

# Absence of the *rotator* phase and evolution of dynamical motions in cluster monolayers

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Alkyl chain dynamics in monolayer protected metal cluster systems has been studied by the quasielastic neutron scattering technique, using two different instruments having very different energy windows. Long chain thiolate protected clusters such as Au-ODT (Au-SC<sub>18</sub>H<sub>37</sub>) are rotationally frozen at room temperature (RT) in a wide time scale of 10<sup>-9</sup> to 10<sup>-12</sup> s. The *rotator* phase is absent at RT even in much smaller chain length systems, Au-OT (Au-SC<sub>8</sub>H<sub>17</sub>) and Au-HT (Au-SC<sub>6</sub>H<sub>13</sub>). Dynamics was found to evolve upon increase in temperature. Alkyl chains in a metal cluster superlattice such as Ag-ODT (Ag-SC<sub>18</sub>H<sub>37</sub>) are also dynamically frozen at RT in the whole time scale range. Evolution of dynamics with temperature is found to be different in the superlattice and isolated cluster systems. In the former, the chains participating in the inter-cluster interaction were found to be dynamically different from those without. On heating just above the chain melting temperature ( $T_{cm}$ ), chains not involved in the inter-cluster interaction become dynamic first. Other chains start softening subsequently and, on increasing temperature near to the superlattice melting, all the chains eventually become dynamic. The uniaxial diffusion motion about the chain axis consistently described the dynamics of the monolayers, both in isolated cluster and in superlattice systems. Direct information on the dynamics of cluster monolayers is obtained for the first time. © 2003 American Institute of Physics. [DOI: 10.1063/1.1544093]

## I. INTRODUCTION

Orientational freedom of the alkyl chain assembly is one of the critical issues concerning the structure of monolayers. Applications of monolayer systems in several areas, utilizing distance specific organization of molecules, depend on the structural and conformational rigidity of the monolayer chain. As a result of this, the phase behavior of self-assembled monolayers (SAMs), being model systems, has been a central point of investigation right from the early period of research in this area. Although the alkyl chain assembly is shown to be all-*trans* in longer chain monolayers, the chain is rotationally disordered down to very low temperatures.<sup>1</sup> The terminal -CH<sub>3</sub> group retains orientational freedom right up to 100 K, according to helium diffraction measurements.<sup>2,3</sup> Infrared spectroscopy<sup>1,4</sup> reveals orientational freedom for the chains above 200 K. The results are in agreement with molecular dynamics studies<sup>5-10</sup> and it is now generally agreed that at room temperature, planar or two-dimensional (2D) monolayers exist in a *rotator* phase.

The monolayer assembly on a metal cluster, alternately referred to as three-dimensional self-assembled monolayers (3D SAMs), is assumed to be similar to that on a planar surface. All the experimental studies<sup>11-16</sup> and molecular dynamics simulations<sup>17,18</sup> point to a picture in which organized alkyl chain bundles are present on cluster surfaces. The packing densities of molecular chains on the cluster surface are higher, but chain disordering temperature is lower than the corresponding planar monolayers as per simulations.<sup>18</sup> Whether alkyl chains possess orientational freedom is an unsolved question. Limited infrared spectroscopic information point to chain length dependent orientational freedom;<sup>19</sup> chains lower than four carbon atoms may exist in a *rotator* phase.

Experiments to resolve this question, such as helium diffraction, are difficult with cluster monolayers. We decided to explore this question using the neutron quasielastic scattering technique. Neutron is a powerful probe<sup>20</sup> to study the dynamics in condensed matter, due to the matching energy scale with the excitations in the system. Further, systems containing protons are more suitable for neutron scattering studies for its large scattering cross-section ( $\sigma_H=80$  barns,  $\sigma_C=5.5$  barns). The random motion of the particles in the system leads to Doppler broadening of the scattered neutrons

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which finally results in the broadening of the elastic line and is known as the quasielastic neutron scattering (QENS) technique. The QENS provides information on the time scale, geometry of motions as well as hindering potential. There are many examples where the QENS technique has been successfully used to elucidate the molecular motions and physical properties related to it.<sup>20,21</sup> These properties make the QENS technique a unique tool to study the dynamics of alkyl chains in systems under investigation. In fact, Barnes<sup>22</sup> had demonstrated application of QENS for studying the “rotator” phase dynamics in *n*-nonadecane way back in 1973.

