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Formation of the Magic Cluster Na_8 in Noble Gas Matrixes†

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The sodium molecules Na_2, Na_4, and Na_8 have been isolated in argon matrixes at 15 K and characterized for the first time by Raman spectroscopy. The vibrational frequencies are compared with density functional (DFT) calculations. The Na_4 cluster possesses a rhombic structure (D_{2h}) with calculated d(Na–Na) = 307.2 and 347.4 pm, respectively. For octasodium, a hypertetrahedral structure (T_d) is predicted in which each side of an inner tetrahedron with d(Na–Na) = 331.5 pm is capped by sodium atoms with a distance of d(Na–Na) = 348.7 pm. The green octasodium cluster is the first example of a matrix-isolated magic number cluster. Its formation from blue tetrasodium is discussed on the basis of the observed sequence of cluster growth.

Introduction

The observation of several unique properties of clusters attracted the interest of scientists during the last 2 decades.[2–4] In particular, the appearance of their surprising size-dependent properties gave rise to the development of theoretical models incorporating these features. The first description of a self-consistent jellium model for clusters using a semiclassical density-variational method was reported by Cini in 1975.[5] This was followed by a parameter-free model that was introduced independently by Ekardt and Beck in 1984.[6–9] The jellium model describes the cluster as a spherical positive background containing an appropriate number of electrons for neutralization. This dramatic simplification ignoring the ionic structure was an object of controversy. Nevertheless, the jellium model is more justified than one might think at first sight, since the sum of the individual effective core potentials forming the positive background is indeed a rather smooth function.[10] Another point is the assumption of sufficiently delocalized electrons, which limits the model to the first and second group and to some extent to the 11th group of elements. Despite these limitations, the jellium model is justified, since appropriate calculations can account qualitatively, and in some cases quantitatively, for many experimental observations, especially the occurrence of magic number clusters in metal cluster beams.[11]

The term *magic number* came up before the spherical jellium model was introduced, following the most obvious way of modeling the cluster geometry by dissection of the crystalline bulk material into small pieces. According to this simple procedure, one can obtain for certain atom numbers polyhedra that are almost spherical in shape and have surface planes with a high incidence of close packing.[11–13] Such clusters with 13, 19, 43, 55, ... atoms were assumed to display higher stability and therefore called *magic clusters*, in analogy to the nuclear phenomenon. The first observation of magic metal clusters in cluster beams was reported in 1984 by Knight and co-workers.[14,15] The appearance of the magic

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† Raman matrix isolation spectroscopy, Part 10. Part 9: Raman spectroscopic investigation of matrix isolated rubidium and cesium molecules: Rb_2, Rb_3, Cs_2, and Cs_3. (See ref 1).

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numbers 2, 8, 20, 40, 58, and 92 for sodium and potassium clusters was explained by closed electron shells in the jellium model. These experiments, as well as quantum mechanical calculations,[16] indicated that the simple picture of modeling the cluster geometry in analogy to the bulk cannot be applied to small alkali metal clusters.

Despite considerable recent efforts, the structures of small atomic metal clusters remain largely unexplored.[17] The sodium clusters are one of the main subjects for cluster beam experiments and theoretical work, but the characterization is restricted to a few spectroscopic methods, and these are difficult or impossible to correlate with the cluster geometries. Several attempts have been made to employ the matrix isolation technique for studies on sodium clusters, but the spectroscopic methods were limited to absorption spectra. These allow the detection of atomic and diatomic species, but the assignment of the broad absorption bands to larger clusters remained speculative, as described by the authors.[18−20] Moreover, this method do not yield any information about the cluster geometries.

In this paper we report the isolation of sodium clusters in noble gas matrixes and their Raman spectroscopic characterization, which provide a reliable way to determine the cluster geometry from quantum mechanical calculations.

Experimental Section

Apparatus and Materials. The apparatus for multichannel Raman matrix isolation spectroscopy and the general procedure have been described elsewhere.[21] The spectra were recorded with an Instruments SA T64000 Raman spectrometer equipped with a Spectra Physics Ar$^+$ laser. Sodium was purifed by vacuum distillation. Argon was dried by passing it through a column filled with P_4O_{10}. Krypton and xenon were used without further purification.

