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Comments

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Chlorine Adsorption Induced Structure and Energetics Change of Vinyl Chloride Physisorbed on Ag(111)

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Abstract:

On the Ag(111) surface pre-adsorbed with Cl, TDS and HREELS studies find that vinyl chloride physisorbs molecularly with a binding energy 8 kJ/mol stronger and an adsorption geometry more parallel to the surface in comparison with adsorption on clean Ag(111). The vinyl chloride in close proximity to the surface Cl has stronger binding energy than the ones further removed from Cl. The binding energy change due to surface Cl can be modeled with charge-dipole interaction between the negatively charged Cl and the large molecular dipole of vinyl chloride.

I. Introduction

The adsorption structure and energetics of vinyl chloride on the Ag(111) surface, one of the few systems of molecules *physisorbed* on metal surfaces that have demonstrated substrate-mediated photochemical activity,¹⁻³ have been characterized⁴ using Thermal Desorption Spectroscopy (TDS) and High Resolution Electron Energy Loss Spectroscopy (HREELS). Vinyl chloride of low sub-monolayer (ML) coverage is found to adsorb molecularly on Ag(111) up to 122 K with a desorption activation energy of 28 kJ/mol. At 126 K vinyl chloride may dissociate into vinyl and Cl, which undergo second order recombination at 190 K with activation energy of 46 kJ/mol. Upon ultraviolet laser irradiation, *physisorbed* vinyl chloride dissociates, via molecular anion formation induced by substrate electron attachment,³ into products chloride and vinyl. Recombination of the latter, through a first order, diffusion limited process at 249 K with an activation energy of 43.5 kJ/mol, forms 1,3-butadiene.

It is generally anticipated that chloride (the Cl atom) would have strong interactions with the Ag surface. Electron transfer from Ag to Cl in the Ag-Cl bonding would result in a chloride adsorption site with negative charge. These charge centers are expected to affect the adsorption of the vinyl chloride molecule, which has a relatively large molecular dipole moment.

In general, adsorbate-adsorbate interactions are in the range of 0.4-40 kJ/mol and can be as strong as adsorbate-substrate interactions in physisorbed systems and consequently affect the adsorption. Adsorbate-adsorbate interactions are mimicked through the space and/or mediated through the substrate.⁵ As an example of the latter, electronegative co-adsorbates may deplete metal states near the Fermi level,⁶ reducing the

degree of back donation of electron density from the metal to the adsorbate. Electronegative adsorbates also increase the local work function.⁷⁻⁹ These adsorbate-substrate interactions would affect long range adsorption structure as the system attempts to minimize the total free energy by maximizing attractive and minimizing repulsive interactions.⁵

One example of the effect of co-adsorbed electronegative adsorbate is found on Ag(100) where sub-monolayer ethene is weakly π bonded with the molecular plane parallel to the surface plane.¹⁰ With co-adsorbed Cl ($\theta_{\text{Cl}}=0.065$), ethene adsorption is enhanced as the Cl withdraws electron density from the metal, which increases ethene's ability to donate π electron density to the metal, resulting in stronger ethene-Ag binding. Ethene was found to first adsorb onto the region around the Cl before regions of the surface away from the Cl.

In this letter, we report the effect of co-adsorbed Cl on the adsorption structure and energetics of vinyl chloride on Ag(111) as a case study for how charged centers on a surface may affect the physisorption of molecules with large dipole moments.