In the first ever report of dynamics of alkyl chains in monolayer protected clusters (MPCs) using QENS, we presented an investigation on two kinds of cluster systems, namely octadecanethiolate protected gold clusters (Au-ODT), in which the cluster along with its monolayers exist as an isolated molecular entity in the solid state, and octanethiolate protected silver clusters (Ag-OT), which form an extended superlattice in the solid state due to interdigitation of the alkyl chains of adjacent clusters. We compared the results of the cluster systems with a layered silver thiolate, which represents a planar alkyl chain assembly.<sup>23</sup> Clearly there were differences in the dynamical behavior between the isolated cluster and the superlattice systems. QENS data were found to be consistent with a model where the chains undergo uniaxial rotational diffusion about the chain axis in all of the three systems considered.

In this article, we report the *absence* of the *rotator* phase in the alkyl chain assembly in MPCs and the evolution of dynamics in them as a function of temperature as studied by quasielastic neutron scattering technique, probing the dynamics in the time scale of  $10^{-9}$  to  $10^{-12}$  s. We show that long chain thiolate protected clusters are rotationally frozen, suggesting that chains form pillars on the lattice planes of the metal cluster. Dynamics evolve slowly, with increase in temperature. Our studies show that the alkyl chain assembly is denser and is distinctly different from the planar systems, offering definite confirmation to the molecular dynamics results.<sup>17,18</sup>

## II. EXPERIMENTAL METHODS

Preparation and characterization of these nanosystems have been discussed previously.<sup>19</sup> Experimental methodology has been presented in an earlier publication.<sup>23</sup> Briefly, the experiments were carried out using two instruments. The first instrument is a medium resolution quasielastic spectrometer<sup>24</sup> at Dhruva reactor in Trombay. The spectrometer is having an energy resolution of  $200 \mu\text{eV}$  with incident neutron energy of  $5.1 \text{ meV}$ . The quasielastic spectra were recorded in the wavevector transfer ( $Q$ ) range of  $0.8$  to  $1.8 \text{ \AA}^{-1}$ . The sample, contained in a sachet of aluminum foil of  $\sim 1 \text{ mm}$  thickness, was placed at an angle bisecting the incident and the scattered beam. The sample thickness was chosen in order to minimize the multiple scattering effects. The second instrument is a high resolution LAM-80ET spectrometer<sup>25</sup> at KENS, KEK, Japan, which was used to extend the dynamical time scale. The (006) reflection of a mica analyzer provides an energy resolution,  $\Delta E_R$  (FWHM)

