Raman Spectroscopic Investigation of Matrix Isolated Rubidium and Cesium Molecules: Rb_2, Rb_3, Cs_2, and Cs_3[†,1]

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The rubidium molecules Rb_2 and Rb_3 and the cesium molecules Cs_2 and Cs_3 were isolated in argon matrixes and characterized for the first time by Raman spectroscopy. The fundamental frequencies of the dimers were observed at 59.1 cm^{-1} for the rubidium dimer and 45.8 cm^{-1} for the cesium dimer. The Raman lines of the rubidium trimer appeared at 38.3 and 53.9 cm^{-1}, and the lines of the cesium trimer, at 24.4 and 39.5 cm^{-1}. The vibrational frequencies were compared with gas-phase frequencies and with density functional theory (DFT) calculations. Furthermore, the lowest vibrational levels of the $^1\Pi_u$ state of Cs_2 isolated in solid argon were observed by Raman matrix spectroscopy.

Introduction

Dimers of alkali metals, especially cesium, have been a topic of investigation since the early decades of this century.[2] The interest in alkali metal dimers first arose because of the special properties of these small molecules. While the electronic structure of these molecules is rather simple, the density of excited states leads to rich absorption and emission spectra which have been extensively studied. The amount of theoretical work done on alkali metal dimers is also immense because several computational methods were developed and refined during the past decade which permit accurate calculations on the electronic and energetic properties. While cesium dimers were an important topic for the first researchers, partly because cesium is used in atomic clocks, nowadays the interest in alkali metal dimers is renewed because of their potential use in quasitunable lasers, the first prototypes of which have already been built.[3]

In comparison to the amount of research done on alkali metal dimers, the study of alkali metal trimers, especially trimers of cesium and rubidium, is very small.[4−18] This may originate from the fact that electron excitation and fluorescence spectra of these clusters are very complex and difficult to interpret. Another problem is the low concentration of larger clusters in the gas phase compared with the concentrations of dimers and single atoms. An attractive alternative is therefore a spectroscopic technique that allows the accumulation of the desired species, yielding less complex spectra. A promising solution for these problems is the isolation of the molecules in a host material of solid noble gas and a subsequent study of the matrix by vibrational spectroscopy. The study of small alkali metal clusters trapped in a solid host was not extensively attempted since the most suitable method for the investigation of matrix-isolated homonuclear molecules is Raman spectroscopy. This technique suffered from the inherent difficulties of Raman matrix measurements. Recently, these problems were largely solved by us.[19] In this paper, we report our investigation on cesium and rubidium trapped in solid argon.

Experimental Section

Matrix Isolation. The cryostat and the laser irradiation geometry are described elsewhere.[19] The spectra were recorded with an Instruments SA T64000 Raman spectrometer equipped with a Spectra Physics Ar^+ laser. Rubidium (purity 99.6%) and cesium (purity 99.95%) (both from Aldrich) were used without further purification. Argon was dried by passing it through a column filled with P_4O_{10}.

Vapor phases of rubidium and cesium were prepared using a Knudsen cell heated externally with a heater jacket. The samples were heated to ca. 85 °C (rubidium) and ca. 55 °C (cesium). The metal vapors were co-condensed with argon on the copper cold tip of a cryostat. The average thickness of the samples was 100 μm.

[†] Dedicated to Prof. R. Schmutzler on the occasion of his 65th birthday.
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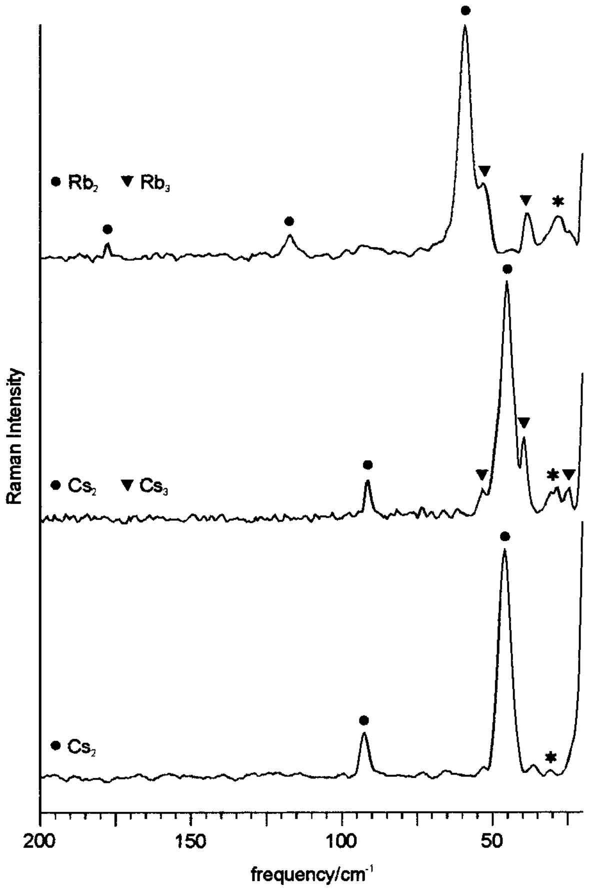