II. Experimental

Two UHV chambers, each with a base pressure of 1×10^{-10} Torr, were used.^{3,4} The first chamber was used for the TDS experiments in which the 1.5 cm diameter Ag(111) sample is mounted on a cryostat that can be cooled with liquid nitrogen to below 85 K or resistively heated at 1 K/sec. Ag(111) is cleaned with cycles of Ne sputter and anneal routinely before each experiment. The sample is positioned with the surface normal parallel to the quadrupole axis of the mass spectrometer, 1 cm from the 0.385 cm

diameter nose cone entrance. The second chamber was used for the HREELS experiments. The sample is mounted on a liquid nitrogen cooled cryostat with a base temperature of 90 K. The sample is Ar sputtered and annealed before each experiment. The HREELS (LK Technologies Model 3000) is a double pass instrument, which consistently achieves less than 4 meV resolution with 10^5 - 10^6 counts per second on the clean Ag(111) surface. Before use, vinyl chloride (Matheson, 99.5% purity) is further purified in a glass vacuum line (10^{-6} Torr) by passing the gas through a series of two cyclohexane slush baths ($\sim 6^\circ\text{C}$). Spectroscopic grade CCl_4 (Acros, > 99 % purity) is thermally dissociated to produce Cl atoms for adsorption onto Ag(111) following the procedure described by Polanyi and coworkers.¹¹ Dosing in both chambers is done through the backfilling method and a series of exposure experiments were used to calibrate dosing in the chamber and determine the coverage-exposure relationship.

III. Results and Discussion

The bottom curve of Figure 1 shows TDS of 0.03 monolayer (ML) vinyl chloride on Ag(111). The very low coverage TDS reveals two features that can be characterized as a first order molecular desorption feature at 122 K and a second order, coverage dependent, recombinative (vinyl plus Cl) desorption feature at 190 K.⁴ Using the Redhead method,¹² the molecular desorption feature can be analyzed to show an activation energy of 28 kJ/mol. Fitting the second order rate equation,¹³ the recombinative desorption feature has an activation energy of 46 kJ/mol.

In contrast, the top curve of Figure 1 shows TDS of 0.03 ML vinyl chloride adsorbed on an Ag(111) surface pre-adsorbed with 0.03 ML Cl. This curve also displays

two desorption features. The molecular desorption on Cl-Ag(111), however, is at 154 K versus 122 K on Ag(111). Redhead analysis gives a desorption activation energy of 36 kJ/mol for the Cl-Ag(111) surface, an 8 kJ/mol increase compared to the clean Ag(111) surface. The second order, coverage dependent, vinyl plus Cl recombinative desorption feature, on the other hand, is at the same temperature of 190 K with an activation energy of 46 kJ/mol for both Cl-Ag(111) and Ag(111) surfaces. This is not surprising, as both surfaces at this temperature have Cl coverage and the recombination depends on the amount of vinyl, which is the same for both cases.

The middle curve of Figure 1 is 0.03 ML vinyl chloride on Ag(111) pre-adsorbed with 0.003 ML Cl. The second order, vinyl plus Cl recombinative desorption feature is at 190 K, the same as with the other two curves. However, there are two molecular desorption features at lower temperatures. One feature is at 154 K with activation energy of 36 kJ/mol, the same as the peak observed in the top curve where the pre-adsorbed Cl coverage is 0.03 ML. In addition, the middle curve has a second molecular desorption feature at 137 K with an activation energy of 32 kJ/mol. This second feature lies between the vinyl chloride molecular desorption feature at 122 K for Ag(111) and 154 K for 0.03 ML Cl-Ag(111).

Figure 2 shows HREELS taken for the vinyl chloride-Ag(111) system. The bottom curve is for 1.0 ML vinyl chloride physisorbed on Ag(111) at 90 K. The top curve is for monolayer saturation coverage of vinyl and Cl, obtained by dosing vinyl chloride continuously with the surface at 126 K where vinyl chloride dissociates on Ag(111) and after saturation, flashing to 155 K to ensure no molecular vinyl chloride is present, then cooling to 135 K to obtain the spectrum. The two HREELS spectra can be

