Formation of Core-Shell Ethane-Silver Clusters in He Droplets

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Abstract

Ethane core - silver shell clusters consisting of several thousand particles have been assembled in helium droplets upon capture of ethane molecules, followed by Ag atoms. The composite clusters were studied via infrared laser spectroscopy in the range of the C-H stretching vibrations of ethane. The spectra reveal a splitting of the vibrational bands which is ascribed to interaction with Ag. A rigorous analysis of band intensities for varying number of trapped ethane molecules and Ag atoms indicates that the composite clusters consist of a core of ethane which is covered by a relatively small Ag clusters. This metastable structure is stabilized due to the fast dissipation in superfluid helium droplets of the cohesion energy of the clusters.

1. Introduction

Helium droplets provide a gentle, low-temperature environment which can be exploited to investigate atomic and molecular species at low energy quantum states.[1-7] Atoms and molecules can be introduced into helium droplets by using a pick-up technique and remain trapped either on the droplet surface or interior depending on their specific interaction potential with helium atoms. Due to the superfluid state of the droplets, trapped species are free to move about once inside the droplet and can combine upon collision. The energy released upon trapping as well as the enthalpy of coagulation is rapidly dissipated as heat which is followed by the rapid evaporative cooling of the droplet to its initial temperature of ~0.4 K.[8] Thus, the droplets can be thought of as ultracold test tubes for the formation of diverse clusters.[9-15]

Previously, we have shown that nanometer-sized clusters [16-17] can be obtained in large droplets consisting of approximately 10^5-10^7 He atoms. These droplets are obtained through a so-called "supercritical" expansion of pressurized helium at low-temperature into vacuum.[7,18-20] In contrast to the more common techniques of aggregation and laser ablation, the helium droplet enables the combination of metal clusters to weakly bounded molecular species. The study of the molecules adsorbed on metal clusters may be of interest in heterogeneous catalysis.[21-22] In this article, we describe our continued IR spectroscopic studies of binary ethane-Ag clusters assembled in large He droplets.

Recently,[16] we have studied composite clusters consisting of up to $\sim10^3$ Ag atoms forming cores, which were covered by several layers of ethane (ET) molecules. The clusters were formed inside He droplets which were doped by Ag atoms and ET molecules in upstream and downstream pickup cells, respectively.[16] The clusters were studied by laser infrared spectroscopy of the C-H stretch region of the ET molecules. The spectra revealed that the vibrational bands of ET were shifted towards lower frequency with respect to their gas phase values due to ET-ET and ET-Ag interactions in the clusters. We found that the ν_7 vibrational band of ET is split into two bands separated by ~15 cm^{-1} and this is due to the two local environments around the ET molecules: molecules were found to exist directly on the Ag core surface or further removed from the metallic core. The two observed bands were designated I- and V-bands, respectively.[16] The I-band is shifted towards lower frequency by a relatively larger amount which is in line with the stronger Ag-ET interaction at the metal-molecule interface as compared to the strength of ET-ET interaction in the outer layers.[16] The intensity ratio of two bands was used for evaluation of the structure of the composite clusters.[16] We found that the number of interface ET molecules is in agreement with a compact-spherical-core-and-shell model for smaller Ag core clusters of less than ~500 atoms. However, larger Ag core clusters consisting of about 3000 atoms, which were obtained in larger He droplets, were noted to have about 5× larger surface area than that predicted by the compact cluster model, indicating a more ramified structure for the larger Ag clusters. This finding is consistent with the formation of the cluster-cluster aggregates [10] or filament shaped clusters on quantum vortices in large He droplets.[9,23-26]

In this work, we employ a similar experimental technique to study clusters obtained by reversing the pickup order; droplets were first doped by ET followed by Ag atoms. We hypothesize, that the particles added upstream will make a stable core of ET molecules covered by shell(s) of Ag atoms after being added downstream. Because Ag has an approximately 10× larger molar enthalpy of sublimation as compared with ET, the reverse ET core-Ag shell structure is energetically unfavorable.[16] We show that such ET core-Ag shell clusters can nevertheless be stabilized in helium droplets due to the low temperature of the helium environment. The results also indicate that the Ag shell may consist of small Ag clusters which likely experience partial submersion into the surface of the ET core.

2. Experiment

The He droplet experiment is similar to that described previously.[16] In this work, however, the droplets are first doped with ET molecules in the upstream pickup cell, then with Ag atoms in the downstream pickup cell. The average size of the droplets $\langle N_{\mathrm{He}} \rangle$ decreases by $\langle \Delta N_{\mathrm{He}} \rangle$ due to capture of Ag atoms and ET molecules, and this decrease is detected by measuring the decrease in the pressure rise due to the He droplet beam, ΔP_{He}, in the terminal chamber which houses a quadrupole mass-spectrometer. The number of captured particles can be estimated according to: [16]

$$N_M = \frac{\langle \Delta N_{\mathrm{He}} \rangle \cdot E_{\mathrm{He}}}{E_M} = \frac{\Delta P_{\mathrm{He}} \cdot \langle N_{\mathrm{He}} \rangle}{P_{\mathrm{He}}} \cdot \frac{E_{\mathrm{He}}}{E_M}, \qquad (1)$$

where $E_{He} = 6.1$ cm^{-1} is the evaporation enthalpy per He atom at T = 0.65 K, as estimated during the pickup.[16] E_M is the energy associated with the pickup of a single particle of either Ag or ethane (i.e., M=Ag, ET) and is due to the particle's kinetic and internal energy as well as the cohesion energy released during the formation of clusters inside of the He droplets. As in Ref. [16], here we assume that the addition of one ET and Ag particle effects evaporation of 330 and 3500 He atoms, respectively. These values are used throughout this work irrespective to the size of the clusters being formed.

