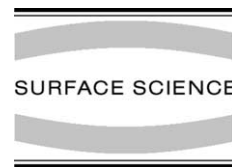




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# An investigation of the surface chemistry of crown ethers: the adsorption and reaction of 12-crown-4 on palladium (1 1 1)

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## Abstract

The adsorption of 12-crown-4 on Pd(1 1 1) is investigated using reflection–absorption infrared spectroscopy and temperature-programmed desorption. Analysis of the infrared spectrum of 12-crown-4 suggests that it adsorbs in a flat-lying geometry with  $C_{4v}$  symmetry with a saturation coverage of  $0.073 \pm 0.008$  monolayers. This implies that the crown ether bonds to the surface via the lone pair orbitals on the ether oxygen atoms. Estimating the saturation coverage for this geometry using Van der Waals' radii yields a value of 0.088 monolayers in good agreement with the measured value. 12-crown-4 thermally decomposes to leave predominantly CO and ethynyl species on the surface where the desorbing CO removes three of the four crown ether oxygen atoms, the fourth remaining on the surface. Small amounts of ethylene are also found to desorb along with a high molecular weight product which is tentatively assigned to the formation of  $C_2H_5OCH_2CHO$ . © 2001 Published by Elsevier Science B.V.

*Keywords:* Ethers; Palladium; Thermal desorption; Infrared absorption spectroscopy; Surface structure, morphology, roughness, and topography

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## 1. Introduction

The concept of “self-assembled” systems has evolved over the past few years [1]. On surfaces, self-assembled monolayers have been synthesized, where the formation of ordered arrays is driven by intermolecular Van der Waals' interactions between the long, anchored chains [2–12]. Rotaxanes provide an example of macromolecular assemblies in homogeneous phase and consist of a linear

spindle molecule threaded through a macrocyclic ring where the spindle is generally trapped in the ring by large terminal groups at either end [13–20]. Variants of these systems, pseudorotaxanes, have been fabricated in which the spindle is not locked in place by the presence of large terminal groups but is merely threaded through the center of the cyclic molecule [21,22]. Such molecular systems have been suggested to have potential for forming the basis for analogs of mechanical devices that operate at the molecular level, such as switches [23–30], ratchets [31,32] and motors [33–36]. Clearly, the long-term utility of such devices rests on the ability to anchor such macromolecular assemblies to surfaces. Rotaxanes have been grafted

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onto gold surfaces by attaching them via thiol functionalities [37]. Our goal, a portion of which is outlined in the following, is to grow rotaxanes directly on a single crystal surface. Our approach is to first prepare a compact overlayer comprising macrocyclic rings using crown ethers and then to allow an axle molecule to penetrate this ring by subsequent absorption onto this surface. Crown ethers have been extensively used in rotaxane syntheses. These are cyclic polyethers having a general formula  $(\text{CH}_2\text{OCH}_2)_n$  so that the oxygen forms an ether linkage [38]. These are named  $3n$ -crown- $n$ , where each of the  $n$  oxygen atoms is bound between two carbon atoms arranged in a ring consisting of  $3n$  (either oxygen or carbon) atoms. 12-crown-4 is depicted in Fig. 1 where the gas-phase molecular structure, in this case, was determined with HyperChem using MM+. In order for the axle molecule to be able to bond to the metal through the orifice in the adsorbed crown ether, it should adsorb with a planar geometry. One of the important properties of crown ethers is their ability to complex with various ionic species through interactions with the oxygen lone pairs providing a simple example of “host-guest” chemistry [39–41]. An analogous bonding configuration on a metal surface would lead to a geometry in which the axle molecule is appropriately oriented to potentially form the rotaxane. It has been

