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Small Magnesium Clusters: Between van der Waals and Valence Bonds

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The magnesium molecules Mg_2, Mg_3, Mg_4, and Mg_5 have been isolated in rare-gas matrixes at 8 K and characterized for the first time by Raman spectroscopy. The vibrational frequencies were compared with those obtained by density functional theory calculations. The fundamental frequency of the dimer was observed at 97 cm^{-1} (Ar matrix), and a bond length of d(Mg—Mg) = 340.8 pm was calculated. The Mg_3 cluster possesses a triangular structure (D_{3h}) with calculated d(Mg—Mg) = 317.8 pm. For tetramagnesium, a tetrahedral structure (T_d) with d(Mg—Mg) = 301.3 pm is predicted. The Mg_5 molecule possesses a trigonal-bipyramidal structure (D_{3h}) with d(Mg—Mg) = 293.1 and 322.5 pm, respectively. The red tetramagnesium cluster is an example of a matrix-isolated magic number cluster.

Introduction

In comparison to the amount of research on alkali metal clusters, studies of the alkaline-earth metal clusters are rare. This may originate from the fact that the generation of alkaline-earth metal clusters is more difficult. Valence-bond theory predicts a single bond for an alkali metal dimer, whereas for an alkaline-earth metal dimer, a bond order of zero is predicted. Therefore, the alkaline-earth metal dimers are expected to be weakly bonded van der Waals clusters. Consequently, another problem is the low concentration of such weakly bonded dimers and larger clusters in the gas phase. Thus, an attractive alternative is the matrix isolation technique, which allows accumulation of the desired species.

The first matrix isolation study on alkaline-earth metal clusters was published in 1971 by Brewer and Wang.[1] The Mg_2 molecule was isolated in an argon matrix at 20 K and characterized by UV spectroscopy. In 1976, Knight and Ebener found additional absorption bands using a similar technique.[2] The additional bands were assumed to originate from Mg_3 and larger clusters. Both authors stated that no further cluster growth was observed upon annealing of the matrixes. This is surprising because annealing cycles usually enable atoms and small clusters to diffuse in the matrix host and subsequently form larger clusters. Later, the absorption bands of Mg_2 were found to vary significantly in different matrix gases. This was explained by perturbation of the $A^1\Sigma_u^+$ ground state of the Mg_2 dimer by matrix effects rather than the presence of higher aggregates.[3,4] These findings seemed to be confirmed in 1978 by Givan and Loewenschuss, who reported only the Raman spectrum of Mg_2,[5] but the results were somewhat contrary to later magnetic circular dichroism (MCD) experiments, which indicated higher clusters of magnesium, particularly Mg_3 and Mg_4.[6]

Similar contradictions on the stability of magnesium clusters are also provided by theoretical studies. Many calculations anticipate the existence of several more stable

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clusters than the weakly bonded van der Waals dimer.[7-28] A recent theoretical study disputes the existence of a Mg_4 molecule and predicts its dissociation into two dimers.[28] The controversial theoretical studies originate from the fact that it is difficult to find an appropriate method to describe the weakly bonded cluster. Because of the leakage of experimental data, the discrepancy in the theoretical predictions is unsolved.

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

Experimental Section

Matrix Isolation. The apparatus for multichannel Raman matrix isolation spectroscopy and the general procedure have been described elsewhere.[29] The spectra were recorded with an Instruments SA T64000 Raman spectrometer equipped with a Spectra Physics Ar^+ and Kr^+ laser. Magnesium (Merck, 99,99%), argon (99.9999%), krypton (99.998%), and xenon (99.998%) were used without further purification.

Magnesium vapor was prepared using a stainless steel Knudsen cell with two effusion holes heated with an external heater jacket to ca. 550 °C. One of the effusion holes was directed to a water-cooled tip of a quartz balance (Inficon XTM) to maintain a persistent condensation rate and determine the amount of evaporated metal. The metal vapor was co-condensed with the rare gas (estimated dilution 1:800) at a continuous flow rate ($0.5-2.0$ mmol h^{-1}) on the copper cold tip (8 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 cycles were carried out by frequently warming the layer to 40 K (argon matrixes) and 55 K (krypton and xenon matrixes), respectively, over a period of $5-30$ min and then cooling to 8 K. These cycles were repeated up to 10 times for each matrix.