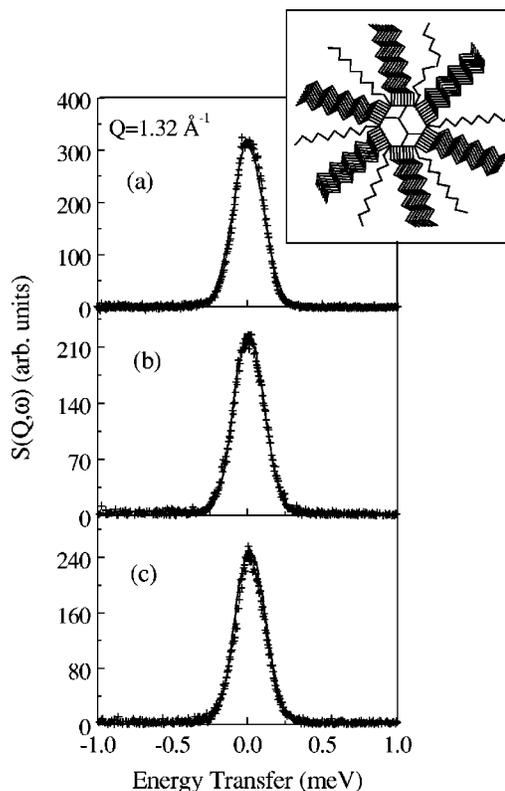


FIG. 1. QENS spectra for (a) Au-ODT (Au-SC<sub>18</sub>H<sub>37</sub>), (b) Au-OT (Au-SC<sub>8</sub>H<sub>17</sub>) and (c) Au-HT (Au-SC<sub>6</sub>H<sub>13</sub>) at room temperature as obtained using QENS Spectrometer at Trombay. The solid line is the resolution function of the instrument. No quasielastic broadening over the instrumental resolution is seen. (Inset) schematic representation of a monolayer protected cluster. The hexagon at the center represents the cluster core and the wiggles represent the alkyl chains. The chains are shown to be all-*trans* as revealed by infrared measurements. The chains form pillars on the cluster surfaces due to interchain interactions. Isolated chains are few and those with defects are rare. One of these isolated chains is shown to possess a *cis*-defect structure. The results reported in this article suggest that pillars without orientational freedom are the most dominant monolayer structures present on cluster surfaces.

of  $17 \mu\text{eV}$  at a fixed final energy of  $1.92 \text{ meV}$  with a  $Q$  range of  $0.25$ – $1.65 \text{ \AA}^{-1}$  and the (004) reflection provides a  $\Delta E_R$  of  $6.5 \mu\text{eV}$ , at a fixed final energy of  $0.85 \text{ meV}$  with a  $Q$  range of  $0.17$ – $1.1 \text{ \AA}^{-1}$ . The raw data in time of flight are normalized with respect to monitor counts and are converted to  $S(Q, \omega)$  using standard programs available at KEK. Measurements were carried out at different temperatures in the range of  $300$ – $400 \text{ K}$ . The temperature measurement was accurate within  $\pm 2 \text{ K}$ .

The systems to be discussed are octadecanethiolate (C<sub>18</sub>H<sub>37</sub>S<sup>-</sup>) stabilized gold clusters (Au-ODT) of  $3 \text{ nm}$  core diameter and two other clusters of shorter chain lengths, namely C<sub>8</sub>H<sub>17</sub>S<sup>-</sup>(Au-OT) and C<sub>6</sub>H<sub>13</sub>S<sup>-</sup>(Au-HT). Results of the measurements with a superlattice of MPCs of similar core dimension, namely Ag-ODT, where the monolayers are strongly interacting, are also presented for comparison. In a superlattice system, the neighboring clusters are anchored to the lattice points as a result of the interdigitation of the monolayer chains.

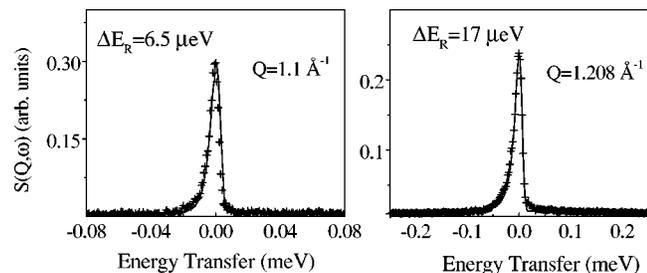


FIG. 2. QENS spectra of Au-ODT (Au-SC<sub>18</sub>H<sub>37</sub>) at RT as obtained using LAM80-ET Instrument at KEK, Japan. The solid line is the resolution function of the instrument. No quasielastic broadening over the instrumental resolution is seen.

### III. RESULTS AND DISCUSSION

#### A. Monolayer protected gold clusters

Schematic of a monolayer protected cluster is shown in Fig. 1 (inset). The hexagonal structure represents the metal core of a MPC and the wiggles are the monolayers anchored on the surface atoms of the cluster core. Alkyl chains may be diverging as they move away from the core.