Sodium vapor was prepared using a Knudsen cell heated with an external heater jacket to 120 °C. The metal vapor was cocondensed with argon (estimated dilution 1:1000) with a continuous flow rate (10−50 cm^3/h) on the copper cold tip (15 K) of the cryostat. The pressure in the area between the Knudsen cell and the cold surface was in the range of 10^{-2} Pa. The average thickness of the formed layers was 100 μm. Annealing was carried out by frequently warming the layer to 40 K over a period of 2 min and cooling to 15 K.

Computational Methods. The appropriate theoretical method for the calculation of alkali metal clusters was chosen by us after comparison of different methods for the alkali metal dimers.[22] For sodium, the SVWN5[23] method along with the 6-31G* basis set employing the Gaussian 94 program package was used.[24] The calculated vibrational frequencies are not scaled by any empirical factor, as this was not found to be needed.

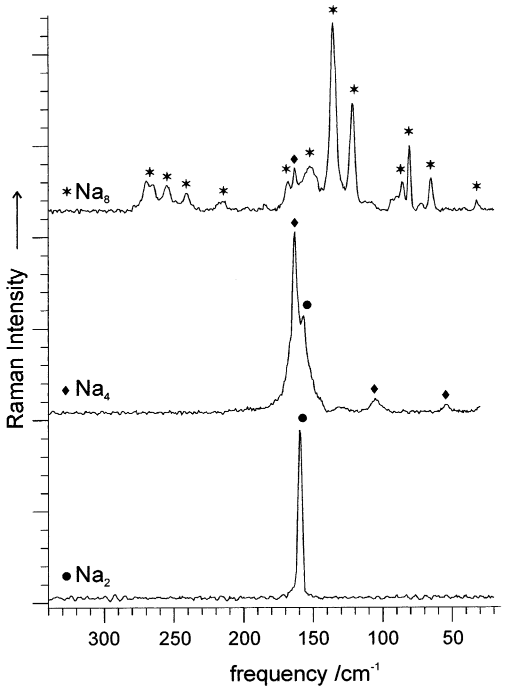

Figure 1. Raman matrix spectra of sodium in argon at 15 K at different stages of cluster formation (experimental conditions: 100 μm layer; laser wavelength 514.5 nm, laser power 125 mW, resolution 1.2 cm^{-1}).

Results and Discussion

Matrix Isolation and Raman Spectra. The experiments were carried out with an apparatus consisting of a regular Knudsen cell connected to our Raman-matrix-isolation setup.[21] The metal sample was evaporated at ca. 120 °C and codeposited with argon on a cold surface, keeping the argon pressure below 10^{-2} Pa. After 1 h of deposition a purple layer was formed. During warm-up cycles of the matrix layer, a diffusion-controlled clustering process occurred, which was monitored by Raman spectroscopy. Three relatively stable clusters were observed in the rare gas matrixes.

At first we observed a single line in the Raman spectrum (Figure 1) of the purple matrix at 160.0 cm^{-1}, which was assigned to diatomic sodium. The fundamental frequency is in excellent agreement with the value obtained from gas-phase experiments (159.1 cm^{-1})[25] as well as density functional calculations with the SVWN5[23] method (159.7 cm^{-1}), which was found to produce data for alkali clusters, in fair agreement with experimental measurements.[22] The formation of disodium can be achieved during matrix deposition by keeping the pressure at 10^{-2} Pa or below to prevent further clustering in the gas phase. It should be noted that such mixtures of disodium and rare gases can be passed through glass tubes of 50 cm length without any observable formation of a sodium mirror on the walls, when the pressure is kept below 10^{-1} Pa. Increasing the pressure to 1 Pa by a higher flow rate of the diluting argon leads to the formation of sodium mirrors within a few minutes.

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Table 1. Experimental and Calculated Raman Frequencies (cm^{-1}) and Vibration Modes for Na_2, Na_4, and Na_8

species	DFT^a	exptl	assignment		species	DFT^a	exptl	assignment	
Na_2	159.7	160.0	ν	Σ_g	Na_8	133.6	134.7	ν_1	A_1
Na_4	49.2	54.2	ν_2	A_g		143.8		ν_6	F_2
	103.4	105.4	ν_3	B_{3g}			152.9	$\nu_2 + \nu_8$	F_2
	163.1	164.0	ν_1	A_g			159.0	$2\nu_7$	F_2
Na_8	17.9		ν_4	E			168.1	$2\nu_2$	A_1
		34.0	$2\nu_4$	E			212.8	$\nu_1 + \nu_7$	A_1
	66.8	66.0	ν_8	F_2			240.5	$2\nu_3$	A_1
	84.5	81.3	ν_7	F_2			255.0	$\nu_1 + \nu_3$	E
	89.2	86.2	ν_2	A_1			264.4	$2\nu_1$	A_1
	120.0	121.4	ν_3	E					

[a] Density functional (DFT) calculations with the Slater's exchange and the local spin density correlation functional of Vosko, Wilk, and Nusair (SVWN5) and the basis set 6-31G*.[23] Frequencies are not scaled.

