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Far-Infrared Spectroscopy of Small Neutral Silver Clusters

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The vibrational spectra of Ag_3 and Ag_4 are recorded in the far-infrared between 100 and 220 cm^{-1} using multiple photon dissociation spectroscopy of their complexes with Ar atoms. For Ag_3−Ar two IR active bands are found at 113 and 183 cm^{-1}, for Ag_4−Ar one band at 163 cm^{-1} and very weak IR activity at 193 cm^{-1} are observed. This, together with recent theoretical studies, allows for a reassignment of the controversial vibrational data reported earlier for the bare Ag_3 cluster. The influence of the number of Ar atoms in the complexes on the frequency of the IR active modes is found to be minor. However, the low-frequency IR-active band of Ag_3 shifts with increasing Ar coverage from 113 cm^{-1} for Ag_3−Ar to about 120 cm^{-1} for Ag_3−Ar_4, the value known for Ag_3 embedded in rare gas matrices.

Introduction

Silver clusters have been the subject of experimental and theoretical studies from the beginning of metal cluster research.[1−6] Initially, studies on clusters of the "simple elements" in the Ia and Ib groups of the periodic table were used to obtain a better understanding of how the properties of metal particles evolve with size. However, the special interest in silver clusters is also triggered by more practical arguments such as the investigation of their chemical reactivity[7−10] that can be relevant for heterogeneous catalytic reactions or for the understanding of their function in the photographic process.[11] In the last years, the optical properties of small silver clusters either in the gas phase or embedded in matrices have been studied intensly.[12−22]

The characterization of small metal clusters grown in rare gas matrices via vibrational spectroscopy has been pioneered by Schulze, who reported Raman spectra for Ag_2 and Ag_3.[2] The group of Moskovits has reported resonance Raman spectra of mass selected silver clusters Ag_n ($n = 3, 5, 7, 9$) deposited in solid Ar.[23−25] Vibrational properties of Ag_3 have also been derived from fluorescence studies and from resonant two photon ionization (R2PI) spectra. The $Ag_3^-/Ag_3/Ag_3^+$ system has been studied in detail using femtosecond pump−probe spectroscopy, but from these studies no information on the vibrational structure could be extracted. The latter has been rationalized in terms of very rapid intramolecular vibrational redistribution.[26,27] At present, there is no consistency between vibrational frequencies and mode assignments of Ag_3 obtained in different experimental studies; a detailed discussion on this can be found in the review on force constants of small metal clusters by Lombardi and Davis.[28] Various theoretical studies agree that the ground-state structure of the silver trimer is an obtuse isosceles triangle with $^2B_2$ electronic configuration.[4−6,29−37] However, Ag_3 is affected by Jahn−Teller-distortion, and its ground-state potential surface is 'mexican hat' shaped. The saddle points between the three $^2B_2$ minima correspond to acute isosceles triangular structures of $^2A_1$ configuration and are ~0.02 eV above the minima. The equilateral $^2E'$ state is reported to be ~0.05 eV higher in energy than the $^2B_2$ minima.[33,37] From the different studies for the $^2B_2$ ground-state configuration the structural parameters converge to a vertex angle of about ~68° and to a length for the shorter bonds of about 2.70 Å. Theory predicts a rhombic structure for Ag_4,[30,31,38−40] but the experimental information that is available on its vibrational properties is rather limited. A vibrational mode at ~45 cm^{-1} has been identified using femtosecond pump−probe spectroscopy.[41]

Here, we present the far-infrared spectra of neutral Ag_3 and Ag_4 clusters that have been obtained by infrared multiple photon dissociation (IR-MPD) spectroscopy of their complexes with rare gas atoms. In these complexes, the metal cluster forms the chromophore, while the weakly bound rare gas atom acts as spectator and as probe for the heating of the clusters that occurs after resonant absorption of far-infrared photons. Recently, we have used the IR-MPD method to obtain the infrared spectra of cationic vanadium clusters[42,43] as well as of neutral and cationic niobium clusters.[44,45] In these studies, the influence of the rare gas atoms on the vibrational spectra of the metal clusters has been investigated, and this influence is seen to be too small to be detected in most cases. The Nb_9 cluster presented an interesting exception. For this particular cluster the dependence of the IR spectra on the rare gas coverage reflected the presence of isomers with different affinities toward the rare gas atoms.[28]