Figure 1(a) presents the QENS spectra for octadecanethiolate stabilized gold clusters, Au-ODT at RT as obtained using the QENS spectrometer at Dhruva. The instrumental resolution function obtained from a measurement using a standard vanadium sample is shown as the solid line. As evident from the figure, the data do not show any QE broadening over the resolution function of the instrument (solid line) indicating absence of dynamical motion of the alkyl chain. As mentioned above, the QENS spectrometer has an energy resolution of  $\sim 200 \mu\text{eV}$ ; absence of observable QE broadening in this instrument suggests no dynamical motion in the time scale of  $\sim 10^{-11} - 10^{-12}$  s. Further measurements were carried out with the smaller chain length Au-OT and Au-HT systems. The spectra from these systems are also shown in Figs. 1(b) and 1(c) along with the resolution function. No observable dynamical motion was found, suggesting that even for much smaller chain length, no *rotator* phase exists at RT in thiolate protected clusters.

To observe possible dynamics at slower time scales, further measurements were carried out using a high resolution spectrometer LAM80-ET, and no QE broadening was found at RT (Fig. 2). As mentioned above, LAM80-ET uses a mica analyzer; (004) and (006) reflections of mica offers energy resolutions of 6.5 and 17  $\mu\text{eV}$ , respectively. Combining the results of these and the QENS spectrometers with resolution of 200  $\mu\text{eV}$ , it can be said that no dynamical motion is present at RT in these systems over a time scale range of  $10^{-9}$  to  $10^{-12}$  s.

#### B. Evolution of dynamics in Au-ODT with temperature

Although the alkyl chains were found to be dynamically frozen at RT, upon increase of temperature to 340 K, significant QE broadening was observed, suggesting the presence of dynamical motion in the system. It may be noted that differential scanning calorimetry (DSC) showed a transition at 335 K on heating corresponding to the chain melting.<sup>26,27</sup>

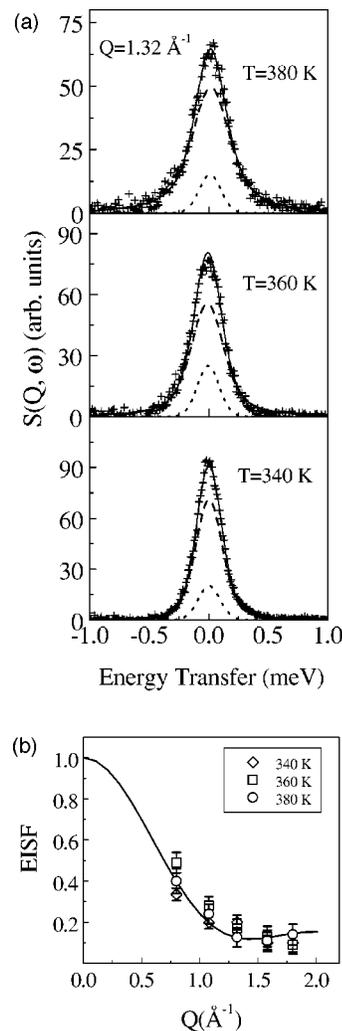


FIG. 3. (a) QENS spectra of Au-ODT (Au-SC<sub>18</sub>H<sub>37</sub>) at different temperatures as obtained using QENS spectrometer at Trombay. Evolution of the dynamics with increase in temperature is evident. (b) Extracted EISF for Au-ODT as obtained from the experimental data. Solid line is as per the model calculation where the alkyl chains undergo uniaxial rotational diffusion about the chain axis.

Therefore, the QENS observation corroborates with DSC results and the observed dynamics should correspond to the motion of the alkyl chains. QENS measurements were also carried out at 360 and 380 K. Typical QENS patterns at different temperatures are shown in Fig. 3(a). To analyze the data for the plausible dynamical behavior, we, in the first instance, separated the elastic and quasielastic components from the total spectrum. As the chains are fixed on the metal cluster, no translational motion is expected for the alkyl chain and therefore, the observed QE broadening should correspond only to the rotational motion of the alkyl chains. Data analysis involves convolution of the scattering law for the molecular rotational motion<sup>20,21</sup> with the resolution function of the instrument, determined by measuring spectra from a standard vanadium sample, and estimating the elastic and quasielastic components by least squares fit to the measured data. From these, the elastic incoherent structure factor (EISF) is evaluated which provides information on the geometry of the motion.<sup>20,21</sup> The extracted EISF is given in Fig.