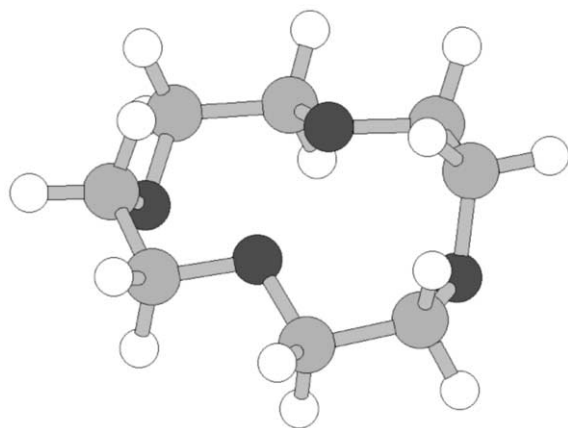


Fig. 1. Ball and stick depiction of 12-crown-2 where the gas-phase geometry was calculated with HyperChem using MM+. Oxygen atoms are indicated in black, carbon in gray and hydrogen in white.

shown previously using infrared spectroscopy that 1,4-dioxane (which, using the crown ether nomenclature, would be 6-crown-2) changes from its gas-phase chair to a boat conformation when adsorbed on Pd(1 1 1) [42], in accord with this idea.

We will subsequently adsorb acetonitrile and methyl isocyanide onto the crown-ether-covered surface to synthesize the rotaxane. These have been investigated previously on Pd(1 1 1) [43]. In particular, acetonitrile was found to adsorb in an  $\eta^2(\text{C},\text{N})$  configuration. The steric constraint imposed by the presence of the crown ether may also cause this to reorient on the surface. In this context, polymeric systems designed to behave as molecular wires have been fabricated using aryl isocyanides ( $\text{CNC}_6\text{H}_4\text{NC}$ ) in which the  $\pi$ -conjugation is maintained throughout [44,45]. Similar crown ether template induced reorientation of adsorbed aryl isocyanides may optimize  $\pi$ -overlap between the isocyanide and the surface.

## 2. Experimental

The experiments were carried out in two stainless-steel, ultrahigh vacuum chambers operating at base pressures of  $1 \times 10^{-10}$  Torr following bakeout and which have been described in detail elsewhere [46,47]. Infrared data were collected from a palladium single crystal sample mounted in a modified 2 3/4 in. six-way cross equipped with infrared transparent, KBr windows. The sample could be resistively heated to 1200 K, or cooled to 80 K by thermal contact with a liquid nitrogen filled reservoir. Light from a Bruker Equinox infrared spectrometer, typically operating at  $4 \text{ cm}^{-1}$  resolution, passes through a polarizer and is focused onto the sample at an incidence angle of  $\sim 80^\circ$  and the reflected light steered onto a liquid-nitrogen-cooled, mercury cadmium telluride detector.

In the second chamber, the sample was mounted to a carousel-geometry manipulator and could similarly be resistively heated to 1200 K and cooled to 80 K by thermal contact to a liquid-nitrogen-filled reservoir. Temperature-programmed desorption (TPD) data were collected using a heating rate of  $\sim 7 \text{ K/s}$  and desorbing species detected using a Dichor quadrupole mass spectro-

meter interfaced to a PC allowing five masses to be monitored sequentially during the same desorption sweep. In order to further minimize spurious signals, the mass spectrometer is enclosed in a shroud with a 1 cm diameter hole in the front. 12-crown-4 was dosed via a tube (6 mm diameter with the end located at  $\sim 5$  mm from the Pd(1 1 1) face) which minimized background contamination and dosing of the supports. This gave a pressure enhancement compared to the background pressure of  $\sim 58$  as measured by carrying out a King and Wells experiment [48] using acetylene and comparing the resulting uptake curve measured by backfilling the chamber [49].

The Pd(1 1 1) sample is cleaned using a standard procedure which consists of heating to 1000 K in  $\sim 4 \times 10^{-8}$  Torr of oxygen and annealing to 1200 K in vacuo to remove any remaining oxygen. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak, Auger spectroscopy is not particularly sensitive to the presence of small amounts of carbon on the surface. It was found that a more sensitive measure of carbon coverage was to saturate the surface with oxygen and to perform a TPD experiment. The presence of surface carbon is manifested by the desorption of CO. As the surface becomes depleted of carbon, the CO yield decreases and the yield of oxygen increases correspondingly. The complete absence of carbon is indicated by the desorption of only O<sub>2</sub>. The Pd(1 1 1) sample was judged to be clean when no CO desorption was detected from the surface.