Experimental Methods

In the present study, complexes of small neutral silver clusters with one or a few argon atoms are generated using a pick-up cluster source.[15,46] The silver cluster complexes are ionized using an ArF-excimer laser, and the cluster distribution is analyzed in a reflectron time-of-flight mass spectrometer. To probe the vibrational spectra of the neutral silver cluster complexes, they are irradiated with the pulsed far-infrared radiation produced by the Free Electron Laser for Infrared eXperiments (FELIX) before they enter the mass spectrometer. Resonant excitation of the complexes may result in the evaporation of one or more argon atoms. Thus, IR spectra are obtained from the intensities of the ion signal of the rare gas complexes as a function of the IR wavelength. A normalization procedure is applied to account for changes in cluster beam intensities and for variation in IR laser fluence, details of which have been described elsewhere.[45]

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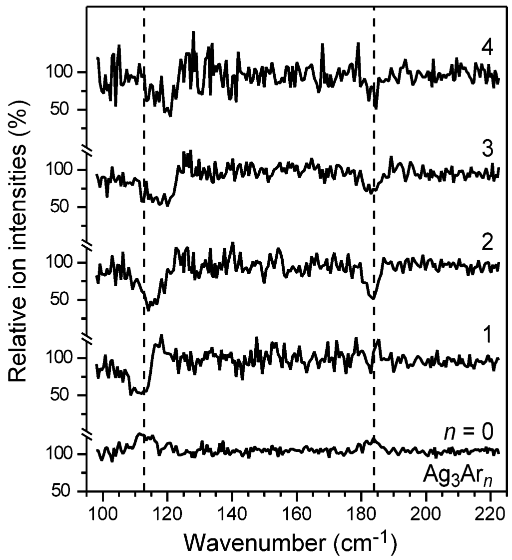

Figure 1. IR-MPD spectra of Ag_3Ar_n ($n = 0-4$) complexes. The various spectra are given an offset for clarity. Intensity growth for a species as a result of IR-MPD of larger complexes is observed together with IR-MPD of the species itself. The positions of the bands of the mono-Ar complex of Ag_3 are indicated by the dashed lines.

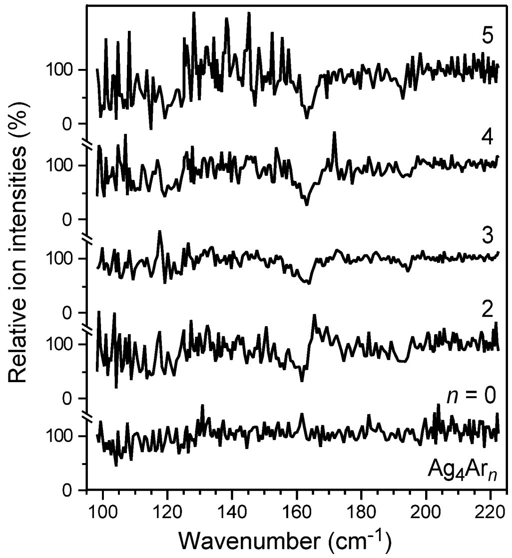

Figure 2. IR-MPD spectra of Ag_4Ar_n ($n = 0, 2-5$) complexes. The various spectra are given an offset for clarity. The increased noise level in the spectra in the range <130 cm^{-1} results from a drop in the intensity of the cluster beam while recording the spectra.

Results and Discussion

The IR-MPD spectra of the argon complexes of neutral Ag_3 and Ag_4 in the 100−220 cm^{-1} range are shown in Figures 1 and 2, respectively. Although the signal-to-noise ratio in these spectra is rather poor due to the low overall cluster beam intensity and due to pulse-to-pulse fluctuations of the ArF ionization laser, several depletion bands are clearly and reproducibly observed.

In the far-infrared range studied here the value of the photon energy is lower than the binding energy of the Ar atoms, which is on the order of ~1000 cm^{-1}. Therefore, absorption of multiple photons is required to evaporate a single Ar atom. Moreover, the absorption cross-sections of the allowed far-infrared transitions in the silver clusters are intrinsically small. As a consequence, the far-infrared excitation of the complexes mainly leads to the loss of single Ar atoms, implying that dissociation of complexes with n Ar atoms distorts the spectra of complexes containing n-1 Ar atoms. In Figures 1 and 2, intensity growth for a species as a result of IR-MPD of larger complexes is observed together with depletion due to IR-MPD of the species itself. Bare silver clusters cannot be fragmented with the far-infrared radiation, and the IR-spectrum observed for Ag_3 closely follows the inverse of the IR-spectrum of Ag_3Ar.

