

# Raman band of matrix isolated $\text{Na}_M\text{Se}_N$ clusters

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## Abstract

Selenium clusters are doped with sodium atoms in the reaction zone of a dual laser vaporization source. Product clusters  $\text{Se}_N$  and  $\text{Na}_2\text{Se}_N$  with  $N = 4-8$  are deposited in a nitrogen matrix and investigated by Raman spectroscopy. Beside the Raman band of pure  $\text{Se}_N$  clusters, a new intense band between  $165$  and  $225\text{ cm}^{-1}$  is observed. Within a simple model of dynamical charge transfer the new band is attributed to certain vibrational modes with considerable changes of Na–Se bond lengths. The assignment is confirmed by density functional calculations. A bonding model for the  $\text{Na}_2\text{Se}_N$  clusters containing horseshoe shaped polyanionic selenium chains is developed.

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## 1. Introduction

Doping of macroscopic semiconductors with suitable metal atoms provides donor electronic states without substantial changes of the geometric bulk structure [1]. The bonding of metal atoms into nanostructured semiconductors, however, is a much more complex problem. For a nanometer sized semiconductor cluster consisting of only a few atoms, the addition of just a single metal atom already corresponds to an extremely high dopant concentration. Moreover, the chemical bonding in the pure semiconductor cluster will deviate significantly from its periodic bulk structure and hence electronic band structure approximations will become useless and a molecular orbital approach is necessary. Metal addition is, therefore, best described as a molecular reaction leading to significant perturbations not only of the electronic but most likely also of the whole geometrical structure of the semiconductor particle. The investigation of such structural effects might become important

for the assembly of smallest semiconductor devices [2] and is an interesting research field of physical and theoretical chemistry.

For a basic understanding of the changes in chemical bonding in a semiconductor cluster due to metal addition one would choose, as a first step, a system where a simple structural model for the semiconductor particles exists. Clusters of, e.g., silicon are not appropriate, since they tend to occur in several isomer structures with complex bonding far from the bulk structure [3,4]. An element forming bonds with a low coordination number as, e.g., selenium is much more suitable. The Se coordination number of two leads to simple ring structures for pure gas phase  $\text{Se}_N$  clusters ( $N = 5-8$ ), as shown by several experiments (electron diffraction [5], photoelectron spectroscopy [6], Stern–Gerlach experiments [7]) and quantum chemical calculations [8–10]. For the metal, a low number of valence electrons per atom is favorable. Then, the expected electron transfer from the metal to the more electronegative selenium can be adjusted in relatively small steps by successive addition of metal atoms. We have, therefore, investigated the addition of sodium providing a single electron per atom to small selenium clusters.

In the bulk, there are several known Se modifications consisting of simple selenium rings or chains [11]. For

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the binary bulk system Na/Se, the phase diagram contains the compounds  $\text{Na}_2\text{Se}_N$  with  $N = 1-4, 6$  [12,13]. Some of them have been isolated [14,15]. An important way of synthesis is the reduction of selenium with sodium dissolved in liquid ammonia. The bonding situation in the selenium rich  $\text{Na}_2\text{Se}_N$  bulk compounds is described as polyanionic corresponding to the formula  $(\text{Na}^+)_2(\text{Se}_N)^{2-}$ . The  $(\text{Se}_N)^{2-}$  polyanions in alkali selenides have chain structure as found by X-ray diffraction for the bulk ( $N = 2-9$  [16,17]), EXAFS measurements on molten selenides [18] and UV/Vis-spectroscopy on ammonia solutions [19].

For small isolated metal/selenium systems, however, only mass spectrometric studies on  $\text{Cu}_M\text{Se}_N$  and  $\text{Ag}_M\text{Se}_N$  clusters are reported [20,21]. The role of polyanion formation in these systems remained unclear, possibly due to a relatively high metal content of the investigated clusters, which makes them also not suitable as model system for the doping process.

The essential question focused in this work is how the simple structures of  $\text{Se}_N$  clusters change when only a few metal atoms are added. The addition of sodium atoms to selenium clusters is carried out in the reactor of a dual laser vaporization source. Products are analyzed by mass spectrometry, followed by deposition in an inert gas matrix and investigation by Raman spectroscopy. The equilibrium geometries of the experimentally found  $\text{Na}_M\text{Se}_N$  clusters are provided by quantum chemical calculations. The vibrational spectra are calculated as well and compared to those obtained by Raman spectroscopy.