Computational Methods. When choosing the appropriate theoretical method for the calculation of Mg_4 clusters, we compared the results of different theoretical calculations with the experimental frequencies. The SVWN5 method along with the 6-31G* basis set employing the *Gaussian94* program package gave the best results.[30] The calculated frequencies were scaled by an empirical factor of 0.95.

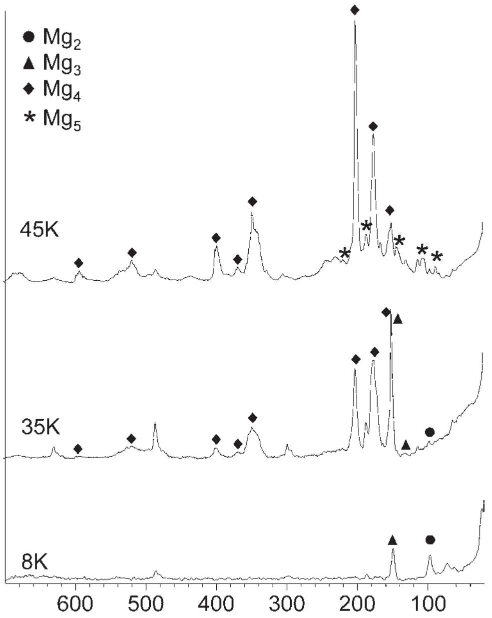

Figure 1. Raman matrix spectra (Ar^+ laser at 514.5 nm) of magnesium in argon at 8 K before and after multiple annealing cycles up to 35 and 45 K, respectively.

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.[29] The metal sample was evaporated at ca. 550 °C and codeposited with the inert gas on a cold surface, keeping the inert gas pressure below 10^{-2} Pa. After 1 h of deposition, a slightly brown layer was formed. During warm-up cycles of the matrix layer, a diffusion-controlled clustering process occurred, which was monitored by Raman spectroscopy. Four clusters were observed in the rare-gas matrixes. Figure 1 shows three representative Raman spectra of one argon matrix containing magnesium clusters at different stages of the cluster growth. The observed and calculated frequencies are summarized in Table 1.

The co-condensation of magnesium vapor with argon, krypton, and xenon, respectively, yielded matrix layers of slightly brown colors. The Raman spectra of argon, krypton, and xenon matrixes displayed two intense Raman lines close to 97 and 147 cm^{-1}. These two Raman lines do not belong to a single cluster. In a series of experiments, it was observed that the intensity ratio between the two lines depended on condensation conditions and it changed during the clustering process. Thus, with a high matrix-to-substrate (M/S) ratio, it was possible to obtain matrixes displaying almost exclusively the line at 97 cm^{-1} in the Raman spectrum. This Raman line is assigned to the smallest cluster species, the Mg_2

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Table 1. Experimental and Calculated (SVWN5/6-31G*) Vibrational Frequencies (cm^{-1}) and Vibrational Modes for Mg_2, Mg_3, Mg_4, and Mg_5 in Different Inert Gas (Ar, Kr, and Xe) Matrixes

	Raman frequencies (cm^{-1})				assignment	
	Ar	Kr	Xe	calcd		
Mg_2 ($D_{\infty h}$)	97	96	98	107	ν	Σ_g
	186	183	186		2ν	Σ_g
Mg_3 (D_{3h})	132			134	ν_2	E'
	149	147	150	153	ν_1	A_1'
Mg_4 (T_d)	150	148	153	147	ν_2	E
	174	174	174	175	ν_3	F_2
	201	199	200	204	ν_1	A_1
	347	346	346		$2\nu_3$	F_2
	374	373	375		$\nu_1 + \nu_3$	F_2
	397	396	397		$2\nu_1$	A_1
	522	516	518		$\nu_2 + 2\nu_3$	F_2
	594	591	590		$3\nu_1$	A_1
Mg_5 (D_{3h})	86	84	85	86	ν_6	E''
	113	111	112	107	ν_5	E'
				127	$\nu_3{}^a$	A_2''
	142	140	144	141	ν_2	A_1'
	185	183	186	184	ν_4	E'
	218	216	217	217	ν_1	$A_{1'}$

[a] Only active in the IR spectrum.

molecule. The calculated fundamental frequency (107 cm^{-1}) has a higher value. This trend is expected because matrix-isolated molecules usually display lower stretching frequencies than those measured in the gas phase free of any interactions.[31] Nevertheless, the difference is larger than that usually observed. It has to be considered that the Mg_2 molecule is very weakly bonded and therefore easily influenced by the surrounding matrix host, but then a stronger dependence on the matrix material should be observed.