During further clustering processes of matrix layers containing disodium we observed a rapid decrease of the 160 cm^{-1} line along with a change in color from purple to blue and the simultaneous appearance of three new lines, which are in satisfactory agreement with DFT-calculated values for tetraatomic sodium (Table 1). Furthermore, the relative intensities of these lines are similar to the recently matrix-isolated tetrapotassium cluster.[22] The absence of trisodium in the Raman spectra during this clustering step is surprising. Matrixes of disodium should contain a considerable amount of remaining single atoms, which would react with disodium to form trisodium. Similar experiments on potassium have shown that tripotassium is formed during such reactions, but only as an intermediate species that reacts further to form the tetraatomic species. The existence of trisodium molecules was already demonstrated by Lindsay et al. on the basis of electron spin resonance (ESR) spectra of matrix-isolated sodium vapor.[26] Although this method is very sensitive, it is restricted to species with unpaired electrons; thus, estimation of the relative concentrations of trisodium and diamagnetic species is difficult. Trisodium may have been a relatively minor constituent in the ESR study. During a series of matrix-isolation experiments, we were not able to observe trisodium by Raman spectroscopy in considerable amounts. These observations support the assumption that trisodium is relatively unstable compared to di- and tetrasodium and appears therefore only in low concentrations.

During annealing experiments on matrix-isolated tetrasodium or mixtures of tetrasodium and disodium, we found a third cluster species, which is enormously stable. The Raman lines of tetrasodium (and disodium, if present) disappeared almost spontaneously upon further warm-up cycles, and the color of the matrix layer changed from blue to green. The remaining Raman spectrum, which we assigned to octasodium, exhibits a complex line structure shown in Figure 1. Further annealing does not change the spectral features, but rougher conditions cause the formation of silvery metallic sodium due to segregation of the sample. To ensure that the spectrum belongs to a single cluster species, we carried out a series of experiments varying the experimental parameters (evaporation temperature, deposition rate, rare gas), but the annealed green matrix layer always displayed the same spectroscopic features. Further, using harsher conditions, such as rapid deposition, high rare gas pressure (10^{-1} Pa), or high substrate/matrix ratios, the green matrix layer was formed during matrix deposition.

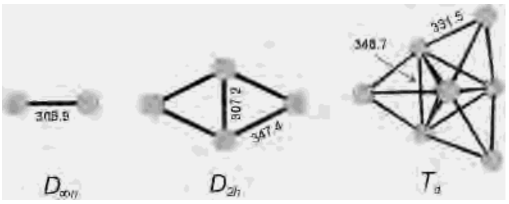

Figure 2. Symmetry and bond lengths of Na_2, Na_4, and Na_8.

The observed fundamental frequencies of the green species are summarized in Table 1. DFT calculations, which are discussed later, give a hypertetrahedral (T_d) structure for octasodium. Consequently, 18 fundamentals, which due to the high-symmetry degenerate to eight modes ($2A_1 + 2E + F_1 + 3F_2$), are expected. Seven modes (species A_1, E, and F_2) are Raman active, whereas only species F_2 is visible in the infrared and species F_1 is inactive in both the Raman and infrared spectra. The assignments for the observed frequencies of Na_8 were made by comparison with the DFT calculated frequencies. The seven Raman-active vibrations, of which six are observed in the spectrum, occur in the region below 150 cm^{-1}. The missing ν_6 vibration is probably overlaid by the nearby intense and broad ν_1 mode, which is the breathing mode of the cluster. There is excellent agreement between DFT-calculated and observed frequencies; only in case of the ν_2 and ν_7 mode are somewhat higher deviations of 3 cm^{-1} observed. Furthermore, the mode expected to be the strongest, ν_1, the totally symmetric stretching mode, is the strongest observed Raman line. Additional support for the assignment is given by the spectral region above 150 cm^{-1}, which displays overtones and combination modes. The appearance of these modes is in agreement with the spectroscopic selection rules for a hypertetrahedral Na_8 cluster of symmetry T_d.