assigned, respectively, to features associated with vinyl chloride (bottom) and vinyl and Cl (top). The HREELS spectrum taken for vinyl and Cl on Ag(111), the top curve of Figure 2, indicates that C_2H_3 adsorbs as vinyl, rather than ethylidene.⁴ The middle curve is for 1.0 ML vinyl chloride physisorbed on 0.03 ML Cl-Ag(111), with assignments made in comparison to vinyl chloride (gas), vinyl chloride (liquid), vinyl chloride on Ag(111), and vinyl and Cl on Ag(111). Table 1 summarizes the HREELS assignments. The vinyl chloride on Cl-Ag(111) spectrum has a prominent feature at 246 cm^{-1} , representing the pre-adsorbed Cl-Ag(111) stretch. The spectrum also has a prominent H-C-Cl twist feature at 658 cm^{-1} , a slight shift upward from the analogous feature at 615 cm^{-1} on Ag(111). The feature at 966 cm^{-1} is assigned to the CH_2 wag and the CH_2 twist, again a slight shift upward from the analogous features at 929 cm^{-1} on Ag(111). The C=C stretch is at 1581 cm^{-1} , a slight shift downward from the same feature at 1605 cm^{-1} on Ag(111). The various CH stretching frequencies are shifted slightly lower than comparable features on Ag(111). The very prominent feature at 794 cm^{-1} on the top curve, representing CH_2 wag – CH wag for the vinyl species, is notably absent for vinyl chloride adsorbed on Cl-Ag(111), indicating no dissociation, consistent with TDS results.

For the vinyl chloride on Cl-Ag(111), the out-of-plane modes (H-C-Cl twist, CH_2 twist, CH_2 wag) are higher intensity than for vinyl chloride on Ag(111) and the in-plane modes (CH_2 scissors, C=C stretch) are lower intensity. These intensity differences indicate, based on HREELS selection rules for dipole active modes, that the vinyl chloride on Cl-Ag(111) has its molecular plane closer to surface parallel than does the molecule on Ag(111). Note also that on Cl-Ag(111), the in-plane modes of C-Cl stretch at 701 cm^{-1} and CH_2 rock at 1027 cm^{-1} on Ag(111) disappear, which is consistent with

the vinyl chloride molecular plane oriented more parallel to the Cl-Ag(111) surface than the Ag(111) surface.

The HREELS spectrum has been analyzed to show⁴ that vinyl chloride physisorbs on clean Ag(111) with its carbon-carbon axis tilted $\sim 64^\circ$ from the surface normal (θ) and its molecular plane $\sim 33^\circ$ from the surface plane (ϕ), as shown in Figure 3. The semi-empirical $\pi\sigma$ parameter¹⁴ describes the extent of rehybridization of π -bonded species upon adsorption and can be applied to the vinyl chloride-Ag(111) system. The $\pi\sigma$ parameter ranges from 1 for sp^3 hybridized chloroethane to 0 for sp^2 hybridized vinyl chloride. For vinyl chloride physisorbed on Ag(111), we determine a $\pi\sigma$ parameter of 0.04, indicating no rehybridization upon adsorption. The middle curve of Figure 2 shows vinyl chloride adsorbed to Cl-Ag(111) at 90 K. Using our previous analysis technique,⁴ vinyl chloride physisorbs on Cl-Ag with its carbon-carbon axis tilted $\sim 77^\circ$ from the surface normal (θ) and its molecular plane $\sim 9^\circ$ from the surface plane (ϕ), as shown in Figure 3. In this case the molecule is more parallel to the Cl-Ag(111) surface than the Ag(111) surface, presumably because the more parallel orientation, with its associated molecular dipole parallel to the surface, maximizes the charge-dipole interaction of the planar vinyl chloride molecule with the negatively charged Cl. The $\pi\sigma$ parameter on Cl-Ag(111) is determined as 0.06, indicating that on Cl-Ag(111) vinyl chloride adsorbs without rehybridization.