The clusters obtained have been studied by pulsed infrared depletion spectroscopy as detailed previously.[16] The intensities of the spectra reported in this work are given in units of absorbed energy per ethane molecule as:

$$E_{\mathrm{abs}} = \beta \cdot \left(\frac{1}{A_{1\mathrm{ET}}} - 1\right) \cdot \left(1 - A_{2\mathrm{Ag}}\right) \cdot E_{\mathrm{ET}} \cdot D, \qquad (2)$$

where $A_{1\mathrm{ET}}$ and $A_{2\mathrm{Ag}}$ is attenuation of He droplet beam due to capture of ET molecules and Ag atoms, respectively, D is the fractional depletion of the mass spectrometer signal upon laser irradiation, and E_{ET} is energy associated with addition of one ET molecule to the cluster.[16] The factor β=3/2 takes into account the dependence of the droplet ionization cross-section on its size which in large droplets scales as $N_{\mathrm{He}}^{2/3}$.

3. Results and Discussion

The normal vibrations in C_2H_6, can be classified in terms of the D_{3d} symmetry group.[27] In the 3 μm region there are two fundamental vibration levels: the ν_7 perpendicular (⊥) band of E_u symmetry located at 2985.4 cm^{-1} and the ν_5 parallel (||) band of A_{2u} symmetry at 2895.7 cm^{-1}. These vibrations are strongly coupled via a cubic anharmonic interaction with the combination vibrational level $\nu_8+\nu_{11}$ and this results in a splitting into || (2953.8 cm^{-1}) and ⊥ (2930.7 cm^{-1}) components of A_{2u} and E_u symmetry, respectively.[27-28] The combination bands source their intensities from the fundamental vibrational bands according to the symmetry rules. In the IR gas phase spectra, the relative intensities of the vibrational bands of C_2H_6 are $I(\nu_5,||):I(\nu_7,\perp):I(\nu_8+\nu_{11},||):I(\nu_8+\nu_{11},\perp)=100:60:40:9$.[28] In Ref. [16], the spectra of the Ag-ET clusters were obtained in a wider spectral range which included the ν_5 band around 2870 cm^{-1}.[29] However, the ν_5 band is a weaker band and does not exhibit characteristic splitting into I and V components. Therefore, the current study of ET-Ag clusters was focused on the spectra of the ν_7 band.