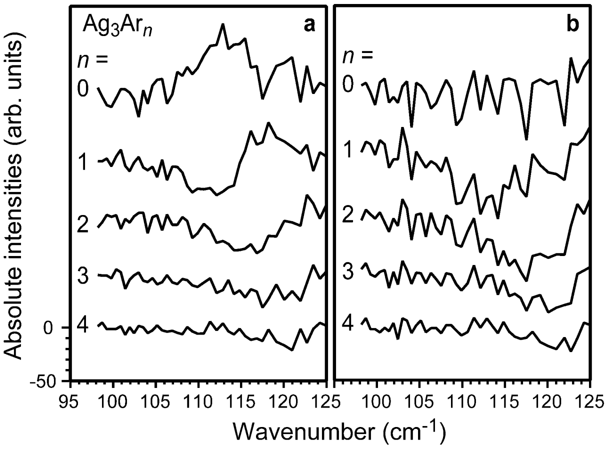

Figure 3. (a) IR-MPD spectra of Ag_3Ar_n ($n = 0, 2-5$) complexes as measured and (b) after subtraction of the IR-MPD contribution from complexes with more Ar atoms. The spectra are plotted all on the same intensity scale but with an offset for clarity.

One can reconstruct the undistorted depletion spectra of the complexes when evaporation of single Ar atoms is assumed. In Figure 3(a) the measured absolute intensities of the ion signal due to the Ag_3Ar_n complexes is shown as a function of the FELIX frequency in the range between 100 and 125 cm^{-1}. After correction for the growth in intensity due to fragmentation of complexes with one more Ar atom, the IR-MPD spectra shown in Figure 3(b) are obtained. From the corrected IR-MPD spectra the band positions are determined by fitting Gaussian profiles to the depletion signals. The values obtained by this method have uncertainties of ±1 cm^{-1} (1σ). The low-frequency band of Ag_3Ar_n is shifted from 113.0 cm^{-1} for the mono-Ar complex to 116.8, 119.1, and 120.5 cm^{-1} for $n = 2$, 3, and 4, respectively. The frequency of the second band of Ag_3, found at 182.8 cm^{-1}, is seen to be hardly affected by the surrounding Ar atoms. For Ag_4Ar_n, at least two bands can be identified at 162.7 cm^{-1} and 192.7 cm^{-1}, independent of the number of Ar atoms attached. A third band might be present at ~120 cm^{-1} but is less clear because of the high noise level.

The experimentally determined frequencies of the IR active vibrational modes of Ag_3 are compared to the vibrational frequencies of Ag_3 obtained by other experimental and theoretical methods in Table 1. Raman spectra for Ag_3 in rare gas matrices display the highest frequency band at ~119 cm^{-1},[2,25,47,48] and an additional mode has been identified at 99 cm^{-1} from a fit of the resonance Raman bands.[25] Although these bands have been assigned to the symmetric stretching and the degenerate bending mode, respectively, polarization analysis of the scattered Raman light, which could substantiate this assignment, has unfortunately not been performed. The band at 119 cm^{-1} nicely matches to the IR-active mode that we observe at 113 cm^{-1} and that is seen to shift to 120 cm^{-1} in the presence of more Ar atoms. The IR-active mode that we observe in our IR-MPD study at ~183 cm^{-1} would be screened in the matrix spectra by the intense Raman transition of Ag_2 at 182 cm^{-1}, also present in the matrix due to photodissociation of the trimer.[25] The frequencies of vibrational modes as extracted from dispersed fluorescence or resonance enhanced two-photon ionization

TABLE 1: Experimentally Determined and Theoretically Predicted Values of the Vibrational Frequencies (in cm^{-1}) of Ag$_3$ in the Ground State[a]

method	ν_{sym}	ν_{asym}[b]	ν_{bend}[b]	state
IR-MPD (this work)	183	113		
Raman, Kr matrix[2]	120			
Raman, Ar matrix[47]	120			
Raman, Xe matrix[48]	111			
Raman, Ar matrix, mass selective deposition[25]	119	99	99	
dispersed fluorescence[49]	≈180	≈67	≈67	X^2E'
R2PI, empirical fit[50,51]	178.6	103.9	103.9	$^2E'$
R2PI, empirical fit, reassignment[52]	121	99	99	$^2E'$
R2PI, empirical fit[53]	157.9	140	140	X^2E'
emission spectrum in superfluid He[54]	≈180			
theory, bond-connectivity force field[55]	235.1	166.3	166.3	
theory, SDCI/CPF[6]		134	68	$^2B_2$
theory, DFT, BP86[31]	170.0	90.4	70.9	$^2B_2$
theory, DFT, BPW91[32]	164.4	112.5	43.1	
theory, full CI[33]	173	113	73	$^2B_2$
theory, CCSD[34]	163.7		62.6	$^2B_2$
theory, DFT, VWN[35]	209	142	66	
theory, MP2[36]	167.5	64.2	58.8	$^2B_2$
theory, DFT, LDA[37]	190		56.1	$^2B_2$

[a] The assignments of the vibrational bands are given as quoted in the original references. [b] Equal values for ν_{asym} and ν_{bend} reflect the double degeneracy of the corresponding bending mode in D_{3h} symmetry.