Figure 1. Raman matrix spectra of rubidium and cesium dimers and trimers trapped in solid argon. The lattice vibration of solid argon is marked by an asterisk.

The spectra of the excited cesium dimers were obtained from a single sample by tuning the Ar^+ laser to the lines at 514.5, 501.7, 496.5, 488.0, and 476.5 nm. After the measurements were completed, the investigated species were checked by a subsequent measurement at 514.5 nm, which proved that no new species were formed in the course of the experiment.

Density Functional Calculations. The appropriate theoretical method for the calculation on alkali metal clusters was chosen by us after comparison of different methods for the case of alkali metal dimers.[20] For rubidium and cesium clusters, the SVWN5[21] method along with the LANL2DZ[22] basis set augmented with polarization and diffuse functions employing the Gaussian 94 program package was used.[23]

Results and Discussion

Matrix Isolation and Raman Spectra. The co-condensation of rubidium and cesium vapors with argon on a cold surface (15 K) yielded matrix layers of intense blue to turquoise colors. A similarly intense color was observed for potassium clusters, and it was confirmed that it is due to the trapped cluster species and does not result from solvated electrons as observed for solutions of alkali metals in aprotic solutions.[20] Representative Raman spectra of the matrix experiments are are shown in Figure 1, and the observed frequencies are listed in Table 1.

The Raman spectra obtained from freshly prepared matrixes of cesium feature one line at 45.8 cm^{-1} and a very small line at 91.2 cm^{-1} (Figure 1). Both lines were assigned to the Cs_2 molecule (fundamental mode and first overtone). The fundamental frequency for Cs_2 determined from fluorescence spectra in the gas phase (42.022 cm^{-1})[24] as well as DFT calculations (41.8 cm^{-1}) shows somewhat lower values. The blue shift of the vibrational frequency by 3.8 cm^{-1} compared to that of the gas-phase reflects an influence of the host material on the isolated species. Usually matrix-isolated species possess stretching vibrations at lower frequencies as in the gas phase, but in case of the relatively large cesium, more energy is required to perform the mode.[25]

Table 1. Vibrational Frequencies (cm^{-1}) of Rubidium and Cesium Clusters

species	obs	calc	assignt
K_2[a]	91.0 (vs)	90.0	ν
	181.5 (w)		2ν
K_3[a]	61.0 (s)	57.2 58.9	δ δ
	81.5 (m)	83.0	ν
Rb_2	59.1 (vs)	59.1	ν
	116.8 (w)		2ν
	177.5 (vw)		3ν
Rb_3	38.3 (w)	35.2	δ
	53.9 (m)	54.0	ν
Cs_2	45.8 (vs)	41.8	ν
	91.2 (w)		2ν
Cs_3	24.4 (vs)	24.7	δ
	39.5 (m)	38.3	ν
	53.4 (vw)		$\delta + \nu$

[a] Data from ref 20.

Matrixes of cesium dimers also contain atoms that are efficiently separated from each other by the host material, which prevents the formation of larger clusters. This situation can be changed by performing warm-up cycles which enable diffusion of the trapped species in the argon layer. Upon such annealing procedures, three additional lines with lower intensity appeared simultaneously, two of which were assigned to the fundamental frequencies of a cesium trimer and the third of which could then be identified as a combination tone (Table 1). Further annealing of the matrix did not produce larger clusters but resulted in the segregation of the matrix sample and formation of golden-colored metallic cesium.

In the case of rubidium, no spectra of the pure dimer in argon were obtained; only spectra of mixtures that were identified as consisting of Rb_2 and Rb_3 were observed (Figure 1). The strongest line at 59.1 cm^{-1} agrees satisfactorily with the DFT-calculated frequency (59.1 cm^{-1}) for Rb_2 as well as with the gase-phase frequency derived from band head measurements (57.31 cm^{-1}).[24] Additionally, overtones at 116.8 and 177.5 cm^{-1} were observed for the Rb_2 molecule. The remaining two lines in the spectra were assigned to the trirubidium cluster.