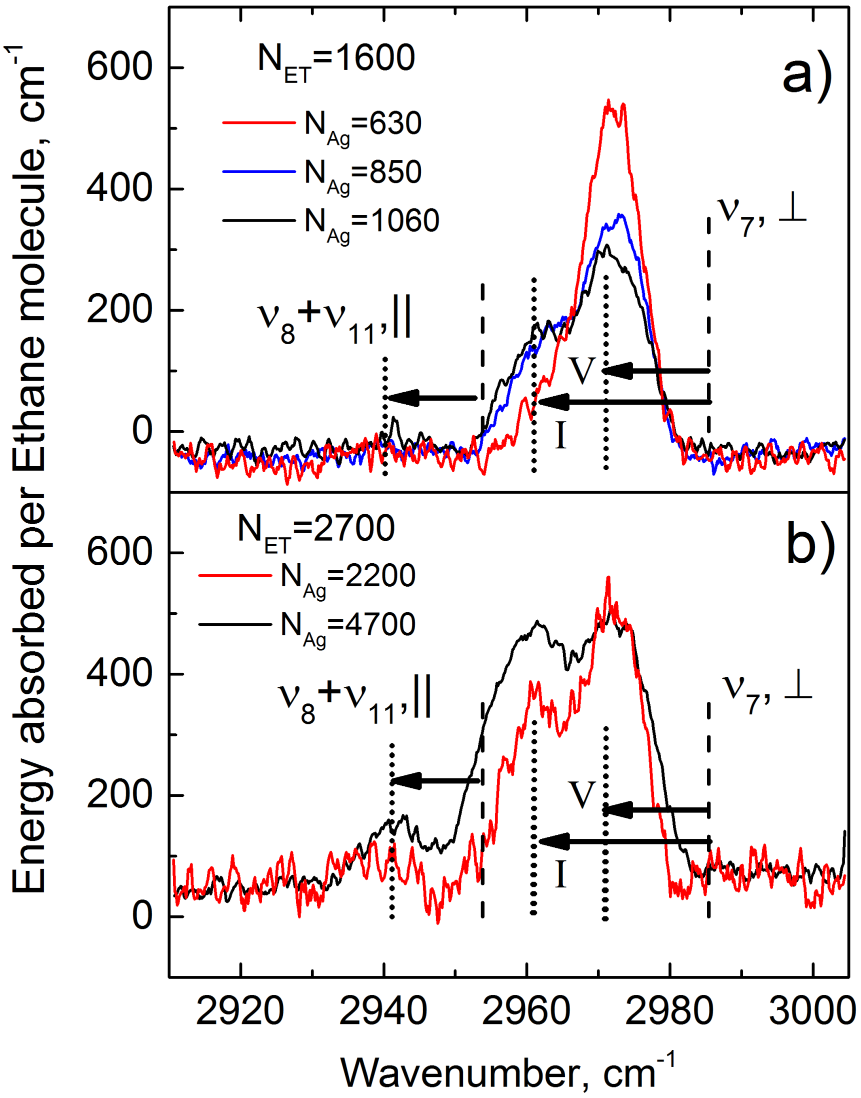

Figure 1. Infrared spectra of clusters obtained upon capture of ET molecules followed by Ag atoms. The clusters were formed in He droplets with initial size of (a) 5×10^6 and (b) 2×10^7 atoms. The average numbers of captured ET and Ag particles is indicated in each trace. Dashed vertical lines show positions of vibrational bands in free molecules. The dotted lines show the band centers observed in clusters and assigned to $\nu_8+\nu_{11}$ and ν_7 (interface: I; volume: V) bands. The horizontal arrows demonstrate the shifts of band frequencies in clusters with respect to free molecules.

Figure 1(a) shows the spectra in the vicinity of the ν_7 band of clusters obtained after doping ~1600 ET molecules in the upstream pickup cell into He droplets (average size $\langle N_{\mathrm{He}} \rangle$= 5×10^6) followed by a varying number of Ag atoms in the downstream pickup cell. The spectra show a splitting of the ν_7 band into two components at about 2962 and 2972 cm^{-1} with widths of ~8 cm^{-1} (FWHM). Fig. 1(b) shows the results of similar measurements for larger ET clusters of 2700 molecules (obtained in larger droplets of $\langle N_{\mathrm{He}} \rangle$~$2\cdot10^7$ atoms) with 2200 or 4700 Ag atoms. Based on the fact that similar band shifts and band splittings were previously obtained in the spectra of the ν_7 band in Ag-core-ET-shell clusters [16] we assign the peaks in Fig. 1 to ET molecules at the interface with Ag atoms and in the volume of the ET cluster, i.e., I and V, respectively. Upon increase of N_{Ag} the intensity of the I-band increases, whereas that of the V band decreases, indicating a corresponding increase in the fraction of the interfacial ET molecules. This behavior is consistent with clusters composed of ET core and a shell of Ag. The weak feature around 2940 cm^{-1} is assigned to the parallel component of the combination band ν_8+ ν_{11} of ET molecules.

The frequencies of band centers measured in clusters of different composition are displayed in Fig. 2. The results show that the frequency of the band centers change by less than 4 cm^{-1} upon increase of the number of Ag atoms in clusters from ~500 to about ~5000 while the band width of each peak in spectra remains at ~8 cm^{-1}.

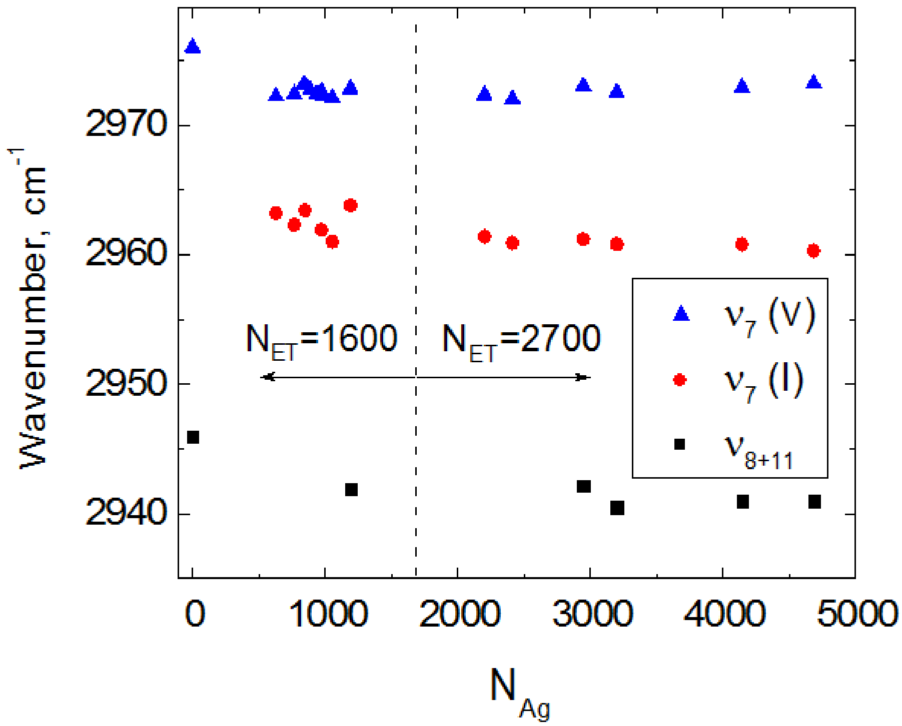

Figure 2. Positions of the band maxima for the ν_{8+11}, ν_7 (I), and ν_7 (V) bands vs N_{Ag} captured upon doping of the He droplets with 1600 and 2700 ET molecules as indicated.