(R2PI) spectra depend strongly on the assumptions underlying the spectral fitting. Interestingly, the earlier interpretations[49−51] resulted in values for the symmetric stretching mode (ν_{sym}) close to the position of the high-frequency band in our experiments, whereas a later reassignment[52] yields a value that agrees with the one from Raman spectroscopy, i.e., with the low frequency band in our spectrum. A third fit of isotopically resolved R2PI spectra resulted in a ν_{sym} of 157.9 cm^{-1}.[53] Because of the high resolution in the latter experiments, it is favored as the most likely value for the symmetric stretch vibration in the review by Lombardi and Davis.[28] However, the values found in this fit[53] deviate significantly from the frequencies of the IR-active modes that we have found in this study.

The high- and low-frequency bands observed for Ag$_3$Ar match reasonably well to the calculated harmonic vibrational frequencies of the symmetric (ν_{sym}) and antisymmetric (ν_{asym}) stretching modes, respectively, of the $^2B_2$ ground state of the bare Ag$_3$ cluster (Table 1). The simple method of assuming a "bond-connectivity" force field[55] clearly overestimates the strength of the Ag−Ag bonds in the trimer. Among the different theoretical studies the best agreement with our experimental data is found for the full CI calculations,[33] even though the use of the harmonic approximation is questionable for the Jahn−Teller system. Vibrational spectra obtained from a simulation of the nuclear dynamics of Ag$_3$ predict that mainly the antisymmetric stretching mode will be affected by the anharmonicities.[33] It might actually well be that symmetry breaking due to the presence of the Ar atom is responsible for a more harmonic potential energy surface around the minimum. A noticeable effect on the shape of the potential energy surface is reasonable, considering that the Ar binding energy of ∼0.1 eV is significantly higher than the (calculated) energy differences between the $^2B_2$ minima and either the $^2A_1$ saddle points or the $^2E'$ state with D_{3h} symmetry (see above). Similarly, significant differences have been found between the optical photodissociation spectra of the copper trimer and of its complexes with argon and krypton and have been related to the fluxional structure of Cu$_3$.[56]

For the silver tetramer several vibrational bands in the 160−200 cm^{-1} range have been identified in ab initio molecular dynamics simulations.[39] Harmonic vibrational frequencies in the relevant range have been reported in three studies at 110, 140, and 181 cm^{-1} (ref 31), 98, 148, and 166 cm^{-1} (ref 36), and at 114, 165, and 196 cm^{-1} (ref 38), depending on the level of theory applied. The latter values, obtained by the Bonačić-Koutecký group using the same methods as those for the trimer, agree very well with our experimental results.

Conclusion

Summarizing, we conclude that the low-frequency band of Ag$_3$Ar at 113 cm^{-1} that shifts with increasing Ar coverage toward 120 cm^{-1} corresponds to the mode at ∼119 cm^{-1} observed via Raman spectroscopy of Ag$_3$ in rare gas matrices. By comparison with DFT calculations and previous molecular dynamics simulations on *bare* Ag$_3$ we assign this band to the antisymmetric stretch vibration of Ag$_3$. The high-frequency band at 183 cm^{-1}, which is not reported in the Raman studies due to congestion with signals from Ag$_2$, is assigned to the symmetric stretch. Our data favor the earlier interpretations of fluorescence and ionization spectra of bare Ag$_3$.[33−35] The frequencies of the two observed IR-active modes of Ag$_4$ agree well with the values from theoretical studies. Both bands correspond most likely to Ag−Ag stretching modes. In general, comparison with theory suggests that the rare gas atoms are not perturbing the vibrational properties of the bare metal clusters significantly, in agreement with earlier findings. However, to understand the coverage dependent shift in the frequency of the asymmetric stretching mode of the Ag$_3$Ar$_n$ complexes, theoretical studies explicitly addressing potential surface distortions relative to that of the bare Ag$_3$ cluster are needed.

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