As shown by HREELS, vinyl chloride does not rehybridize upon adsorption on Ag(111) or Cl-Ag(111). The TDS of Figure 1 provide insight into the nature of the adsorption interaction. For 0.03 ML vinyl chloride, the density of adsorbate molecules is sufficiently small that there is little vinyl chloride-vinyl chloride interaction. The

desorption energy difference of 8 kJ/mol between the top and bottom curves of Figure 1, then, must be due to the presence of Cl. Cl is electronegative and is expected to withdraw electron density from the surface, causing Cl to carry a partial negative charge. Ag has little ability to donate electron density to vinyl chloride and likewise, vinyl chloride has little ability to donate π electron density to the silver d bands, which are about 3.9 eV below Fermi level. As a result, and consistent with HREELS, there is no vinyl chloride rehybridization on Ag(111) or Cl-Ag(111). Therefore, the 8 kJ/mol increase in desorption activation energy must be due to direct interaction between Cl and vinyl chloride, rather than via a through-the-metal interaction.

Since the Cl carries a partial negative charge and vinyl chloride has a dipole moment of 1.4 D, a first order approximation of the interaction can be modeled with a charge-dipole interaction. In calculating the charge-dipole attraction between the negative Cl and vinyl chloride, the charge-dipole repulsion between the positive image charge in the metal and the vinyl chloride must also be included. In the calculation, we use the Cl adsorbed on Ag(111) with a full -1 point charge at 2.7 Å above the surface,¹⁵ and based on the geometry of vinyl chloride, approximate the dipole moment center to be 5 Å from the point charge. The result is a first order approximation of ~13 kJ/mol attraction and ~4 kJ/mol repulsion, for a total of ~9 kJ/mol difference between adsorption of vinyl chloride on Cl-Ag(111) versus Ag(111), consistent with the 8 kJ/mol experimentally determined difference.

The middle TDS curve of Figure 1, 0.03 ML vinyl chloride adsorbed on 0.003 ML Cl-Ag(111), warrants further comment. The middle TDS curve arises from a surface with the same coverage of vinyl chloride as the other two curves, however, this surface

has an order of magnitude less pre-adsorbed Cl than the top-curve surface. The middle curve has the same vinyl plus Cl recombinative desorption feature at 190 K as the other two curves. Its 154 K feature appears at the same temperature as the one in the top curve representing physisorbed vinyl chloride more tightly bound because of interaction with the pre-adsorbed Cl. However, the 154 K feature of the 0.003 ML Cl surface is smaller than in the top curve from the 0.03 ML Cl surface. In the top curve, the quantities of vinyl chloride and Cl are such that all of the vinyl chloride molecules are adsorbed similarly relative to Cl, therefore, there is a single desorption feature. In contrast, the middle curve has two (137 K, 32 kJ/mol activation energy and 154 K, 36 kJ/mol) desorption features, indicating physisorbed vinyl chloride with two different types of adsorption relative to the pre-adsorbed Cl. For the surface with low quantity of pre-adsorbed Cl (0.003 ML), we propose that only a portion of the 0.03 ML of vinyl chloride is able to adsorb in positions relative to the Cl that result in a desorption temperature of 154 K. The adsorption sites nearest to the Cl with the greatest binding energy are saturated first. The remaining vinyl chloride then adsorbs in positions with less binding energy, presumably farther away from the negative Cl, and desorb in the second feature at 137 K. The implication of these two physisorbed desorption features in the middle curve is that the pre-adsorbed Cl induces some type of ordering of vinyl chloride around Cl on the surface.

IV. Conclusion

We have determined that vinyl chloride physisorbs molecularly on Cl-Ag(111) with no rehybridization and an adsorption energy 8 kJ/mol higher than on Ag(111). On

both surfaces the vinyl chloride adsorbs with its molecular plane approximately parallel to the surface, but on the Cl-Ag(111) surface, the vinyl chloride plane is more parallel to the surface plane. The Cl-vinyl chloride interaction may be modeled with a simple charge-dipole interaction that is consistent with the experimentally determined desorption activation energy. TDS peaks also indicate that vinyl chloride adsorbed closer to the Cl atom has a stronger binding energy to the surface.