The intensity of the dimagnesium line decreased rapidly in the Raman spectrum after the first annealing cycle with only slightly increased temperature, regardless of the matrix host. The decrease of the Mg_2 line is accompanied by an increase of the 147 cm^{-1} line, which is assigned to the stretching vibration of trimagnesium. This value is in agreement with the calculated frequency of 153 cm^{-1}. For the triangular molecule (D_{3h}), two Raman-active vibrations (species A_1' and E') are expected. The vibrational line calculated at 134 cm^{-1} is predicted to be of weak intensity and is therefore only observable at a larger content of Mg_3 in the Raman spectrum.

Further annealing of the matrixes containing Mg_2 and Mg_3 molecules led to fast and dramatic changes of the Raman spectra together with a change of the matrix color, turning from slightly brown to intense red. The lines of Mg_2 and Mg_3 molecules decreased, and three relatively intense Raman lines appeared simultaneously together with several weaker lines at higher wavenumbers. These lines are assigned to the tetrahedral Mg_4 cluster. The six fundamental modes of the Mg_4 molecule are degenerated because of the tetrahedral structure to three vibrational modes [$\Gamma(T_d) = A_1 + E + F_2$] all of which are Raman-active. The intense three lines in the matrix spectra agree with the theoretical calculations and display an intensity ratio [$\nu_1(A_1):\nu_3(F_2):\nu_2(E) \approx 100:80:40$] that is typical for tetrahedral molecules like P_4 or As_4.[31] The spectral region above 200 cm^{-1} displays overtones and combination modes, but it is probably overlaid by a weak fluorescence responsible for the variation of the background. Therefore, only the lines with a constant intensity ratio have been assigned to overtones and combination modes. Their appearance is in agreement with the spectroscopic selection rules.

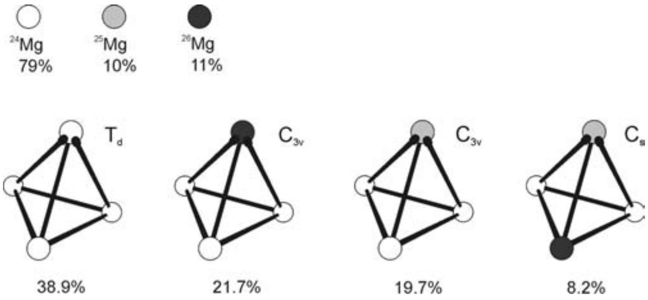

Figure 2. Distribution of isotopic isomers of Mg_4 from natural magnesium.

The formation of tetramagnesium is accompanied by the formation of at least one larger cluster. Raman spectra containing mainly tetramagnesium displayed in the region below 220 cm^{-1} five additional Raman lines of weak intensity. The intensity of these lines varied with matrix deposition conditions, but the intensity ratio between these lines did not change. The Raman lines show a satisfactory agreement with the calculated frequencies for pentamagnesium. The nine fundamentals of the Mg_5 molecule are degenerated because of the trigonal-bipyramidal (D_{3h}) structure to six vibrational modes [$\Gamma(D_{3h}) = 2A_1' + A_2' + 2E' + E''$], of which five are Raman-active. The tetramagnesium and small amounts of pentamagnesium were rapidly formed during annealing cycles of diluted matrixes. Harsh condensation conditions, such as a low M/S ratio, favored the formation of Mg_4 and Mg_5 already during matrix deposition. Matrixes containing tetramagnesium displayed a red color, and the intensity depended only on the dilution of the matrix. Further annealing did not change the spectral features significantly, but harsher conditions caused the formation of silvery metallic magnesium due to segregation of the sample.