A comparison of rubidium with cesium shows that rubidium forms clusters more readily under our conditions. This can be due to its higher mobility in the argon layer during matrix deposition. The size distribution of the guest material, i.e., trimers, dimers, and remaining atoms, was already achieved during matrix preparation, and temperature cycles did not alter the sample composition in the case of rubidium. Prolonged annealing resulted, as was observed for cesium, in sample segregation. The occurrence of larger clusters such as tetramers, as was recently found for potassium, was not observed.[20]

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Table 2. Bond Lengths (pm) of Alkali Metal Dimers and Trimers

species	exp (gas phase)	calc
K_2	390.5[a]	386.9[c]
Rb_2	420.99[b]	409.1
Cs_2	447[a]	454.7
K_3		428.5; 432.5[c]
Rb_3		453.2
Cs_3		503.4

[a] Data from ref 24. [b] Data from ref 26. [c] Data from ref 20.

DFT Calculations. The DFT-calculated (SVWN5[21] method with LANL2DZ[22] basis set) frequencies for dimers and trimers of potassium, rubidium, and cesium are given in Table 1 and compared with observed frequencies of the matrix-isolated species. We find reasonable agreement for all vibrational modes.

The calculated bond lengths of the dimers and trimers are summarized in Table 2 together with known bond lengths of the dimers determined on the basis of laser-induced fluorescence spectra.[24,26] For the dimers, we find satisfactory agreement between calculated and experimentally derived values. The deviations are in the range 3.6−12 pm, but compared to the large absolute values, these differences are relatively small. In general, the bonds in Rb_2 and Cs_2 are very weak in comparison to common chemical bonds. This is more obvious when one compares the force constants 0.083 N cm^{-1} (Rb_2) and 0.069 N cm^{-1} (Cs_2), which indicate the weak bonding between the atoms and the fragility of these species.

The calculations of the geometry of the trimers yielded equilateral triangles with bond lengths of 453.2 pm for Rb_3 and 503.4 pm for Cs_3. These values are remarkably larger than those of the corresponding dimers. A similar observation was made in the case of potassium clusters,[20] and it is in accordance with the expected trend predicted by theoretical studies dealing with the transition between single atoms and the bulk material. These studies, carried out on different elements, show altogether that the strongest bonding is always found for the dimers.[27] An increasing cluster size accompanies an increasing bond distance approaching the value of the interatomic distance in the crystalline bulk material. It should be noted that the change in bond length is more dramatic for weakly bonded metal clusters, as in our case. The calculated bond lengths for tricesium are 48.7 pm longer than those of dicesium but only 22.4 pm shorter than the interatomic distance in the body-centered cubic lattice of cesium.

The D_{3h} symmetry found for the trirubidium and tricesium clusters is in accordance with the experimentally observed Raman spectra, which possess two fundamental frequencies ($A_1' + E'$). This result is rather surprising because the alkali metal trimers are subject to Jahn−Teller distortion, which should lead to an equilibrium geometry with C_{2v} symmetry due to the vibronic splitting of species E'.[28] One should then observe three fundamental frequencies ($2A_1 + B_2$). ESR studies have shown that the lightest alkali metal trimers Li_3 and Na_3 appear to be pseudorotating dynamic Jahn−Teller molecules.[29−32] Similar experiments on K_3 show a different situation, and the results can be interpreted by a static Jahn−Teller effect or by a model taking ionic interactions into account.[33] However, ESR spectra yield information about the symmetry of an open-shell cluster with the uncertainty that the electronic states might be strongly influenced by the matrix environment; only the magnitude of the Jahn−Teller distortion is difficult to estimate. Recently, matrix experiments together with DFT calculations on K_3 have shown that the Jahn−Teller effect is too small to be resolved in the Raman spectra.[20] This is in accordance with the observation that Jahn−Teller distortions acting along a nontotally symmetric normal coordinate have in general small amplitudes (on the order of 1% of a bond length).[34] Furthermore, the amplitude of this interaction is limited by the very small force constants of the corresponding vibrations of the heavier alkali metal trimers. Consequently the Jahn−Teller effect is observable for the lighter alkali metal trimers, but it is a negligible for the very weakly bonded trirubidium and tricesium molecules.