The intensity of a Raman signal depends on the magnitude of the change in the clusters electric polarizability due to a vibration [22]. Here, one can expect strong effects due to electronic charge transfer from the Na to the Se. This charge transfer is expected to depend sensitively on the distance between Na and Se atoms, i.e., on the Na–Se bond length, as can be easily shown by a comparison of atomic and ionic polarizabilities. An isolated Na atom has a polarizability of  $24 \text{ \AA}^3$  and a Se atom of  $3.8 \text{ \AA}^3$ . In the ionic  $\text{Na}_2\text{Se}$  bulk, however, for the  $\text{Na}^+$  ion one finds a polarizability of only  $0.18 \text{ \AA}^3$  and for the  $\text{Se}^{2-}$  ion  $10.5 \text{ \AA}^3$  [23]. This means that during the formation of the ionic bond, the polarizability of the Na is reduced because it loses essentially its unpaired electron while the polarizability of the Se increases. The increase through anion formation, however, is much too small to compensate the decrease due to cation formation. If a pair of initially separated atoms are approaching each other, this charge transfer leads to a significant reduction in the polarizability of the pair with decreasing distance. Therefore, one can expect a strong dependence of the cluster polarizability on changes of the Na–Se bond lengths, that should reflect itself in intense Raman bands for vibrations where the Na–Se bonds are involved.

## 2. Experimental

Sodium/selenium clusters are generated in a dual laser vaporization source by separate vaporization from a Se and a Na rod into pulsed helium gas flows (Fig. 1). The vapors are mixed together in the reaction zone, where  $\text{Na}_M\text{Se}_N$  clusters are formed and expanded through a nozzle into a first vacuum chamber forming a cluster beam. The beam passes through a differential pressure stage in a second chamber. There clusters are photoionized using a VUV flash lamp (spectral range 120–1100 nm) and the cluster distribution is analyzed in a home-built Wiley/McLaren time-of-flight mass spectrometer (TOF-MS) [24]. In a third vacuum chamber the cluster deposition rate is determined with a quartz microbalance (Intellemetrics) which can be moved into and out of the cluster beam. The deposition rate is 5–200 pm/s on a substrate area of  $30 \text{ mm}^2$  at a distance of 1.8 m to the cluster source. Last, the clusters enter a UHV chamber where they are deposited into a growing argon or nitrogen matrix on a gold plated sapphire substrate, cooled by a continuous flow liquid He cryostat to  $T = 15 \pm 1 \text{ K}$ . Optical interferometry is used to calibrate the deposition rate of the matrix. High dilution of the clusters (1:1000) prevents them from interacting. The typical matrix thickness is 12 nm. Due to the low kinetic energy of the clusters which is determined by means of a retarding electric potential at the TOF-MS to be less than 10 eV, there should be no cluster fragmentation during deposition [25]. The support can be turned towards the optics of a Fourier transform Raman spectrometer (Bruker RFS100/S with modified optics and liq.  $\text{N}_2$  cooled Ge detector). The clusters frozen in the matrix are irradiated by Nd:YAG laser light (1064 nm, 10–110 mW) and a Raman spectrum is recorded.

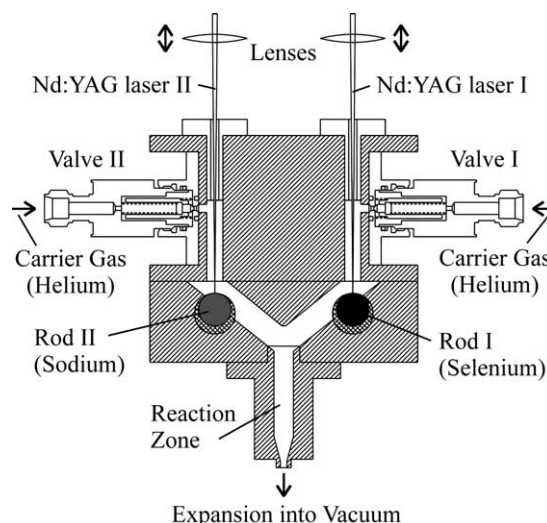


Fig. 1. Dual laser vaporization source.

### 3. Computational methods

For the calculation of the equilibrium geometries and the harmonic vibrational wavenumbers of  $\text{Na}_M\text{Se}_N$  clusters density functional theory (B3LYP functional) as implemented in the GAUSSIAN 98 program package [26] is used. Starting geometries are well-known selenium ring and chain structures [10,11] with sodium atoms added at different positions. As a first step the optimization is performed with a 6-31G\* basis set, followed by reoptimization with a 6-311G\* basis set. Additionally, Mulliken population analysis is used to gain some information about the partial charge distribution.