Overall, the Raman lines of the magnesium cluster are relatively broad for matrix-isolated species, for which small half-line widths are expected. One reason is the isotopic composition of the magnesium cluster formed from magnesium with a natural isotopic distribution (79% ^{24}Mg, 10% ^{25}Mg, and 11% ^{26}Mg). The Mg_4 cluster consists of four isotopomers with an abundance larger than 5% (Figure 2). Additionally, the mixed isotopomers have a lower symmetry, which lifts the degeneracy of the vibrational modes. The isotopic splitting is in the region of up to 3 cm^{-1}, and it is not resolved in the Raman spectra. Therefore, the superposition of all isotopomers leads to broader Raman lines. The isotopic splitting alone would not cause such a line broadening as is observed. The main reason is the weak nature of the bonds, which are easily influenced by the matrix host, as was observed for rubidium and cesium clusters.[31,32]

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Our Raman spectroscopic investigations on matrix-isolated magnesium clusters are consistent with our investigations on the heavier alkaline-earth metals,[33] but they are in contrast with previously reported Raman spectra on matrix-isolated magnesium clusters and gas-phase studies.[3−6,34] Primarily, Balfour and Douglas reported absorption spectra of magnesium vapor.[34] The observed band system was tentatively assigned to a Mg_2 molecule. A fundamental frequency of 51.12 cm^{-1} has been derived under the assumption that the lower state of the observed transition is the ground state of the Mg_2 molecule. These findings seemed to be confirmed in 1978 by Givan and Loewenschuss, who reported the only known Raman spectrum showing only Mg_2.[5] The authors observed only slight changes of these lines using different matrix deposition conditions. The band shape is rather atypical for a Raman line, and it is very close to the broad Raleigh line. It could be an artificial stray light of the triple monochromator, of which the two stages had been used for stray-light rejection (subtractive mode). A closer inspection of the Raman spectrum shows a significant Raman line in the region of 100 cm^{-1}. Compared to our studies, this line could originate from Mg_2 molecules. Andrews et al. have reported photoluminescence and MCD spectra of matrix-isolated Mg_2 molecules.[4,6] The authors derived a fundamental frequency of 90.8 cm^{-1} from the observed band system. The difference of ca. 6 cm^{-1} to the Raman line reported here might be caused by an influence of the two states involved in the optical band. The authors have discussed this possibility in their work.[4] The MCD studies of Andrews et al. are remarkable because they were able to assign other optical band systems to Mg_3 and Mg_4 and predicted the cluster symmetries as D_{3h} for Mg_3 and T_d for Mg_4.[6]

DFT Calculations and Cluster Structure. Usually we have chosen theoretical methods by comparison of the calculated data with the known experimental data of the dimers.[32,35−37] This turned out to bear difficulties in the case of magnesium because the Mg_2 molecule is very weakly bonded and therefore possesses a low gradient in the energy surface. Furthermore, the gas-phase fundamental frequency turned out to be incorrect. Therefore, the Mg_4 cluster was considered to be the benchmark molecule for a comparison of different theoretical methods. The SVWN5/6-31G* method for the quantum-mechanical calculations has been chosen because it is in good agreement with the experimentally measured Raman frequencies of the Mg_4 molecule. The calculated vibrational frequencies are summarized in Table 1, and the calculated geometries are presented in Figure 3.

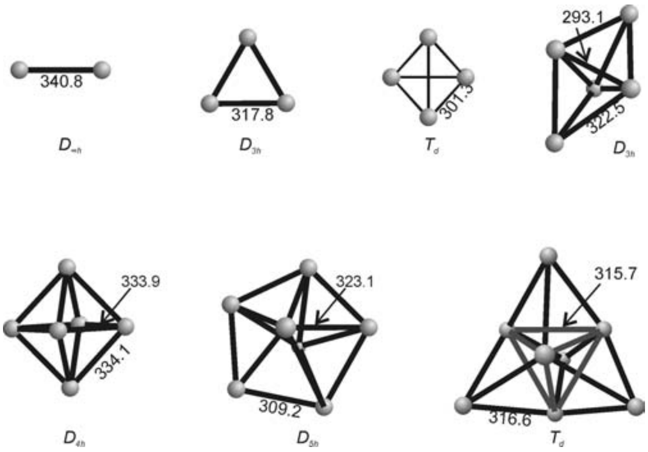

Figure 3. Calculated (SVWN5/6-31G*) geometries for small magnesium clusters.

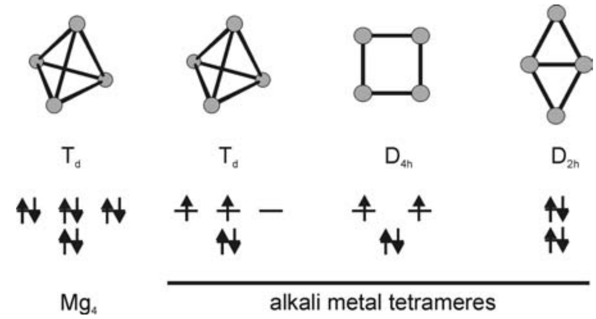

Figure 4. Configuration of Mg_4 and tetraatomic alkali metal clusters and corresponding bonding molecular orbital occupation.