DFT Calculations. The DFT-calculated (SVWN5[24] method with 6-31G* basis set) frequencies for Na_2, Na_4, and Na_8 are given in Table 1, where they are compared with observed frequencies of the matrix-isolated species. We find excellent agreement for all vibrational modes.

The DFT-calculated geometries for Na_2, Na_4, and Na_8 are presented in Figure 2. For the Na_2 molecule we find satisfactory agreement between the calculated (306.9 pm)

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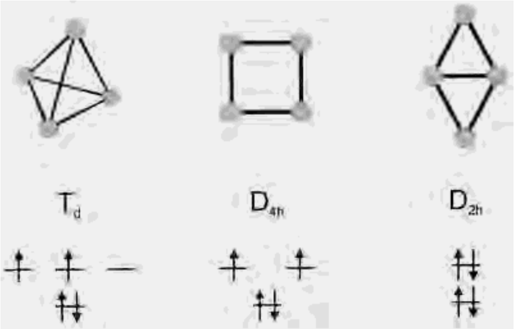
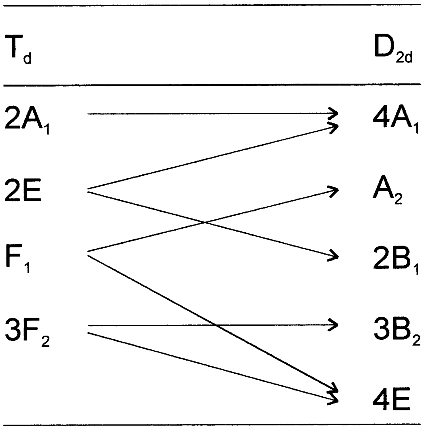


Figure 3. Configurations of tetraatomic alkali metal clusters and corresponding bonding molecular orbital occupation.

and measured (307.88 pm)[25] bond length, as deduced from laser-induced fluorescence spectra. For tetrasodium, the minimal energy is found for a rhombic planar arrangement of D_{2h} symmetry with one Na−Na bond (307.2 pm) slightly longer than that calculated for disodium and four much longer Na−Na bonds (347.4 pm). The bonding situation in Na_4 is similar to that found recently for matrix-isolated K_4.[22] The tetrapotassium cluster with symmetry D_{2h} possesses one short K−K bond of 391.8 pm, slightly longer than in K_2 (386.9 pm), and four considerably longer bonds with $d(\mathrm{K{-}K}) = 437.3$ pm. The rhombic shape of tetrasodium agrees with previous predictions made on the basis of quantum mechanical calculations.[16] One way to rationalize why this structure is favored instead of a higher symmetry square or a tetrahedron can be found by comparing the occupation of the corresponding molecular orbitals shown in Figure 3. Both the tetrahedron and the square have two unpaired electrons. This unfavorable electronic situation is subject to Jahn−Teller distortion into the rhombic structure, with electron pairing to form a singlet ground state. It is interesting to note that the same molecule orbital scheme can be used to explain that tetraatomic alkaline earth clusters should have a tetrahedral structure, since the four orbitals are then fully occupied. This example illustrates that the structures of small metal clusters result from the particular electronic situation rather than the previously postulated tendency to form close-packed structures, at least for the main group metals.

Octasodium has been an object of various theoretical investigations since it was observed in 1984 by mass spectroscopy in cluster beams as a magic cluster.[14,15] Three symmetries were considered for octasodium: hypertetrahedron (each side of an tetrahedron is capped by an atom, T_d), square antiprism (D_{4d}), and a distorted tetrahedron (D_{2d}). The analysis of the absorption spectrum of Na_8 in the gas phase along with theoretical calculations could exclude the D_{4d} structure for Na_8.[27] The remaining question, whether Na_8 has a $\mathrm{T_d}$ or D_{2d} symmetry, could not be answered on the basis of the experimental data. Theoretical calculations, however, indicated that the hypertetrahedron is the most stable conformation. The minimal energy for the octasodium cluster was found by us for a hypertetrahedral structure with Na−Na bonds of 348.7 pm for the inner tetrahedron and Na−Na distances of 331.5 pm to the capping sodium atoms. The T_d structure of octasodium is confirmed by the Raman spectrum discussed above. A less symmetrical D_{2d} structure would display a much more complex Raman spectrum. The alternative D_{2d} structure can be described as a distortion of a hypertetrahedron, which lifts the degeneracies of species E, F_1, and F_2 (Scheme 1). Consequently, one would expect 13 Raman-active modes ($4A_1 + 2B_1 + 3B_2 + 4E$) instead of seven.