### 4. Results and discussion

In a first experiment pure selenium clusters are generated by vaporization of selenium only. The conditions in the source can be tuned easily to a state where small selenium clusters with 5–8 atoms strongly dominate the cluster beam as observed by the TOF-MS (similar to Fig. 3, pure  $\text{Se}_N$  only). The typical Raman signal of this cluster mixture deposited in a nitrogen matrix is shown in Fig. 2a. One observes a Raman band in the range of 235–280  $\text{cm}^{-1}$ . The use of argon as matrix material does not change the signal significantly. This is in agreement with investigations on other semiconductor clusters [27] as well as the well-known fact that vibrational wavenumbers of clusters in an inert matrix are shifted usually less than 1% against the gas phase values [22,28]. The resolution of the spectrometer is about 4  $\text{cm}^{-1}$  and hence much smaller than the width of the observed band. Vibrations of the smallest clusters  $\text{Se}_2$ ,  $\text{Se}_3$ , and  $\text{Se}_4$ , which were determined in previous work to be in the range of 311–385  $\text{cm}^{-1}$  [23,29,30] are not observed in our experiments. This is consistent with the low abundances of these clusters in the mass spectra.

The observed Raman band can be explained by a superposition of vibrations of  $\text{Se}_N$  clusters with  $N = 5-8$ .

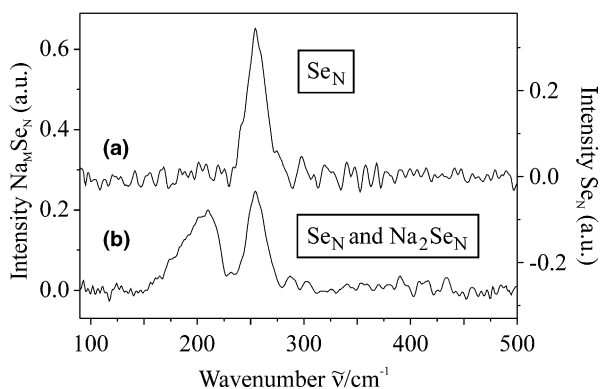


Fig. 2. Raman spectrum of selenium clusters (a) and sodium/selenium clusters (b) in a nitrogen matrix ( $T = 15$  K, laser power 110 mW).

Calculations of the Raman spectra for isolated ring-like  $\text{Se}_N$  of these sizes with ab initio methods give strongest lines between 239 and 287  $\text{cm}^{-1}$  [10], well matching the experimentally observed Raman band. Other investigations for ring-like selenium clusters in zeolites or microporous silicate show also wavenumbers in this region [31,32].

On the other hand, wavenumbers in the same range are also attributed to vibrations of small selenium chains [31,33]. Hence, Raman spectra seem to be not a possible way for a clear distinction between isolated selenium rings and chains. However, since for gas phase  $\text{Se}_N$ , as mentioned in the introduction, all experiments and calculations support ring structures, they are plausible for our experiments as well.

In a second step both Na and Se are vaporized in the cluster source producing mixed  $\text{Na}_M\text{Se}_N$  clusters. The amount of sodium is kept low to dope the  $\text{Se}_N$  clusters with a few Na atoms only. Beside pure  $\text{Se}_N$ , one finds predominantly product clusters with two Na atoms,  $\text{Na}_2\text{Se}_N$  ( $N = 3-8$ , Fig. 3). The mixture of  $\text{Se}_N$  and  $\text{Na}_2\text{Se}_N$  is deposited in the matrix and the corresponding Raman spectrum is shown in Fig. 2b. Again a band at 235–280  $\text{cm}^{-1}$  is observed which is identical to that of pure selenium clusters. Furthermore, there is a new broad signal between 165 and 225  $\text{cm}^{-1}$  with a maximum at 210  $\text{cm}^{-1}$ . This signal can be attributed to the mixed  $\text{Na}_2\text{Se}_N$  clusters, since it does not occur in the spectrum of the pure selenium clusters nor in the spectrum when pure NaN clusters are deposited. The latter was also measured and shows one band which does not overlap with the signal of the  $\text{Na}_2\text{Se}_N$ . Moreover, we expect strong Raman signals for vibrations of Na–Se bonds due to their large polarizability changes during the oscillation as explained in the introduction. Hence, we attribute the signal at 210  $\text{cm}^{-1}$  to Na–Se vibrations in the  $\text{Na}_2\text{Se}_N$  clusters, whereas we expect the Se–Se vibrations to contribute much less to the spectrum. Even if the Se–Se vibrations would give an observable signal, it would probably vanish under the signal of the pure

