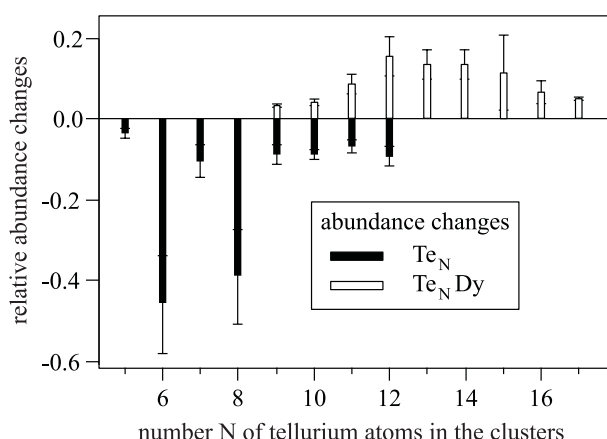


Fig. 4. Mean abundance changes in cluster mixtures with and without dysprosium atoms, with respect to the overall cluster intensity (with error bars).

4.2 Influence of metal impurities on cluster growth

Figure 4 shows the changes in cluster abundances in cluster mixtures with and without dysprosium atoms. It is demonstrated, that presence of dysprosium atoms leads to formation of relatively large Te_NDy clusters (positive values in Fig. 4), whereas abundances of small tellurium clusters decrease simultaneously (negative values in Fig. 4). However, the production of large Te_NDy clusters cannot be explained by simple addition of one dysprosium atom to a tellurium cluster, since no changes in abundance of the corresponding Te_N cluster are observed in most cases. Hence, the formation of large Te_NDy can be achieved only by a stepwise reaction mechanism



Taking the observation, that the maximum of the size distribution is shifted to larger clusters in presence of dysprosium, we conclude that Te_NDy clusters are much more reactive towards addition of further tellurium clusters than pure Te_N clusters. The higher reactivity of Te_NDy can be explained by a simple chemical model, considering an ionic chemical bonding of the type $\text{Dy}^{3+}(\text{Te}_N)^{3-}$ in analogy to the Zintl concept for bulk materials [12,13]. According to the electronic configurations (Te: $5s^2p^4$, Dy: $4f^{10}6s^2$), the polyanion $(\text{Te}_N)^{3-}$ has an unpaired radical electron, whereas pure Te_N clusters have always an even number of valence electrons. For bulk TeDy , the existence of a radical electron was already shown by magnetic and conductivity measurements [14]. This compound is reported to consist of Dy^{3+} and Te^{2-} ions and one delocalized radical electron e^- per formula unit. In clusters, one effect of the radical electron is, that bond formation to other clusters should be much easier. As a second effect, the collision cross sections are increased: The delocalized radical electron [15] can easily be polarized, *i.e.* the clusters have a high polarizability α . This leads to strong attractive long-range van-der-Waals interactions between clusters and hence large collision cross sections. As a result, collision frequencies with other clusters are dramatically

increased and addition reactions occur at larger extend, serving as a satisfactory explanation for the higher reactivity of Te_NDy clusters compared with Te_N .

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft (Be-1350/5-1). C.H. acknowledges a grant from the Fonds der Chemischen Industrie.

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7. From the mass increase of the rod ($\Delta m = 280 \mu\text{g}$), we conclude the number of deposited Te_N clusters per laser shot assuming a mean cluster size of 10 atoms. To roughly estimate the cluster concentration in the reaction chamber, we presume that nearly all clusters are deposited at its inner walls (and the rod) and almost no clusters leave through the nozzle compared to deposition. This is somewhat justified by the order of magnitude of the diffusion constant $D = 5 \times 10^{-2} \text{ m}^2/\text{s}$ for clusters in helium, calculated assuming an ideal gas. Within the dwell time of approximately 1 ms in the chamber, the clusters move a distance of 10 mm, which is more than the diameter of the chamber (6 mm). The ratio of clusters deposited at the inner walls of the chamber to clusters deposited on the rod equals the ratio of the inner area of the chamber to the surface area of the rod. The concentration of dysprosium atoms is too low to be determined by deposition and is considered to be much smaller than the concentration of tellurium atoms.
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