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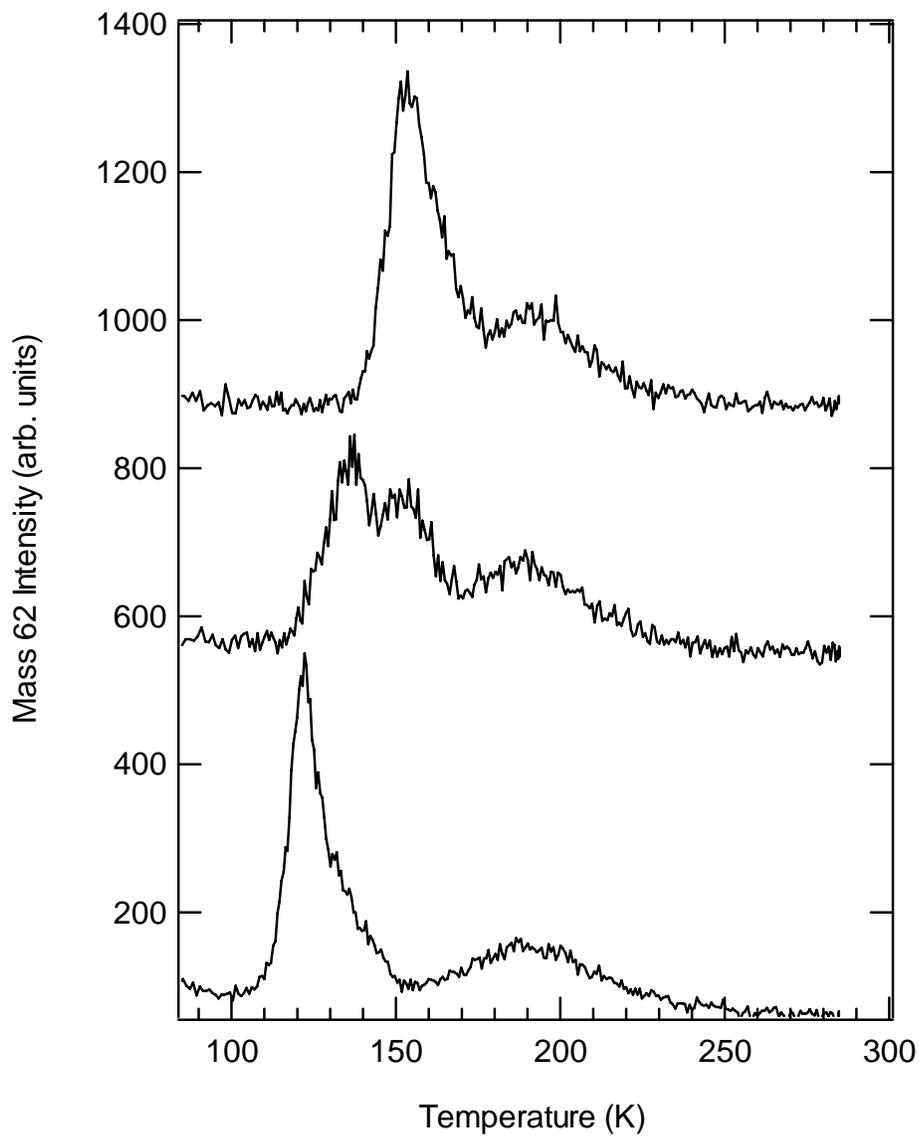


Figure 1. Mass 62 (vinyl chloride) TDS spectra for 0.03 ML vinyl chloride. Top curve has 0.03 ML pre-adsorbed Cl on Ag(111), middle curve has 0.003 ML pre-adsorbed Cl on Ag(111), and bottom curve has no pre-adsorbed Cl.