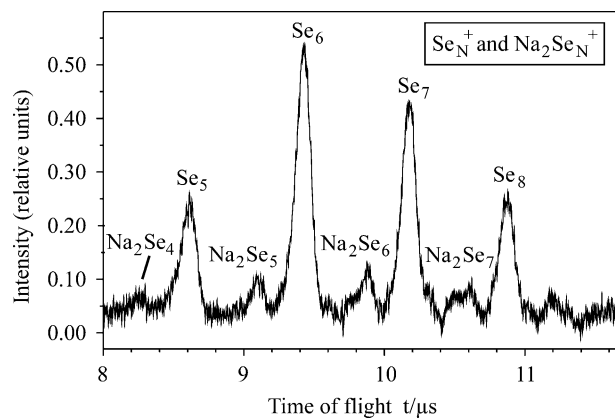


Fig. 3. Mass spectrum of  $\text{Se}_N$  and  $\text{Na}_M\text{Se}_N$  clusters after ionization by a flash lamp.

Se<sub>N</sub> clusters which are much stronger present than the Na<sub>2</sub>Se<sub>N</sub> (cf. Fig. 3).

In order to support this assignment, we compare the experimental results to density functional calculations for the Na<sub>2</sub>Se<sub>N</sub> clusters ( $N = 4-6$ ) that are prominent mixed species in the mass spectra. The optimized geometries with the lowest energies are shown in Fig. 4. The two Na atoms are located in the front, above and below the selenium plane. Other possible isomers have at least 60 kJ/mol higher energies. One can interpret the calculated geometries in terms of two single Na atoms opening a selenium ring to form a chain with the Na at its ends. This would explain the absence of clusters with one Na atom, because a Se<sub>N</sub> chain with only one end saturated by a Na has an unpaired electron at the other end, which would be quickly saturated by picking up a second Na in the cluster source. The known bulk compounds, Na<sub>2</sub>Se<sub>N</sub> ( $N = 2, 3, 4, 6$ ) have also just two Na atoms per formula unit. As already mentioned, they are understood as polyanionic structures (Na<sup>+</sup>)<sub>2</sub>(Se<sub>N</sub>)<sup>2-</sup> with ionic Na–Se and covalent Se–Se bonds leading to selenium chains in the bulk crystal structure with a sodium atom at each chain end.

However, the selenium chains in the bulk are stretched [16,17], whereas in the clusters they remain strongly bent to a horseshoe-like shape. This indicates an attractive interaction between the two Na which come very close together. The Na–Na distances in Na<sub>2</sub>Se<sub>4</sub> (3.57 Å) and Na<sub>2</sub>Se<sub>6</sub> (3.40 Å) are similar to that of a free Na<sub>2</sub><sup>+</sup> ion (3.54 Å [34]). The Mulliken population analysis gives a positive charge of 0.4–0.5e for each sodium atom in Na<sub>2</sub>Se<sub>4</sub> and Na<sub>2</sub>Se<sub>6</sub>, which fits to the model that a Na<sub>2</sub><sup>+</sup> ion is inserted into a selenium ring. The corresponding negative charge

is located at the two end atoms of the selenium chain (Table 1). For the Na<sub>2</sub>Se<sub>5</sub> a stronger charge transfer is observed, one obtains 0.4e for one Na and 1.0e for the other. Because of the odd number of Se atoms in the chain one Na is much closer to a chain end as shown in Fig. 4. This leads to a stronger charge transfer to the semiconductor and weakens the Na–Na bond as reflected in a longer Na–Na distance (3.87 Å in Na<sub>2</sub>Se<sub>5</sub>). All findings support the idea of polyanionic selenium chains in the isolated Na<sub>2</sub>Se<sub>N</sub> clusters just as in the bulk compound. The amount of charge transfer in the Na–Se bonds, however, varies. The overall bonding situation is well described as something between the border cases (Na<sub>2</sub>)<sup>+</sup>(Se<sub>N</sub>)<sup>-</sup> and (Na<sup>+</sup>)<sub>2</sub>(Se<sub>N</sub>)<sup>2-</sup>. These findings demonstrate that the interaction between the donor atoms can become crucial for the understanding of doped nanostructures, whereas it is essentially negligible for the understanding of doped bulk structures.

The vibrational wavenumbers of the Na<sub>2</sub>Se<sub>N</sub> clusters ( $N = 4-6$ ) are calculated to be in the range of 20–300 cm<sup>-1</sup>. The calculation of Raman intensities, however, has a relatively high uncertainty due to the elaborate calculation of the polarizability tensor of the molecule with respect to normal coordinates [35]. We have, therefore, preferred to make a much more simple but likewise significant correlation with the experimental spectrum by separating the cluster vibrations in those with mainly Na–Se and those with mainly Se–Se bonds oscillating. For this purpose the vibrational amplitudes of the different bonds in a cluster for the different cluster vibrations are calculated from the coordinates  $\vec{r}$  of the atoms in their equilibrium position and their oscillation  $\Delta\vec{r}$  during a vibration by a simple vector subtraction.