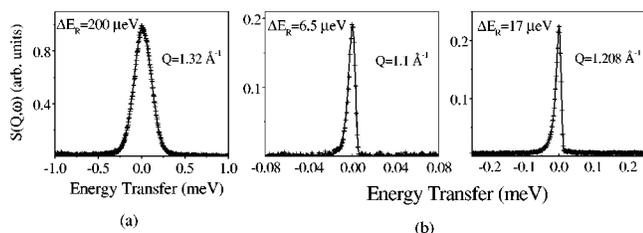


FIG. 4. QENS spectra of Ag-ODT (Ag-SC<sub>18</sub>H<sub>37</sub>), a superlattice MPC sample at RT, as obtained using (a) QENS spectrometer at Trombay and (b) LAM80-ET spectrometer at KEK, Japan. No QE broadening over the resolution of the instrument is observed. Solid line corresponds to the resolution function of the instrument.

3(b). As found in our earlier work,<sup>23</sup> uniaxial rotational diffusion or jump motion among  $N$  equivalent sites on a circle<sup>20–22</sup> with  $N=6$  described the data very well for the MPC system; here also the same model was assumed and found to be adequate. The theoretical EISF as per this model is also shown in Fig. 3(b) as the solid line. In summary, it is found that the alkyl chains are dynamically frozen at room temperature and, upon heating above the chain melting temperature ( $T_{cm}=335$  K), the chains become dynamic and the motions evolve further on heating. The observed dynamics is compatible with a model where the chains undergo uniaxial rotation diffusion or jump diffusion among  $N$  equivalent sites on a circle about the chain axis. A radius of gyration of 2.1 ( $\pm 0.1$ ) Å is also determined from the data. This means that the hydrogens, on the average, are lying on a cylinder of radius 2.1 Å. The residence time, defined as the time between the jumps assuming an instantaneous jump is found to follow the Arrhenius law. The activation energy of rotation is found to be  $6.3 \pm 0.4$  kcal/mol for Au-ODT.

### C. Octadecanethiolate (C<sub>18</sub>H<sub>37</sub>S-) stabilized silver clusters: Ag-ODT

Figure 4 presents the QENS spectra at RT for this system as obtained using the QENS spectrometer at Dhruva as well as the high-resolution spectrometer at KEK. The resolution of the instrument is shown by the solid line. As evident from the figure, data from both the instruments suggest the absence of any QE broadening over the resolution function of the instrument, indicating absence of dynamical motion of the alkyl chain. Combining the results of the two instruments, it can be said that no dynamical motion is present in the system over a time scale range of  $10^{-9}$ – $10^{-12}$  s. However, upon increase of temperature to 340 K, significant QE broadening was observed. It may be noted that DSC showed a transition at 335 K on heating which was attributed to chain melting<sup>26,27</sup> and so the QENS observation is consistent with the DSC results. QENS measurements were also carried out at 360 and 380 K. Typical QENS patterns at different temperatures are shown in Fig. 5(a). As before, we have separated the elastic and quasielastic components from the total spectrum. The extracted EISF at different temperatures are shown in Fig. 5(b). The value of EISF is unexpectedly large even at large  $Q$  ( $\sim 2$  Å<sup>-1</sup>). Large EISF at large  $Q$  values implies that some hydrogen atoms are static and are not participating in the dynamics. Since the hydrogen atoms that are