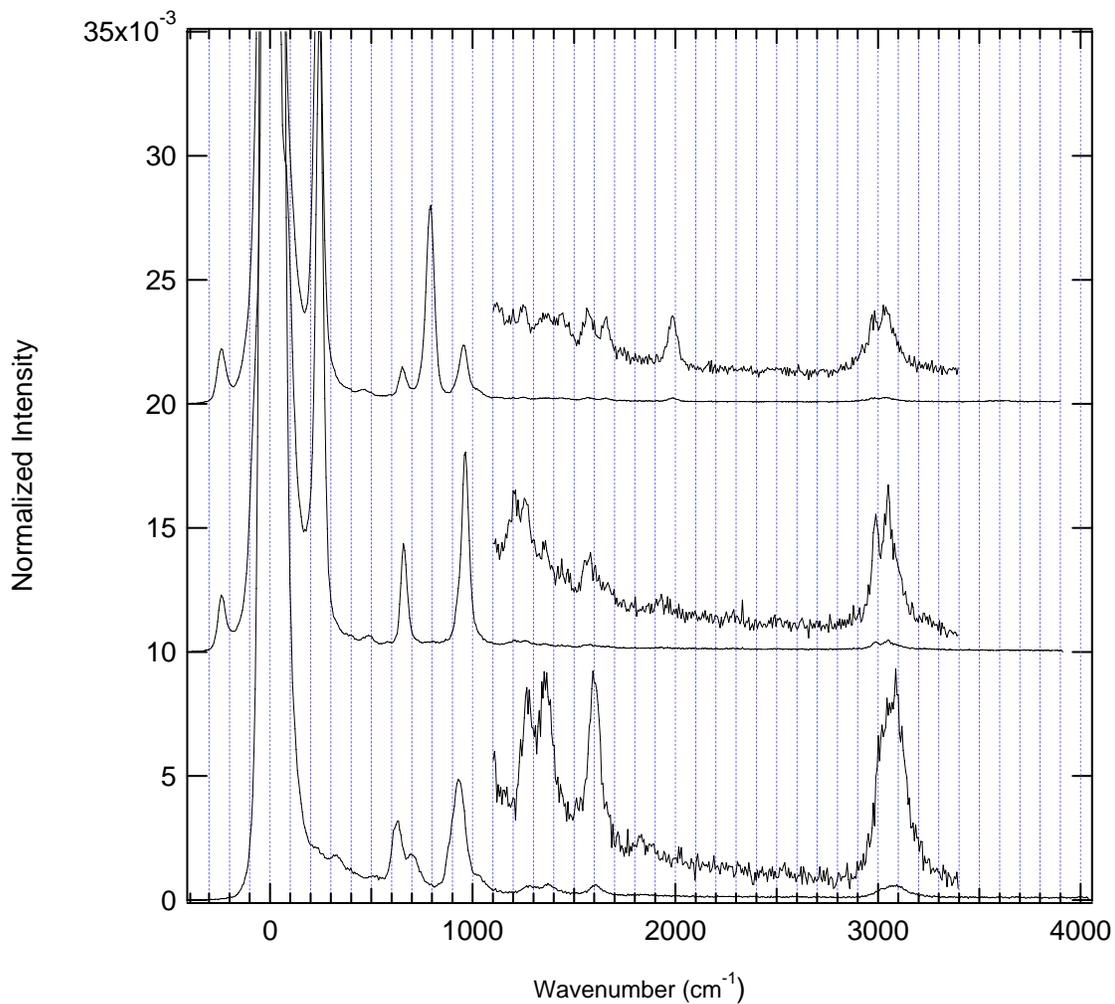


Figure 2. HREELS of vinyl and Cl adsorbed on Ag(111) (top), vinyl chloride physisorbed on Cl-Ag(111) (middle), and vinyl chloride physisorbed on Ag(111) (bottom). Expanded curves are $\times 15$ for 1100 cm^{-1} to 3400 cm^{-1} .