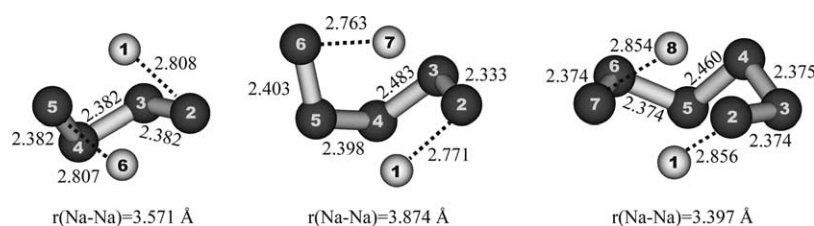


Fig. 4. Calculated equilibrium geometries of Na<sub>2</sub>Se<sub>4</sub>, Na<sub>2</sub>Se<sub>5</sub> and Na<sub>2</sub>Se<sub>6</sub> (all bond lengths in Å).

Table 1

Calculated atomic charges according to Mulliken (in elementary charges), atom numbers according to Fig. 4

Na <sub>2</sub> Se <sub>4</sub>		Na <sub>2</sub> Se <sub>5</sub>		Na <sub>2</sub> Se <sub>6</sub>	
Atom	Charge	Atom	Charge	Atom	Charge
1 (Na)	0.470	1 (Na)	0.988	1 (Na)	0.398
2 (Se)	-0.445	2 (Se)	-0.556	2 (Se)	-0.350
3 (Se)	-0.025	3 (Se)	-0.096	3 (Se)	0.028
4 (Se)	-0.025	4 (Se)	-0.134	4 (Se)	-0.079
5 (Se)	-0.445	5 (Se)	-0.030	5 (Se)	-0.076
6 (Na)	0.470	6 (Se)	-0.588	6 (Se)	0.030
		7 (Na)	0.416	7 (Se)	-0.348
				8 (Na)	0.397

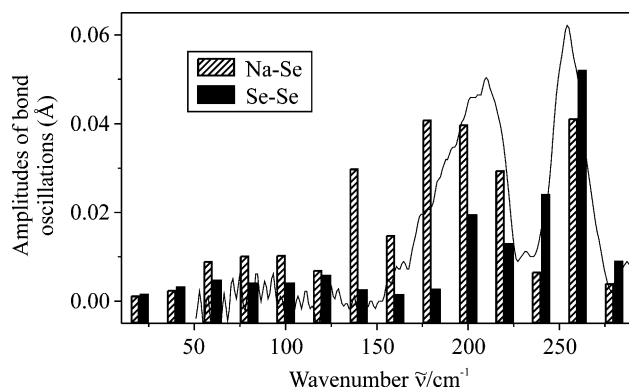


Fig. 5. Averaged vibrational amplitudes for all Na–Se and all Se–Se bonds in  $\text{Na}_2\text{Se}_N$  ( $N = 4-6$ ) as function of the calculated vibrational wavenumbers ( $x$ -axis is divided in intervals of  $20 \text{ cm}^{-1}$ ). The experimental Raman spectrum is shown in the background.

The parameters  $\bar{r}$  and  $\Delta\bar{r}$  are provided by the quantum chemical calculations. The average of the vibrational amplitudes for all Se–Se bonds on the one hand and for all Na–Se bonds on the other hand for all clusters  $\text{Na}_2\text{Se}_4$ ,  $\text{Na}_2\text{Se}_5$ ,  $\text{Na}_2\text{Se}_6$  are shown in Fig. 5 as a function of the vibrational wavenumber. In the background the experimental Raman spectrum is plotted (cf. Fig. 2). Obviously, the experimental Raman signal at lower wavenumbers corresponds to vibrations where mainly Na–Se bonds oscillate and the signal at higher wavenumbers corresponds to vibrations where mainly Se–Se bonds oscillate. This supports the conclusion that the Raman signal between  $165$  and  $225 \text{ cm}^{-1}$  is due to the vibration of the Na atoms against the semiconductor chain.

In summary, the addition of only a few sodium atoms to small selenium clusters leads to considerable structural changes from selenium rings to polyanionic selenium chains. Bonding interactions between the sodium atoms significantly influence the structures of the emerging sodium/selenium clusters. The dynamic charge transfer during Na–Se bond elongation leads to high Raman intensities for vibrations involving these bonds.

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