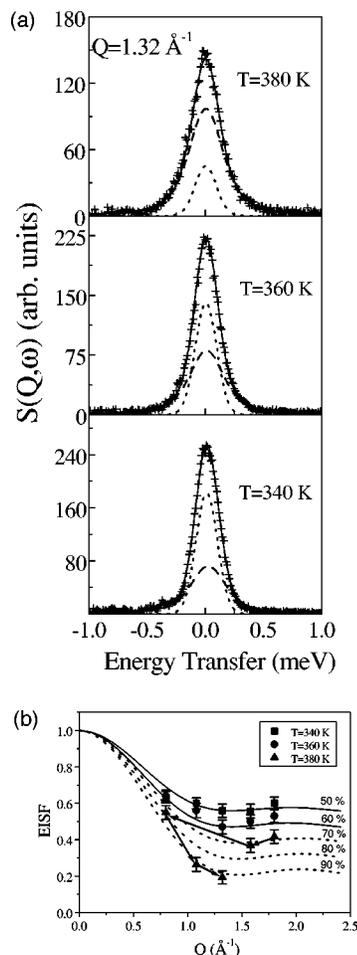


FIG. 5. (a) QENS spectra of Ag-ODT (Ag-SC<sub>18</sub>H<sub>37</sub>), a superlattice MPC at a typical value of  $Q=1.32$  Å<sup>-1</sup> at different temperature as obtained using QENS spectrometer at Trombay. The evolution of the dynamical motion with temperature is evident with the increase of QE component. (b) Extracted EISF for Ag-ODT at different temperatures. The sequence of measurements done at 380 K is also indicated by arrows and the slow melting is evident. The first measurement was done at  $Q=1.8$  Å<sup>-1</sup> and that corresponds to about 70% of the chains being mobile while the last one was done at  $1.32$  Å<sup>-1</sup> which indicates more than 90% of the chains are mobile. This slow melting was checked with repeat measurements also.

not in motion will contribute to the elastic scattering only, the generalized scattering law in such case can be written as

$$S(Q, \omega) = (1 - p_x) \delta(\omega) + p_x [A_0 \delta(\omega) + (1 - A_0) L(\omega, \Gamma)], \quad (1)$$

where  $p_x$  is the fraction of hydrogen atoms in the system participating in the dynamics.  $A_0$  is the EISF and will depend on the model. The first term on the right hand side is the elastic contribution from the static hydrogen atoms in the total spectrum whereas second term is the scattering law for rotational motion weighted with the fraction of hydrogen atoms in the alkyl chains participating in rotational motion. The total elastic fraction can be written as

$$\text{EISF}_{\text{Tot}} = [p_x A_0 + (1 - p_x)]. \quad (2)$$

We attempted to determine  $p_x$  by least squares fit of the extracted EISF from the experimental data using Eq. 2 assuming a suitable model which will determine  $A_0$ . It is known that the variation of EISF for molecules performing

TABLE I. Residence time  $\tau$  (ps) and the fraction of mobile alkyl chain,  $p_x$ , as obtained from the QENS data.

$T$ (K)	Ag-ODT (Ag-C <sub>18</sub> H <sub>37</sub> -)		Au-ODT (Au-C <sub>18</sub> H <sub>25</sub> -)	
	$\tau$ (ps)	$p_x$ (%)	$\tau$ (ps)	$p_x$ (%)
300	...	...	...	...
340	3.5	50	6.2	100
360	3.0	60	3.7	100
380	Time dependent		2.3	100

jump diffusion among  $N$  equivalent sites on a circle<sup>28</sup> for  $N \geq 6$  does not differ significantly<sup>29</sup> from that of a uniaxial rotational diffusion model for  $Q \leq 2.5 \text{ \AA}^{-1}$ . It may be noted that the EISF also depends on the radius of gyration and was kept as a parameter in the least squares fit. The solid line in Fig. 5 represents the least squares fit to the experimental EISF using Eq. (2). It is found that at room temperature about 50% of the chains are contributing to the dynamics. It may be noted that the MPCs exist in the superlattice structure as the chains among neighboring clusters are interdigitated which makes the clusters fixed. Thus the 50% correspond to the fraction of chains, which take part in interdigitation.<sup>23</sup> At 360 K, EISF is found to be lower, indicating that more protons start contributing to the dynamics. The value of  $p_x$  was 0.6 at 360 K. It may be noted that the obtained proportion of the mobile chains is an average number, so more than 50% of the chains are mobile would suggest that chains taking part in the interdigitation start contributing to the dynamics. At 380 K, the behavior of the EISF showed that, even at a constant temperature, the proportion of chains contributing to the dynamics increases slowly with time. Some kind of annealing effect is observed. The contribution towards the elastic part went on reducing. It may be noted that in the spectrometer used for the present study, measurements are done at a particular  $Q$  value at one time. In Fig. 5 we have presented the order in which the spectra were recorded at different  $Q$  values at 380 K. At 380 K, initially about 70% of the chains were contributing to the dynamics and afterwards the contribution went up to 90%. The chains participating in the interdigitation, and static at lower temperatures, are now contributing to the observed dynamics. Again, it was found that data correspond to a model in which the hydrogen atoms of the alkyl chains are lying, on the average, on the surface of a cylinder of radius of about 2.1  $\text{\AA}$ . This result is in accordance with alkyl chain packing as mentioned above. The model  $S(Q, \omega)$  assuming a sixfold jump diffusion model, or uniaxial rotational diffusion about the chain axis with radius of gyration,  $a$  ( $=2.1 \text{ \AA}$ ), was found to give a very good fit to the data over the whole temperature range. The obtained values of the quasielastic fraction ( $p_x$ ) and the residence times at each temperature are given in Table I. When the interdigitated chains also start contributing to the dynamics, the residence time obtained will be an average of the interdigitated and noninterdigitated chains and it is expected that interdigitated ones may have slower motion compared to the noninterdigitated ones.