For the Mg_2 molecule, a bond length of 340.8 pm has been calculated. It is somewhat shorter than the sum of the van der Waals radii (346 pm)[38] but remarkably longer than the distance of magnesium atoms in the bulk metal (320 pm).[39] The relatively weak Mg−Mg bond is also reflected by the force constant of 0.071 N cm^{-1}. For trimagnesium, the minimal energy was found for an equilateral triangle (D_{3h}) with bond lengths of 317.8 pm. This value is remarkably smaller than that for the dimer.

The trend in bond shortening by increasing the cluster size continues up to the tetrahedral Mg_4 cluster with a calculated bond length of 301.3 pm and a stretching force constant of 0.263 N cm^{-1}. At first sight, a tetrahedron and therefore closed-packed structure would be expected for a tetraatomic metal cluster, but our previous studies on alkali metal clusters have shown that the structures of small clusters are rather determined by the electronic situation.[35−37] Therefore, alkali metal clusters have a rhombic shape, which can be rationalized by comparing the occupation of the corresponding molecular orbitals shown in Figure 4. For an alkali metal tetramer, the tetrahedron and the square have two unpaired electrons and are therefore subject to Jahn-Teller distortion into the rhombic structure. In the case of Mg_4, a tetrahedral structure is favored because of the complete occupation of all bonding molecular orbitals.

Tetramagnesium is a magic cluster with respect to the jellium model, which was introduced by Ekardt.[40−43] The jellium model describes metal clusters as spheres of uniform positive charge with an appropriate number of

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electrons. Despite its extreme simplicity, this model depicts the real situation surprisingly well. In particular, it predicts for alkali metals the existence of clusters with 8, 20, 40, 58, and 90 atoms, which should exhibit an exceptionally high stability and therefore are called magic clusters. The magic numbers for alkali metal clusters have been confirmed by cluster beam experiments.[44,45] Nevertheless, the jellium model ignoring the ionic structure was an object of controversy. Despite the dramatic simplification, it is more justified than one might think at first sight. The sum of the individual effective core potentials forming the positive background is indeed a rather smooth function.[46] Another point is the assumption of sufficiently delocalized electrons, which limits the model to the first and second groups, and to some extent to the 11th group, of the elements. The appearance of the magic numbers for alkali metals is explained by closed electron shells in the jellium model. Therefore, for alkaline-earth metal clusters, the expected magic cluster sizes should be 4, 10, 20, 29, and 45 atoms. The predominant formation and stability of Mg_4 in matrixes are comparable to our observations on the magic clusters Na_8 and Li_8.

The Mg_4 cluster possesses, with 301.3 pm overall, the shortest Mg−Mg bonds. A shorter Mg−Mg bond has only been calculated for the trigonal-bipyramidal Mg_5 cluster in the equatorial position (293.1 pm) but at the expense of longer bonds to the apical atoms (322.5 pm). The average bond distant slightly decreases with cluster sizes beyond the Mg_4 molecule. Only the Mg_6 cluster possesses exceptionally long bonds, and after Mg_2, it is the weakest bonded cluster. The calculations yielded a structure very close to an octahedral geometry, but because of the flat energy surface, it cannot be excluded that the cluster might be elongated along one axis, which results in a D_{4h} structure. It is noteworthy that the Mg_8 cluster has the same hypertetrahedral structure as that observed for Na_8 and Li_8 clusters; however, the geometries of the smaller alkali metal clusters differ from those of the magnesium clusters.[36,37]

The average bond distances of the small magnesium clusters show an unexpected trend. Studies dealing with the transition between single atoms and the bulk material have shown that the strongest bonds are found for the dimers. The number of experimentally determined geometries of a series of cluster sizes is restricted to very few examples like lithium, sodium, and silver clusters, and the trends found in these few examples have often been generalized for all metals.[47,48] The average bond lengths of sodium and magnesium clusters normalized on the distance in the metallic bulk are shown in Figure 5.