The 12-crown-4 (Aldrich, 99+%) used for these experiments was transferred to a glass vial and further purified by repeated freeze-pump-thaw cycles and its cleanliness monitored mass spectroscopically. The purity was further established using infrared spectroscopy by condensing a multilayer on the sample and by comparing the infrared data with the published gas-phase spectrum.

### 3. Results

Shown in Fig. 2 are a series of TPD spectra monitoring 28 amu as a function of 12-crown-4

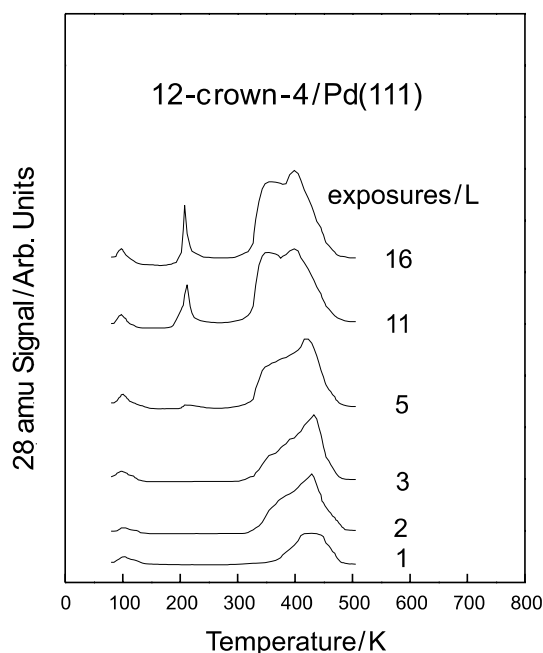


Fig. 2. 28 amu TPD spectra following adsorption of 12-crown-4 on Pd(1 1 1) at 80 K as a function of exposure. The exposures are marked adjacent to each spectrum and are uncorrected for ionization gauge sensitivity.

exposure (in Langmuirs,  $1 \text{ L} = 1 \times 10^{-6}$  Torr s). The exposures, calculated using the enhancement factor referred to above, are marked adjacent to the corresponding spectra and are not corrected for ionization gauge sensitivity. The spectrum consists of a broad feature between 350 and 450 K and a sharp peak at  $\sim 210$  K. In order to establish the nature of the desorbing species, spectra were collected following an 11-L exposure at various masses (Fig. 3). Note that, since only five masses could be monitored in one TPD sweep, a common mass (28 amu) was included as one of the masses monitored in all of these spectra to ensure reproducibility between different sets of data. These spectra reveal that the feature between 350 and 450 K is predominantly due to the desorption of CO. The relative yields of the sharp feature at  $\sim 210$  K correspond extremely well with the mass spectrum ionizer fragmentation pattern of 12-crown-4 [50]. Note that a fragment of the crown ether is also present in the 28-amu spectrum (Fig. 2) but only appears for exposures of 11 L or greater. This

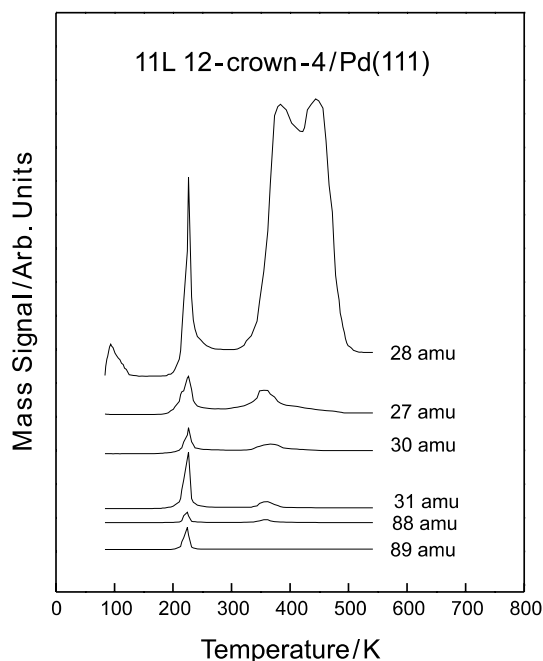


Fig. 3. TPD spectra of 11 L of 12-crown-4 adsorbed on Pd(111) at 80 K collected at various masses. The mass detected is marked adjacent to the corresponding spectrum.