The relative intensities of the I and V bands in Fig. 1 (a) and (b) as measured for varying number of added Ag atoms can be used to infer the structure of the clusters. The fraction of the ET molecules on the surface of a dense, spherical cluster containing 1600 ET molecules, as in Fig. 1 (a), can be estimated from the liquid drop model to be ~35%; *i.e.*, ~540 ET molecules reside in the surface layer of the compact spherical ET cluster. Thus, the predicted ratio of band intensities $I_V/I_I = 1.9$ is in a quantitative agreement ratio obtained from Fig. 1 (a) with 1060 Ag atoms, $I_V/I_I \approx 1.8$. The number of Ag atoms which can be accommodated in the first shell around the ET_{1600} cluster is estimated to be ~1500, based on compact spherical core-shell model.[16] Therefore, the largest amount of silver used here $N_{Ag} = 1060$ in Fig. 1(a) is not sufficient for formation of a continuous and close-packed monolayer of Ag atoms around the ET core cluster. However, adding 850 and 1060 Ag atoms seems to be sufficient to affect nearly all of the surface ET molecules, which could for example be achieved upon random attachment or Ag atoms and small clusters on the surface of the ET cluster. Thus nearly all of the ET molecules on the surface can closely interact with at least one Ag atom. The resulting interaction between the closely spaced ET and Ag causes a large red shift of the ν_7 band of ET molecules on the interface. Due to the fact that the Ag-Ag binding energy is substantially higher than Ag-ET binding energy,[16] one may expect that some rearrangement of the randomly attached Ag atoms will lead to formation of small Ag clusters on the ET surface. Fig. 1 (a) shows that the relative intensity of the I band decreases with decreasing N_{Ag}. In the case of the smallest $N_{Ag} = 630$ in Fig. 1 (a), $I_V/I_I \approx 5$ was found, in qualitative agreement with the expected smaller number of interfacial ET molecules in contact with Ag atoms.

The intensity ratio of the I and V bands can also be discussed in terms of metallicity of the Ag shell. If the layer of Ag atoms were metallic as in the case of Ag core [16] then the I-band would lose about a half of its IR intensity because in the double degenerate $\nu_7(E_u)$ band at least one Cartesian component of vibration dipole moment would be parallel to metallic surface and yield zero IR intensity according to the selection rule for transitions on the metallic surfaces. So, instead of ratio obtained from Fig. 1 (a) with 1060 Ag atoms $I_V/I_I \approx 1.8$ in the case of metallic Ag shell around ET cluster the ratio would be $I_V/I_I \approx 4$. However, the observed ratio $I_V/I_I \approx 1.8$ suggests that both components of $\nu_7(E_u)$ are IR active. Therefore, we conclude that ET clusters produced in smaller He droplets of $N_{He}=5\cdot 10^6$ are likely compact and that the Ag layer does not show metallic properties.

For larger clusters consisting of $N_{ET} = 2700$, see Fig. 1 (b), the measured intensity ratio of $I_V/I_I \approx 1.6$ was determined from a Gaussian peak fit of the spectrum taking a shell of 2200 Ag atoms. For a compact ET core, however, one would expect a number ratio of $N_V/N_I \approx 2.4$. Increasing the number of added Ag atoms to 4700 gives $I_V/I_I \approx 1$ which is even less than the expected ratio of 2.4. This discrepancy is consistent with the formation of ramified ET clusters which will have lower values of N_V/N_I and require a larger number of Ag atoms to saturate the surface of such molecular core. A similar effect has been observed in case of large Ag-ET clusters.[16] A ramified cluster may form in large He droplets via cluster-cluster aggregation, a mechanism discussed previously in Ref. [10]. On the other hand, vortices in large droplets induce the formation of the filament shaped clusters [9,23-26] with larger surface area as compared with the compact spherical clusters.