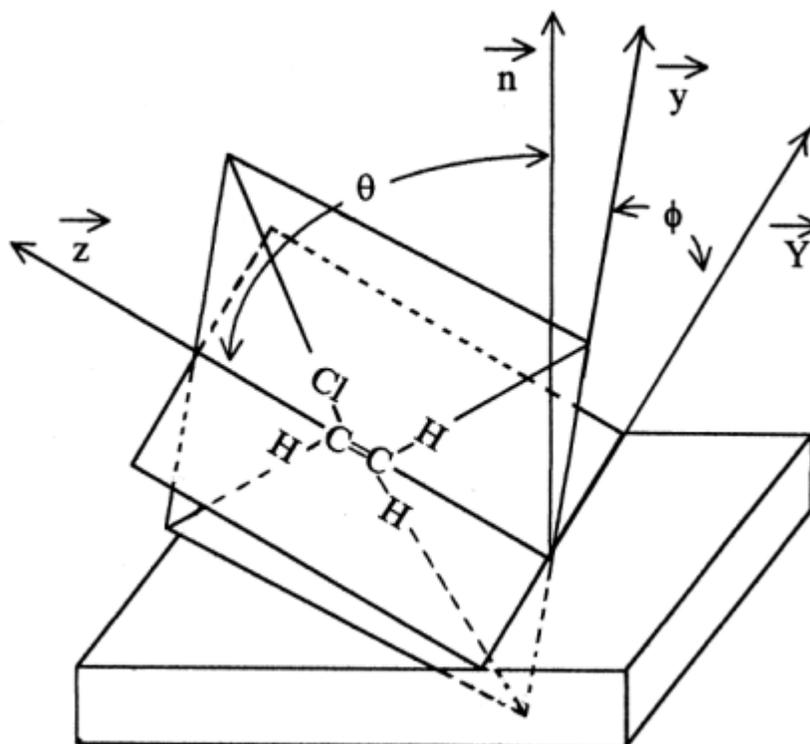


Figure 3. Orientation of vinyl chloride with respect to the surface as determined by comparison of HREELS and IR frequencies and intensities for vibrational modes.¹ For vinyl chloride physisorbed on Ag(111), $\theta=64\pm 1^\circ$ and $\phi=33\pm 1^\circ$. For vinyl chloride physisorbed on Cl-Ag(111), $\theta=77\pm 11^\circ$ and $\phi=9\pm 7^\circ$.

Table 1

Assignments of HREELS spectra to vinyl chloride, vinyl, and Cl on Ag(111). For comparison the gaseous and liquid vinyl chloride IR spectra assignments are also listed.

Vibrational Motion	C ₂ H ₃ Cl _(g) ¹⁶	C ₂ H ₃ Cl _(l) ¹⁷	HREELS 1.0 ML C ₂ H ₃ Cl on Ag(111) ⁴	HREELS 1.0 ML C ₂ H ₃ Cl on Cl-Ag(111)	HREELS H ₂ C=CH- & Cl on Ag(111) ⁴
Cl-Ag stretch				246	240
C=C-Cl rock	395	398	326		
C-Ag stretch					462
H-C-Cl twist	620	626	615	658	
Cl-Ag + C-Ag					652
C-Cl stretch	720	705	701		
CH ₂ wag – CH wag					794
CH ₂ twist	896	903	929	966	
CH ₂ wag	941		929	966	
CH ₂ wag + CH wag					954
CH ₂ rock	1030	1026	1027		
CH ₂ rock + CH rock					1127
CH rock					1249
CH deformation	1279	1275	1267	1255	
CH ₂ scissors	1369	1365	1353	1359	1348
C=C stretch	1608	1605	1605	1581	1563, 1661
CH stretch	3030	3028	3087	2989	3028
CH ₂ sym stretch	3086	3080	3087	2989	2984
CH ₂ asym stretch	3121	3112	3087	3051	3028