suggests that this feature is due to the adsorption of second and subsequent layers of 12-crown-4. Smaller additional features are also noted at  $\sim 340$  K in the 27-amu spectrum and at  $\sim 370$  K at 30, 31 and 88 amu. The 27-amu spectrum is displayed as a function of 12-crown-4 exposure in Fig. 4 and is assigned to the presence of a small amount of ethylene desorbing from the surface. The corresponding 28-amu fragment is obscured by the leading edge of the intense CO desorption (Fig. 2). Possible origins of the small 30, 31 and 88 amu features will be discussed below. These results indicate that the majority of the 12-crown-4 thermally decomposes on the surface to desorb CO (and hydrogen). This is illustrated by the data of Fig. 5 which plots the CO desorption yield, measured from the 28-amu peak area, as a function of 12-crown-4 exposure. This increases with increasing crown ether exposure up to approximately 11 L, following which it saturates. Note that the multilayer peak at 210 K (Figs. 2–4) appears after the saturation of the monolayer. In order to gauge

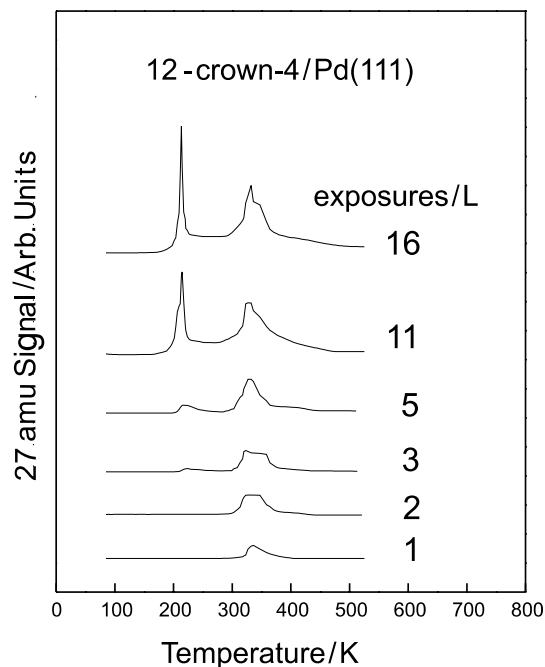


Fig. 4. 27 amu TPD spectra following adsorption of 12-crown-4 on Pd(111) at 80 K as a function of exposure. The exposures are marked adjacent to each spectrum and are uncorrected for ionization gauge sensitivity.

the proportion of the adsorbed crown ether that decomposed to yield CO or form adsorbed carbon and oxygen, Auger spectra were collected of a crown-ether-saturated surface (11 L exposure) heated to 250 K to desorb the multilayer (Fig. 2), and to 550 K, so that the crown ether had completely decomposed and all CO had desorbed. Gauging the oxygen coverage from the peak-to-peak ratio of the oxygen Auger transition at  $\sim 510$  eV kinetic energy to that of the intense palladium transition at  $\sim 330$  eV indicates that  $25 \pm 2\%$  of the oxygen initially present in a 12-crown-4 saturated surface remains after heating to 550 K. This implies that three of the four oxygen atoms in 12-crown-4 desorb as carbon monoxide. The yield of CO from the saturated 12-crown-4 overlayer (Fig. 5) can be compared with the yield of a saturated CO overlayer from the same surface [51], using exactly identical experimental conditions, and shows that the CO yield from a saturated crown ether layer corresponds to  $0.21 \pm 0.02$  monolayers