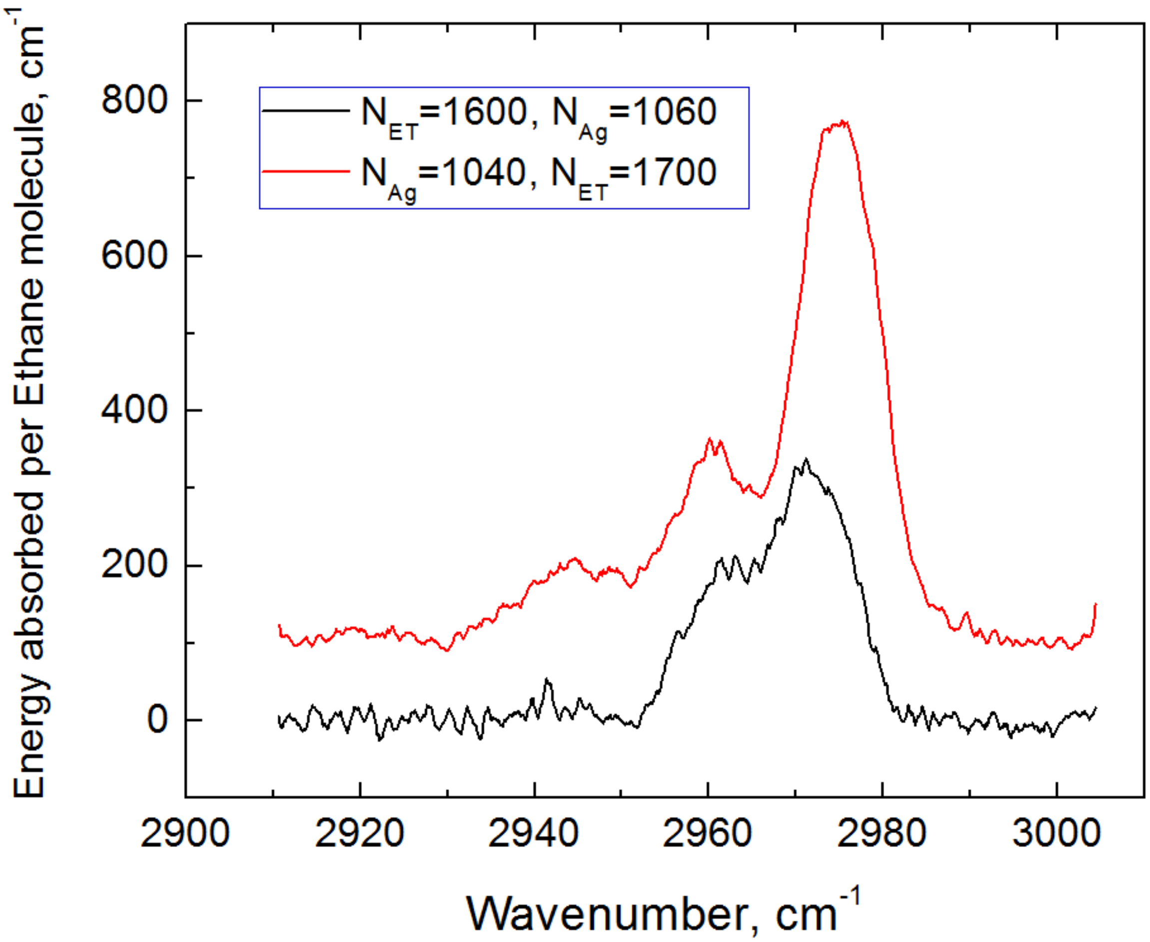

Figure 3. Comparison of the spectra of clusters obtained by doping He droplets of $5 \cdot 10^6$ atoms with ~1000 Ag atoms and ~1600 ET molecules for two different pickup orders. Black trace: doped with ET first, then Ag (same trace as in Fig. 1 (a)); red trace: doped with Ag first, then ET. The larger total integral intensity of the red trace spectrum is likely due to inconsistencies in the alignment of the laser beam during the two measurements on different days.

Figure 3 shows a comparison of the spectra obtained for clusters containing an almost equal number of Ag and ET particles ($N_{Ag} \approx 1000$ and $N_{ET} \approx 1600$), which have been assembled in He droplets of $5x10^6$ atoms. These clusters were, however, produced using two different pickup orders of ET and Ag species. It is seen that in both the spectra the I and V bands are of similar width. The positions of I bands are also very similar, i.e. 2961 and 2960 cm^{-1}, for clusters containing either an ET core or ET shell, respectively. On the other hand, the V band of the ET core - Ag shell clusters is at 2972 cm^{-1} compared to 2975 cm^{-1} in the Ag core - ET shell clusters. The lower frequency of the V band in the ET-Ag clusters is in agreement with the picture of ET molecules being surrounded by Ag. On the other hand, in the Ag - ET clusters the ET molecules on the surface of the clusters have a higher C-H stretch frequency which contributes to the overall higher average frequency of the V band. Due to smaller spacing of the I and V bands in the spectra of the ET-Ag clusters, the two bands appear somewhat less resolved compared to those measured in the Ag-ET clusters.

The ratios of the integrated band intensities I_V/I_I of the two spectra in Fig. 3 were found to be 1.8 and 3.0 in ET-Ag and Ag-ET clusters, respectively. The larger value of I_V/I_I in the Ag-ET is expected because of the smaller fraction of the interface molecules in contact with Ag atoms. Indeed, the compact core of 1040 Ag atoms would have the diameter ≈16 Å and be able to accommodate about 220 ET molecules in the interface layer out of the total 1700 molecules, giving $N_V/N_I \approx 6.7$. The fact that theoretical N_V/N_I ratio is larger than the experimental is in agreement with the ramified structure of the core Ag clusters as has been discussed earlier.[16] Remarkably, no continuum in the spectra due to the absorption of Ag was observed in the ET-Ag clusters (black trace in Fig. 3) while it was pronounced in the Ag-ET clusters such as shown by the red trace in Fig. 3. A similar continuum was observed in the visible and near-infrared part of the spectrum for neat Ag clusters,[10,16] where it was ascribed to formation of Ag cluster− cluster aggregates in large He droplets. The absence of such continuum, is consistent with the presence of Ag on the ET surface in the form of small clusters.