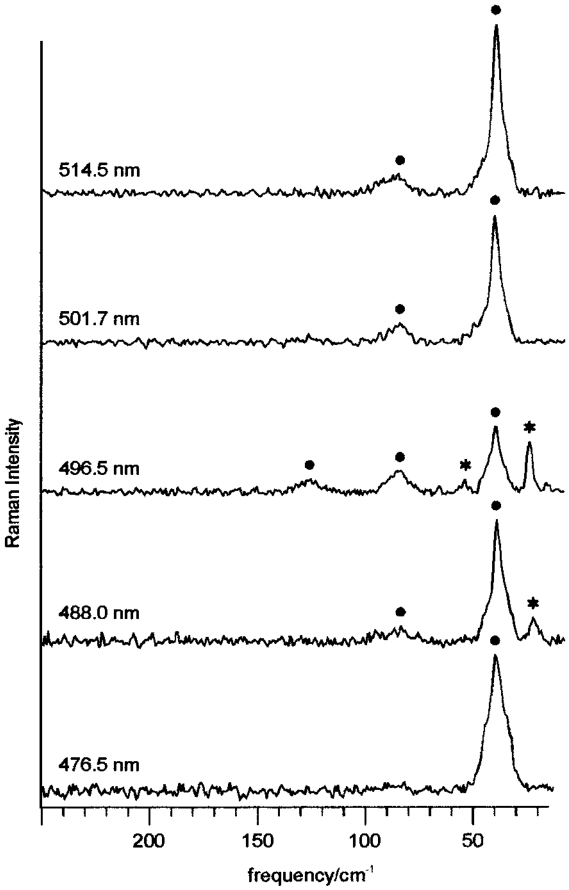

Figure 2. Raman matrix spectra of cesium dimers excited by different lines of an argon ion laser.

Laser Excitation of Cs_2. Besides the general problems accompanying the identification of new matrix-isolated species, the effect of laser radiation has to be determined for each sample when Raman spectroscopy is used as a means of investigation. During such a routine determination, changing the wavelength of the laser, we found that Cs_2 can be optically pumped into an excited state. For the experiment, we chose a deep blue matrix sample containing only cesium dimers isolated in solid argon without accompanying trimers. The sample was subsequently irradiated by Ar^+ laser lines of 514.5, 501.7, 496, 488, and 476 nm wavelengths. The Raman matrix spectra are shown in Figure 2, and the Raman lines are summarized in Table 3.

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Table 3. Vibrational Frequencies of Cesium Dimers in the $^1\Sigma_g^+$ and $^1\Pi_u$ States

laser wavelength, nm	Raman lines, cm^{-1}		assignt
	$^1\Sigma_g^+$ state	$^1\Pi_u$ state	
514.5	45.1		ν
	90.0		2ν
501.7	45.1		ν
	90.0		2ν
496.5	45.1	28.4	ν
	90.0	57.4	2ν
	129.5		3ν
488.0	45.1	28.4	ν
	90.0		2ν
476.5	45.1		ν

At a laser wavelength of 476.5 nm, only the fundamental vibration of Cs_2 is observable. The situation changes when the laser is tuned to 488.0 nm. Two new lines apper at 28.4 and 90.0 cm^{-1}, the second apparently being an overtone of the fundamental vibration. At a laser wavelength of 496.5 nm, the intensity of the first overtone increases and a second overtone at 129.5 cm^{-1} appears. Also a new line of low intensity can be found at 57.4 cm^{-1}. After the laser is tuned to 501.7 and 514.5 nm, only the fundamental vibration of Cs_2 and its first overtone can be observed. The formation of observable amounts of new cluster species under laser irradiation can therefore be excluded.

The origin of the two Raman lines at 28.4 and 57.4 cm^{-1} was revealed by comparison with data from fluorescence spectra of Cs_2 in the gas phase.[24,35] The lines can be assigned to the stretching vibration of the excited state $^1\Pi_u$ of Cs_2, which was accessed by optical pumping of the ground state $^1\Sigma_g^+$.[8,10,15,16] The vibrational frequency of the excited Cs_2 molecule is somewhat smaller than that observed in the gas phase (30.398 cm^{-1}).

Conclusion

Small clusters of rubidium and cesium were isolated in rare gas matrixes and characterized by Raman spectroscopy. The results of the Raman spectroscopic measurements and the corresponding density functional calculations are in good agreement. The analytical method which was demonstrated to work well for potassium clusters can be extended to the even more fragile heavier alkali metal clusters. An excitation of isolated cesium dimers by the radiation of an argon ion laser leads to the first Raman matrix measurements of cesium dimers in the $^1\Pi_u$ state.

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