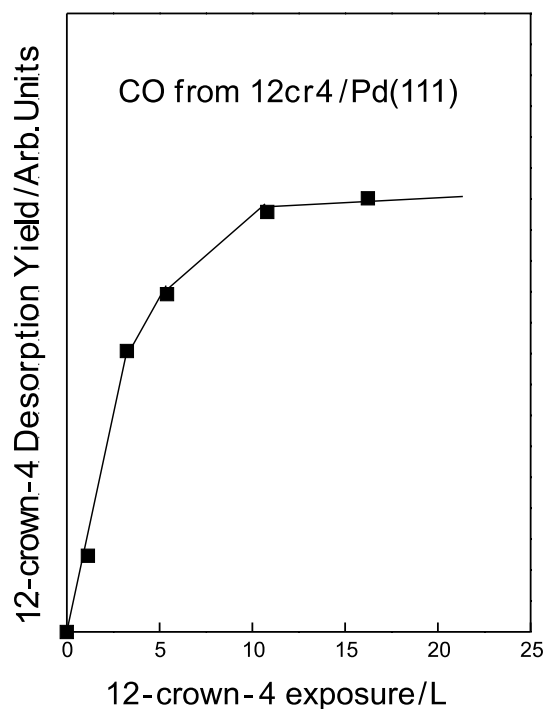


Fig. 5. Plot of the 28-amu yield from the  $\sim 400$  K desorption states as a function of 12-crown-4 exposure.

of CO (where coverages are referenced to the number of exposed palladium atoms on the (1 1 1) face). This corresponds to  $\sim 75\%$  of the oxygen atoms in the crown ether so that the oxygen coverage for a saturated 12-crown-4 overlayer can be calculated as  $0.29 \pm 0.03$  monolayers, yielding a saturation 12-crown-4 coverage of  $0.073 \pm 0.008$  monolayers. Hydrogen desorption was also found and the corresponding 2 amu TPD spectra are displayed in Fig. 6.

The corresponding reflection-absorption infrared spectra are shown in Fig. 7. At low exposures (1 L) at 80 K, the spectrum consists of two intense features at 848 and 1024  $\text{cm}^{-1}$ . Increasing the exposure to 5 L (approximately 75% the overlayer saturation exposure) causes these features to broaden somewhat and an additional feature to appear at 1150  $\text{cm}^{-1}$ . An exposure of 14 L produces a complex spectrum. All of these features in the spectrum found after a 14-L exposure agree well with the gas-phase spectrum of 12-crown-4 [52] which emphasizes that this molecule can be

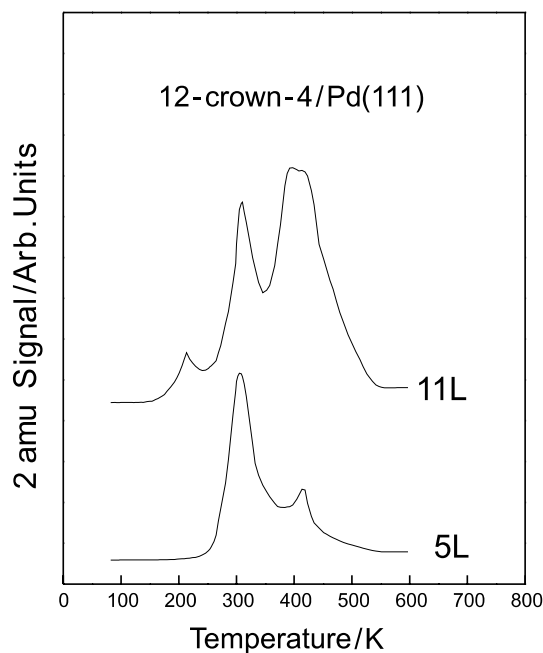


Fig. 6. Hydrogen (2 amu) TPD following adsorption of 12-crown-4 on Pd(1 1 1) at 80 K.

cleanly deposited onto the surface. These surface features are compared with those in the gas phase in Table 1. This table also shows proposed assignments for the features and these will be discussed in detail below. Annealing the sample to 250 K, just above the multilayer desorption temperature (see Figs. 2–4), removes the multilayer peaks and leaves features at 1730, 1685, 1306, 1145 and 848  $\text{cm}^{-1}$ . Note that the 1024  $\text{cm}^{-1}$  peak is now absent. The features at 1306, 1145 and 848  $\text{cm}^{-1}$  have counterparts in the spectrum of condensed 12-crown-4 and are presumably due to the presence of molecular 12-crown-4, the reduced number being due to a high-symmetry adsorption geometry on the surface. This will be discussed in greater detail below. The additional features at 1730 and 1685  $\text{cm}^{-1}$  do not correspond to any 12-crown-4 modes and must be due to intermediate thermal decomposition products. The peak at 1730  $\text{cm}^{-1}$  is likely to be due to an aliphatic aldehyde (which has C=O stretching modes between 1720 and 1740  $\text{cm}^{-1}$  [53]). The origin of the 1685  $\text{cm}^{-1}$  mode is not clear but may be due to some