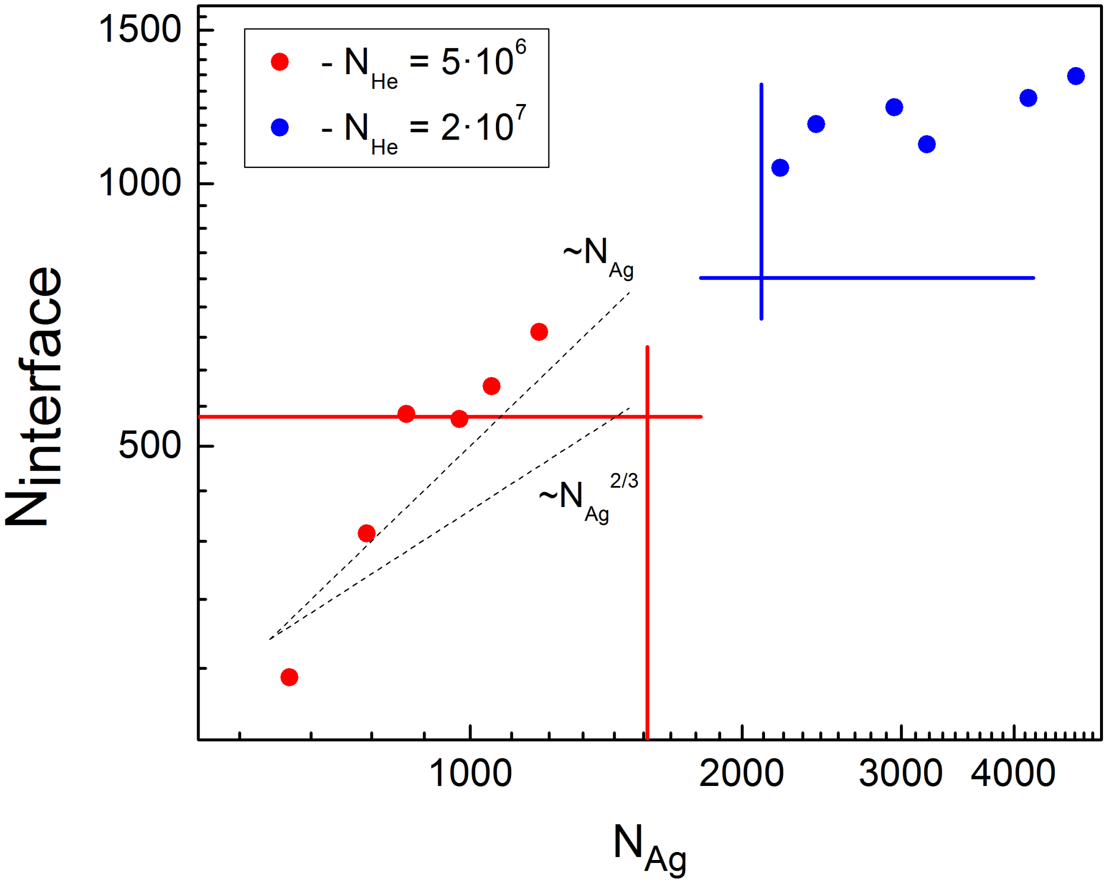

Figure 4. Number of the interfacial ET molecules, N_I, versus the number of added Ag atoms, N_{Ag}, at constant total number of ethane molecules N_{ET} =1600 (red symbols) and N_{ET} =2700 (blue symbols). The number of the interfacial ET molecules and Ag atoms in the compact spherical ET core- Ag shell clusters is shown by the horizontal and vertical lines, respectively. Dashed lines illustrate two different scalings of $N_I \sim N_{Ag}$ and $N_I \sim N_{Ag}^{2/3}$ as indicated in the figure.

Figure 4 shows the number of the interfacial ET molecules, N_I, vs the number of the added Ag atoms, N_{Ag}. The results were obtained from the measured I_V/I_I values at constant N_{ET} =1600 (red symbols) and N_{ET} =2700 (blue symbols). Solid lines show the predictions of the compact spherical cluster models. The horizontal lines give the number of the surface ET molecules, and the vertical lines the number of the Ag atoms in the dense monolayer on the surface of the spherical cluster, calculated as described in Ref. [16]. In the case of the rigid core shell (RCS) structure, upon increase of N_{Ag}, N_I is expected to increase linearly, as it is illustrated by the upper dashed line in Fig. 4, and saturate when N_{Ag} exceeds the number of atoms in the monolayer, at the level shown by horizontal lines. The lower dashed line illustrates the N_I~$N_{Ag}^{2/3}$ scaling which would be observed if for example Ag atoms coagulate into a compact core embedded into the ET cluster. Clearly, the experimental data are better described by the N_I~N_{Ag} scaling indicating that inside the cold helium droplet Ag atoms are trapped one-by-one and do not aggregate into a compact core, despite the fact that this would be the most energetically favorable configuration. Such rearrangement is presumably prevented by the fast cooling of the clusters upon addition of each Ag atom.

Saturation is indeed observed in the larger clusters depicted in Fig. 4 by blue symbols. However, it is seen that in both cases the N_I number exceeds the predictions of the RCS model. This discrepancy may stem from at least two different effects. Firstly, the ET clusters may possess a larger surface are due to deviation from being spherically shaped as discussed previously. [16] Moreover, the model of a monolayer of Ag atoms on the ET cluster surface is likely not very realistic. Calculations indicate that small Ag_n clusters (n=2-6) have planar geometry, whereas larger clusters are three dimensional.[30-31] The weak interaction of Ag atoms with the ET surface may not be sufficient to stabilize a Ag monolayer, and the Ag layer will likely contain a collection of small clusters. In addition, large energy of about 1-2 eV is released upon addition of Ag atoms to those sub clusters [30], which may cause some the submersion of the Ag clusters into the ET cluster, leading to the larger fraction of the interfacial ET molecules. Finally, the formation of clusters containing a homogeneous mixture of the ET molecules and Ag atoms can also be ruled out. In such clusters the saturation will be achieved at much smaller N_{Ag} or about 1/12 of the N_{ET}, which is in disagreement with the experimental results in Fig. 4.