Scheme 1. Symmetry Distortion of Octasodium ($T_d \rightarrow D_{2h}$)



Cluster Growth and Formation of Na_8. The aim of this study was to isolate small sodium clusters at the very first steps of the transition from atoms to bulk material. An unexpected result is that the cluster growth that occurs upon matrix annealing does not proceed randomly, producing a complex cluster population as it was presumed but not spectroscopically demonstrated in previous investigations.[28]

Cluster growth proceeds differently in cluster beam experiments and depends strongly on the technique.[29] Knudsen-cell effusion probes the equilibrium vapor composition,[30] but clusters larger than tetraatomic cannot easily be studied by this technique.[31] High yields of larger molecules are produced by supersonic expansion of neat and seeded metal-vapor beams. The size distribution depends strongly on experimental conditions, such as orifice diameter and shape, auxiliary seed-gases, and stagnation pressure. It should be noted that such systems are not in thermodynamical equilibrium; thus, inferences made from such studies are dangerous, especially when assigning stability to clusters based on their abundance in the size distribution. Therefore, the observation of magic clusters by Knight et al. was an object of controversy. Nevertheless, some clues exist for the assumption that the observed distributions are instantaneous pictures of a process that preserves cluster sizes of predominant stability.[29] This is exemplified by the discovery of buckminsterfullerene.[32]

Although the stability of clusters in cluster beams can be assigned to some extent, nucleation is more difficult to

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comprehend, and derivation of the cluster growth sequences is a difficult task. By comparing the cluster growth sequence of our matrix experiments with Knudsen-cell effusion, the similarity concerning the odd−even alternation in cluster size is evident and clearly pronounced in the matrix. Already the smallest odd cluster (Na_3) is not formed in considerable amounts. It was previously observed for potassium clusters in matrixes that K_3 is formed as an intermediate from K/K_2 mixtures and that it reacts completely under conditions favorable for formation of K_4. A similar process is likely for sodium, but it probably proceeds more rapidly. The removal of odd clusters at the very beginning of nucleation together with an absence of their formation by dissociation processes of even clusters would explain the odd−even alternation for both the matrix and cluster beam experiments.

The outstanding observation of this study is the formation of octasodium. In previous experiments on the heavier alkali metals, a tetraatomic species (K_4) was observed as the largest cluster in a matrix environment. This is probably due to the lower mobility of the potassium clusters compared with the corresponding sodium species. Alternatively, this may be due to the fact that the bond strength is considerably higher for sodium molecules, at least as judged by the harmonic force constants [$f(K_2) = 0.093$ N cm^{-1}, $f(Na_2) = 0.173$ N cm^{-1}]. Summarizing our experimental observation on the Na_8 cluster, it seems that its formation proceeds via Na_4 molecules. However, it was not possible to stop the clustering of Na_2 at a point where the Raman spectra displayed pure Na_4, which then would form the Na_8 species. The absence of a Na_6 cluster implies this assumption. A possible mechanism for the formation of the highly symmetrical octasodium from two approaching Na_4 clusters is shown in Figure 4. At the last step only a butterfly motion is required to form the spherical magic cluster.

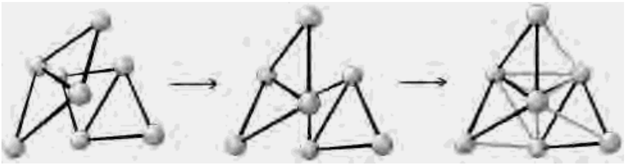

Figure 4. Formation of the magic number cluster Na_8 from Na_4 clusters.

Conclusion

The sodium molecules Na_2, Na_4, and Na_8 have been formed and characterized in rare gas matrixes by Raman spectroscopy. This has shown that the formation of clusters in matrixes does not proceed in a random manner. The Raman spectroscopic data together with DFT calculations confirm a rhombic structure (D_{2h}) for Na_4 and a hypertetrahedral symmetry (T_d) for the Na_8 molecule. The octasodium cluster is the first magic number cluster that has been previously observed in cluster beams to be isolated in a rare gas matrix in nearly pure form. It possesses an exceptional stability in rare gas matrixes. Though impossible to prepare Na_8 in pure condensed phase, it will be interesting to study its properties at higher temperatures by embedding it in more stable matrix environments.

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