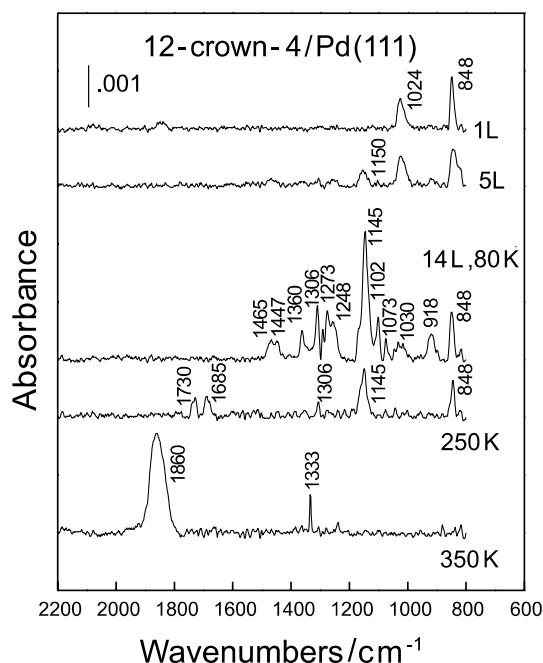


Fig. 7. Reflection/absorption infrared spectra of 12-crown-4 adsorbed on Pd(111) at 80 K as a function of exposure, and after annealing to various temperatures. The exposures and annealing temperatures are marked adjacent to the corresponding spectra and the absorbance scale is marked as a vertical line on the figure.

Table 1  
Vibrational assignments for 12-crown-4 assuming that it adopts  $C_{4v}$  symmetry

Gas-phase frequency <sup>a</sup>	Assignment	Symmetry	Condensed layer on Pd(111)
848	COC stretch	$A_1$	848
921	COC stretch	E	918
971	$CH_2$ rock	–	1030, 1070
1142	COC stretch	E	1145
1255	$CH_2$ twist	–	1248, 1273
1295	$CH_2$ twist	–	1306
1362	$CH_2$ wag	–	1360
1454	$CH_2$ scissor	–	1447, 1465

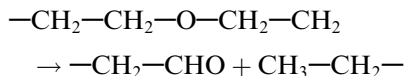
<sup>a</sup> NIST Chemistry Web Book, <http://webbook.nist.gov/chemistry>.

unsaturation of the chain due to some dehydrogenation [53]. Further heating to 350 K, corresponding to the onset of CO desorption (Figs. 2

and 3), causes all of the crown ether features to disappear leaving a broad feature at  $1860\text{ cm}^{-1}$  and a sharp peak at  $1333\text{ cm}^{-1}$ . Both of these peaks disappear on heating to 450 K (not shown).

#### 4. Discussion

12-crown-4 adsorbs as a chemisorbed overlayer on Pd(111) at 80 K with the majority of the crown ether thermally decomposing to yield CO (Fig. 2) and hydrogen (Fig. 6). A small amount of ethylene desorption is detected (Fig. 4) at  $\sim 320\text{ K}$ . Since ethylene desorbs from Pd(111) at  $\sim 250\text{ K}$  [54], this implies that the crown ether has undergone substantial thermal decomposition by this temperature. Ethylene desorption is also found from dioxane at a similar temperature although, in this case, a substantial proportion of the dioxane overlayer desorbs intact [42]. This immediately suggests that 12-crown-4 is more strongly adsorbed on the palladium surface than 1,4-dioxane since, in the former case, no desorption is observed from the overlayer. Another decomposition product is found at  $\sim 360\text{ K}$  where the highest mass detected at this temperature is at 88 amu (Fig. 3). This is clearly a relatively large and complex intermediate decomposition product which is difficult to identify unequivocally from the mass spectral fragmentation pattern. However, the infrared spectra of 12-crown-4 on the surface heated to 250 K shows features at 1730 and  $1685\text{ cm}^{-1}$  which cannot be associated with adsorbed 12-crown-4 and are therefore assigned to surface decomposition products. It has been found that the ether linkage in linear polyethers can react forming an aldehyde group as follows [55]:



The detection of aldehyde functionalities on the surface using infrared spectroscopy is in accord with this reaction pathway. This reaction route has been proposed to be responsible for the thermal decomposition of polyether lubricants on magnetic disks [55]. The occurrence of this reaction at two opposite ether linkages in 12-crown-4 would lead

to the formation of  $C_2H_5-O-CH_2CHO$  which has a molecular weight of 88 amu and may account for the appearance of a peak at this mass at 88 amu in the TPD spectrum (Fig. 3). Note, however, that the yield of all of these species is substantially lower than that of CO which is the major thermal decomposition product. This allows the coverage of the crown ether adsorbed onto the Pd(111) surface to be gauged from the CO desorption yield and the plot of CO yield versus 12-crown-4 exposure is shown in Fig. 5. The crown ether coverage increases with increasing exposure up to an exposure of 11 L and saturates. This exposure is taken to correspond to saturation of the overlayer on Pd(111). The sharp feature at 210 K in Figs. 2 and 3 is thus assigned to desorption from second and subsequent layers. Note that there is initial evidence for the appearance of this feature at 12-crown-4 exposures of 3 and 5 L implying that second-layer condensation commences before the chemisorbed overlayer is completed. A similar effect has been noted for 1,4-dioxane adsorbed on Pd(111) [42]. This suggests that the infrared spectrum for a 5-L exposure of 12-crown-4 on Pd(111) already contains contributions from the second layer. It appears, however, that the amount of second-layer adsorption at an exposure of 1 L is negligible and that the features at 848 and 1204  $cm^{-1}$  are due to 12-crown-4 adsorbed on the Pd(111) surface. It is striking that the overlayer spectrum contains far fewer features than are present for the condensed overlayer indicating that a large number of surface modes have been rendered inactive by the surface selection rules. This in turn implies that the 12-crown-4 has a relatively high symmetry on the surface. Clearly a relatively large molecule like 12-crown-4 can adopt a large number of conformations in the liquid or gas phase. Many or all of the vibrational modes of low-symmetry conformers of randomly adsorbed molecules will be allowed. This effect is evident in the condensed multilayer which consists of at least 13 easily identifiable features. It was found previously that 1,4-dioxane adsorbed on Pd(111) via the oxygen lone pairs on the ether linkages and that the conformation changed from the usual gas-phase chair to a boat conformation [42]. The vibrational spectrum of 12-crown-4 will therefore be