The present results are in agreement with the literature<sup>14-16</sup> which suggest that long chain monolayers (of

the order of C<sub>18</sub>) anchored on clusters do not exhibit dynamics in the shorter time window. The interlocked alkyl chains of the all trans assembly prohibit free rotation of the chains. This occurs as the individual chains are more closely held (with a chain radius of 2.1  $\text{\AA}$ ) whereas the distance between chains in planar monolayers is  $\sim 5 \text{ \AA}$ . A shorter interchain distance suggests closer surface binding of the monolayers. As the number of sites on each of the planes of the cluster surface is of the order of 10, it is most likely that the available chains form a bundle. Such a bundle, of course, can have only longer time scale motions. It is important to see that this picture of cluster monolayers is valid for shorter chain lengths also. This would imply that the closer surface binding and concomitant interlocking of the chains (and not the van der Waals interactions between the chains) are the dominant aspects controlling dynamics. Thus it is expected that dynamics in different surface planes will be different. A variation in dynamics is expected for different metal clusters as well as chemically different surface binding groups.

#### IV. SUMMARY

Dynamical behavior of the alkyl chains in monolayer protected metal cluster superlattice systems has been studied by the quasielastic neutron scattering technique. The studies have definitively established that monolayers in long chain thiolate protected clusters such as Au-ODT (Au-SC<sub>18</sub>H<sub>37</sub>) are rotationally frozen at room temperature and dynamics evolve upon increase in temperature. The absence of the rotator phase was found to be in a wide time scale of  $10^{-9}$ – $10^{-12}$  s, as studied using two different instruments having very different energy windows. The *rotator* phase is absent even in much smaller chain length systems, Au-OT (Au-SC<sub>8</sub>H<sub>17</sub>) and Au-HT (Au-SC<sub>6</sub>H<sub>13</sub>). Monolayers were found to be dynamically frozen in the superlattice system Ag-ODT (Ag-SC<sub>18</sub>H<sub>37</sub>) also. This was also checked using two different spectrometers providing information over the above mentioned time scale range. The evolution of dynamics with temperature in the superlattice is found to be different than that in the isolated cluster system. Here, the chains participating in the intercluster interaction were found to be dynamically different from those without. On heating just above the chain melting temperature ( $T_{cm}$ ), those chains not involved in the intercluster interaction become dynamic first and, upon further heating, other chains start softening and, on increasing temperature near to the superlattice melting, all the chains eventually become dynamic. Proportion of the mobile chains is found to increase with time at a constant temperature of 380 K.

The data put together suggest that alkyl chains form bundles on the surface of the clusters and within each of these bundles, interchain interaction is significant and the chains get locked up (radius of the chain  $\sim 2.1 \text{ \AA}$ ). It appears that in a superlattice structure, both bundles and isolated chains exist. It may also be that monolayers exist only as bundles, even in these systems as well, but they are of two distinctly different kinds, with different temperature evolution of dynamics.

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