The results in Fig. 4 in smaller and larger droplets correspond to linear and saturated regimes, respectively. Ideally, it would be desirable to span these regimes using He droplets of the same average size. Unfortunately, such experiments are not feasible for ET - Ag clusters. In smaller droplets the limitation is posed by the evaporation of the entire droplet upon capturing of the large number of Ag atoms. On the other hand, experiments with small ET clusters in large He droplets are challenging due to low signal to noise ratio in the infrared spectra.

4. Conclusions

Here we have demonstrated the utility of the helium droplet techniques in the formation of composite clusters consisting of a molecular core with adsorbed Ag atoms . The clusters were assembled via sequential doping of helium droplets with ethane molecules then Ag atoms. Infrared spectroscopic study shows that the vibrational bands of ET exhibit a characteristic splitting which is assigned to two different environments surrounding the molecules, namely either in contact with Ag atoms or not. A similar splitting has been observed previously in clusters consisting of a Ag core and a molecular shell.[16,32] Analysis of the band intensities with varying number of dopant Ag atoms suggests that in spite of the strong pair interaction of Ag-ET and Ag-Ag, the ET core cluster persists leaving the Ag atoms to reside on the surface of the ET cluster. This effect likely relates to the fast dissipation of the heat of formation of the Ag and ET clusters in superfluid helium droplets. We argue that the obtained composite clusters consist of ethane core covered with small Ag clusters having different degree of submergence on the surface. ET clusters of ~500 molecules are likely compact while lager ET clusters of ~3000 molecules have ramified structures. The successive pickup of Ag atoms leads to saturation in the intensity of the interface band as more and more ET molecules with the majority of ET molecules in the outer layer in contact with Ag atoms. The shell of Ag atoms which is formed around the ET core does not display metallic properties in IR spectra of ET which suggests that coagulation of Ag atoms into one large cluster does not take place. Thus, more likely the Ag atoms randomly stick onto the ET surface one-by-one which at higher coverage leads to numerous smaller Ag clusters.

Acknowledgments

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References:

(1) Toennies, J. P.; Vilesov, A. F. Spectroscopy of atoms and molecules in liquid helium. *Ann. Rev. Phys. Chem.* **1998**, *49*, 1-41.
(2) Toennies, J. P.; Vilesov, A. F. Superfluid helium droplets: a uniquely cold nanomatrix for molecules and molecular complexes. *Angew. Chem. Int. Ed.* **2004**, *43*, 2622-2648.
(3) Stienkemeier, F.; Lehmann, K. K. Spectroscopy and dynamics in helium nanodroplets. *J. Phys. B* **2006**, *39*, R127-R166.
(4) Choi, M. Y.; Douberly, G. E.; Falconer, T. M.; Lewis, W. K.; Lindsay, C. M.; Merritt, J. M.; Stiles, P. L.; Miller, R. E. Infrared spectroscopy of helium nanodroplets: novel methods for physics and chemistry. *Int. Rev. Phys. Chem.* **2006**, *25*, 15-75.
(5) Callegari, C.; Ernst, W. E. Helium droplets as nanocryostats for molecular spectroscopy—from the vacuum ultraviolet to the microwave regime. In *Handbook of*

High-resolution Spectroscopy.; Quack, M., Merkt, F., Eds.; John Wiley & Sons, Ltd.: Chichester, 2011; pp 1551-1594.

(6) Callegari, C.; Lehmann, K. K.; Schmied, R.; Scoles, G. Helium nanodroplet isolation rovibrational spectroscopy: methods and recent results. *J. Chem. Phys.* **2001**, *115*, 10090-10110.

(7) Tanyag, R. M.; Jones, C. F.; Bernando, C.; O'Connell, S. M. O.; Verma, D.; Vilesov, A. F. Experiments with large superfluid helium nanodroplets. In *Cold chemistry: molecular scattering and reactivity near absolute zero*; Osterwalder, A., Dulieu, O., Eds.; Royal Society of Chemistry: Cambridge, in press, 2017.

(8) Hartmann, M.; Miller, R. E.; Toennies, J. P.; Vilesov, A. Rotationally resolved spectroscopy of SF_6 in liquid-helium clusters - a molecular probe of cluster temperature. *Phys. Rev. Lett.* **1995**, *75*, 1566-1569.

(9) Gomez, L. F.; Loginov, E.; Vilesov, A. F. Traces of vortices in superfluid helium droplets. *Phys. Rev. Lett.* **2012**, *108*, 155302-1-5.

(10) Loginov, E.; Gomez, L. F.; Chiang, N.; Halder, A.; Guggemos, N.; Kresin, V. V.; Vilesov, A. F. Photoabsorption of Ag_N (N~6-6000) nanoclusters formed in helium droplets: A transition from compact to multi-center aggregation. *Phys. Rev. Lett.* **2011**, *106*, 233401-1-4.

(11) Loginov, E.; Gomez, L. F.; Vilesov, A. F. Surface deposition and imaging of large Ag clusters formed in He droplets. *J. Phys. Chem. A* **2011**, *115*, 7199-7204.