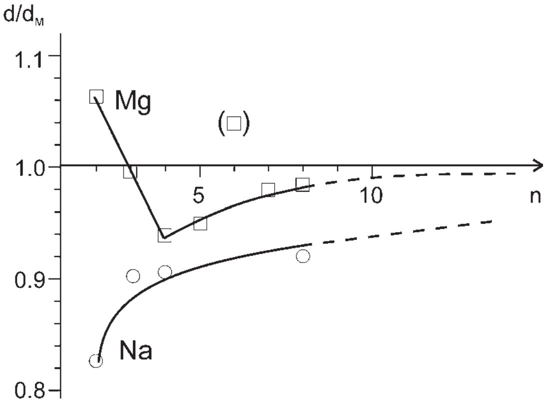

Figure 5. Relative average bond lengths of sodium and magnesium clusters normalized on the distance in the metallic bulk.

The bond length of Na_2 (307.88 pm) is 17% shorter than the distance of the sodium atoms in the bulk (371.6 pm). It has the strongest Na−Na bond among sodium clusters, which is also reflected by the stretching force constant of 0.173 N cm^{-1}. The average Na−Na bond length in the sodium clusters increases with the cluster size toward the Na−Na distance in the metallic bulk. For magnesium clusters, the dimer has the weakest bond. The calculated bond length of 340.8 pm is even longer than the Mg−Mg distance in the metallic bulk (320 pm),[39] and the bond can be described as a van der Waals bond. The bond situation changes dramatically toward Mg_4, which has a bond length of 301.3 pm and is 5.8% shorter than the distance of the magnesium atoms in the bulk. The change is better reflected by the stretching force constant, which is 0.071 N cm^{-1} in Mg_2 molecules and increases to 0.263 N cm^{-1} in Mg_4. The stretching force constant of Mg_4 is larger than that for Na_2 molecules and is even comparable to that Li_2 molecules (0.257 N cm^{-1}). This indicates that Mg_4 is rather better described as a weakly covalent bonded cluster than a van der Waals cluster. Further progression of the bond lengths for larger magnesium clusters is similar to that for sodium clusters.

Cluster Growth. The aim of this study was to isolate small magnesium clusters at the very first steps of the transition from atoms to bulk material. Our previous studies on alkali metal clusters have shown that the cluster growth that occurs upon matrix annealing does not proceed randomly, producing a complex cluster population. This is overall similar for magnesium clusters but with some essential differences.

The distribution of initially observed clusters varies with the condensation conditions. Highly diluted matrixes with a M/S ratio above 1000:1 combined with high evaporation temperatures result in matrixes containing only atoms. At slightly lower dilutions or after gentle annealing, Mg_2 along with Mg_3 is formed. In the case of sodium and lithium, the trimers have not been observed in considerable amounts, sufficient to be visible in the Raman matrix spectra. This is in accordance with cluster beam experiments, which show a pronounced odd−even alternation in the cluster size caused by the instability of alkali metal trimers as well as larger odd clusters. Such odd−even differences cannot occur for magnesium clusters; thus, the Mg_3 molecule is formed in considerable amounts. Further cluster growth of the Mg_2/Mg_3 cluster population leads to matrixes of Mg_4 clusters with a small content of Mg_5 clusters. This shows that the cluster growth of magnesium clusters does not proceed randomly because then one should expect a larger amount of Mg_5 and a considerable amount of Mg_6 clusters. The Mg_4

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cluster is relatively stable under matrix conditions, and further annealing does not lead to the formation of larger clusters. This is probably not due to a low mobility of Mg_4 clusters because the larger Na_4 cluster undergoes further cluster growth, forming the Na_8 magic cluster. Similar to our previous observations on Na_8 and Li_8 clusters, the end of cluster growth in matrixes is rather due to an exceptional stability of these species.

Conclusion

The magnesium clusters Mg_2, Mg_3, Mg_4, and Mg_5 have been characterized in rare-gas matrixes by Raman spectroscopy for the first time. The experiments have shown that the formation of magnesium clusters does not proceed randomly. The Raman spectroscopic data together with DFT calculations yielded reliable geometric parameters for the magnesium clusters. The previously reported gas-phase fundamental frequency (51 cm^{-1}) of the weakly van der Waals bonded Mg_2 molecule seems to be inaccurate. It has been measured in this work at 97 cm^{-1} (calculated 107 cm^{-1}). The bond strength of small magnesium clusters increases dramatically with the cluster size; thus, the tetrahedral Mg_4 molecule can be described as a weakly covalent bonded cluster. According to the jellium model, it belongs to magic clusters.

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