(12) Volk, A.; Thaler, P.; Knez, D.; Hauser, A. W.; Steurer, J.; Grogger, W.; Hofer, F.; Ernst, W. E. The impact of doping rates on the morphologies of silver and gold nanowires grown in helium nanodroplets. *Phys. Chem. Chem. Phys.* **2016**, *18*, 1451-1459.

(13) Thaler, P.; Volk, A.; Knez, D.; Lackner, F.; Haberfehlner, G.; Steurer, J.; Schnedlitz, M.; Ernst, W. E. Synthesis of nanoparticles in helium droplets-a characterization comparing mass-spectra and electron microscopy data. *J. Chem. Phys.* **2015**, *143*, 134201-1-10.

(14) Yang, S. F.; Ellis, A. M. Helium droplets: a chemistry perspective. *Chem. Soc. Rev.* **2013**, *42*, 472-484.

(15) Emery, S. B.; Xin, Y.; Ridge, C. J.; Buszek, R. J.; Boatz, J. A.; Boyle, J. M.; Little, B. K.; Lindsay, C. M. Unusual behavior in magnesium-copper cluster matter produced by helium droplet mediated deposition. *J. Chem. Phys.* **2015**, *142*, 084307.

(16) Loginov, E.; Gomez, L. F.; Vilesov, A. F. Formation of core-shell silver-ethane clusters in He droplets. *J. Phys. Chem. A* **2013**, *117*, 11774-11782

(17) Mozhayskiy, V.; Slipchenko, M.; Adamchuk, V. K.; Vilesov, A. F. The use of helium nanodroplets for assembly, transport and surface deposition of large molecular and atomic clusters. *J. Chem. Phys.* **2007**, *127*, 094701-1-6.

(18) Buchenau, H.; Knuth, E. L.; Northby, J.; Toennies, J. P.; Winkler, C. Mass-spectra and time-of-flight distributions of helium cluster beams. *J. Chem. Phys.* **1990**, *92*, 6875-6889.

(19) Henne, U.; Toennies, J. P. Electron capture by large helium droplets. *J. Chem. Phys.* **1998**, *108*, 9327-9338.

(20) Gomez, L. F.; Loginov, E.; Sliter, R.; Vilesov, A. F. Sizes of large helium droplets. *J. Chem. Phys.* **2011**, *135*, 154201-1-9.

(21) *Handbook of Nanophysics*; Sattler, K. D., Ed.; CRC Press, 2010; Vol. 2 and 6.

(22) Lang, S. M.; Popolan, D. M.; Bernhardt, T. M. Chemical reactivity and catalytic properties of size-selected gas-phase metal clusters; Elsevier: New York, 2007; Vol. 12.

(23) Gomez, L. F.; Ferguson, K. R.; Cryan, J. P.; Bacellar, C.; Tanyag, R. M. P.; Jones, C.; Schorb, S.; Anielski, D.; Belkacem, A.; Bernando, C.; et al. Shapes and vorticities of superfluid helium nanodroplets. *Science* **2014**, *345*, 906-9.

(24) Tanyag, R. M. P.; Bernando, C.; Jones, C. F.; Bacellar, C.; Ferguson, K. R.; Anielski, D.; Boll, R.; Carron, S.; Cryan, J. P.; Englert, L.; et al. X-ray coherent diffraction imaging by immersion in nanodroplets. *Struct. Dynam.* **2015**, *2*, 051102-1-9.

(25) Spence, D.; Latimer, E.; Feng, C.; Boatwright, A.; Ellis, A. M.; Yang, S. F. Vortex-induced aggregation in superfluid helium droplets. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6903-6906.

(26) Jones, C. F.; Bernando, C.; Tanyag, R. M. P.; Bacellar, C.; Ferguson, K. R.; Gomez, L. F.; Anielski, D.; Belkacem, A.; Boll, R.; Bozek, J.; et al. Coupled motion of Xe clusters and quantum vortices in He nanodroplets *Phys. Rev. B.* **2016**, *93*, 180510(R)-1-6.

(27) Herzberg, G. Molecular spectra and molecular structure, II Infrared and Raman spectra of polyatomic molecules; Van Nostrand: Princeton, New Jersey, London, 1968.

(28) Hepp, M.; Herman, M. Weak Combination bands in the 3-mm region of ethane. *J. Mol. Spectrosc.* **1999**, *197*, 56-63.

(29) Abe, H.; Charle, K. P.; Tesche, B.; Schulze, W. Surface-plasmon absorption of various colloidal metal particles. *Chem. Phys.* **1982**, *68*, 137-141.

(30) Chen, M. Y.; Dyer, J. E.; Li, K. J.; Dixon, D. A. Prediction of structures and atomization energies of small silver clusters, Ag_n, $n < 100$. *J. Phys. Chem. A* **2013**, *117*, 8298-8313.

(31) Mancera, L. A.; Benoit, D. M. Vibrational anharmonicity of small gold and silver clusters using the VSCF method. *Phys. Chem. Chem. Phys.* **2016**, *18*, 529-549.

(32) Loginov, E.; Gomez, L. F.; Sartakov, B. G.; Vilesov, A. F. Formation of large Ag clusters with shells of methane ethylene, and acetylene in He droplets. *J. Phys. Chem. A* **2016**, *120*, 6738-6744.

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