analyzed assuming that 12-crown-4 adopts  $C_{4v}$  symmetry. In addition, since the CO stretching modes are likely to be the most intense in the vibrational spectrum, the C–O stretch is used as a basis for the group theoretical analysis. The irreducible representations for these vibrations are  $A_1 + B_1 + A_2 + B_2 + 2E$  in the  $C_{4v}$  point group. Of these, only the  $A_1$  and E modes are infrared active so that the gas-phase spectrum has only three active modes involving C–O stretches, the rest of the vibrations being due to the  $CH_2$  species. As far as we are aware, there have been no spectroscopic assignments for 12-crown-4. However, the vibrational spectrum of 1,4-dioxane has been fully assigned [52] and it is found that the antisymmetric C–O–C modes have vibrational frequencies of  $\sim 1220$   $cm^{-1}$  ( $A_u$  at 1136  $cm^{-1}$  and  $B_g$  at 1110  $cm^{-1}$ ) and the symmetric C–O–C modes at  $\sim 860$   $cm^{-1}$  ( $A_g$  at 837  $cm^{-1}$  and  $B_u$  at 889  $cm^{-1}$ ). In order to ascertain which of the above irreducible representations are due to either symmetric or asymmetric C–O–C modes, each of these are used as bases for the group theoretical analysis, again assuming  $C_{4v}$  symmetry. This reveals that the symmetric C–O–C modes have symmetries of  $A_1 + B_1 + E$ , of which the  $A_1$  and E are infrared active. These modes, as noted above, should have vibrational frequencies around 860  $cm^{-1}$ . The  $A_1$  mode involves the in-phase vibration of all the symmetric C–O–C vibrations and therefore should be lower in frequency than the E mode. A similar analysis using the asymmetric C–O–C vibrations as bases shows that these have  $A_2 + B_2 + E$  symmetries, of which only the E mode is infrared active and should have a characteristic frequency of  $\sim 1220$   $cm^{-1}$ . Both the gas-phase [52] and condensed layer spectra (Fig. 7) of 12-crown-4 have low-frequency vibrational modes around 860  $cm^{-1}$  at 848 and 918  $cm^{-1}$ . Furthermore, these frequencies are away from any modes that might be assigned to  $CH_2$  vibrations so that the 848  $cm^{-1}$  mode is assigned to the  $A_1$  mode and the 918  $cm^{-1}$  feature to the symmetric C–O–C stretching mode of E symmetry. The asymmetric E mode should be intense and have a vibrational frequency of  $\sim 1120$   $cm^{-1}$ . The most intense mode in the gas-phase infrared spectrum of 12-crown-4 is at 1142  $cm^{-1}$  [52]. The intense mode at 1145  $cm^{-1}$  for the

condensed layer of 12-crown-4 on Pd(1 1 1) (Fig. 7) is therefore assigned to this mode. The remaining features are due to CH<sub>2</sub> vibrations and can be straightforwardly assigned by comparison with the corresponding modes for 1,4-dioxane, and the resulting assignments are summarized in Table 1.

The surface infrared selection rules [56] can be used to establish the orientation of species on the surface. The infrared spectrum for 1 L of 12-crown-4 adsorbed on Pd(1 1 1) is shown in Fig. 7 and exhibits two features at 848 and 1024 cm<sup>-1</sup>. Reference to Table 1 indicates that the 848 cm<sup>-1</sup> mode is due to the asymmetric C–O–C stretch of A<sub>1</sub> symmetry and the 1024 cm<sup>-1</sup> feature is due to a CH<sub>2</sub> rocking mode. Note that there is no evidence for the presence of modes of E symmetry which should appear at ~918 and 1145 cm<sup>-1</sup>. Modes of A<sub>1</sub> symmetry transform as *z* in the C<sub>4v</sub> point group (where the *z*-axis is oriented along the principal C<sub>4</sub> symmetry axis of the molecule), while the E modes transform as *x* and *y*. The presence of a single C–O–C mode with A<sub>1</sub> symmetry at 848 cm<sup>-1</sup> suggests that 12-crown-4 adopts C<sub>4v</sub> symmetry on the Pd(1 1 1) surface with the principal C<sub>4</sub> axis oriented perpendicular to the surface and with the *x*–*y* plane of the molecule parallel to the (1 1 1) plane. This implies that the molecule bonds to the surface via the lone-pair orbitals on the oxygen atoms in the ring where the bonding is similar to that found for 1,4-dioxane [42]. Similar multiple bonding of cyclic ethers has been investigated on Ru(001) where it was suggested that the heat of adsorption could be estimated by summing over the oxygen–metal bonds formed on the surface [57]. The desorption activation energy for 1,4-dioxane from Pd(1 1 1) is estimated, using Redhead analysis [58] to be ~16 kcal/mol suggesting an approximate O–metal bond strength of ~8 kcal/mol. The infrared data suggest that 12-crown-4 bonds via four bonds so that the heat of adsorption should be ~32 kcal/mol. A Redhead analysis, using a preexponential factor of 1 × 10<sup>13</sup> s<sup>-1</sup> and the experimental heating rate of 7 K/s, indicates that this species would desorb at ~460 K. This temperature is significantly higher than the decomposition temperature of ~300 K on Pd(1 1 1) and rationalizes the complete thermal decomposition of 12-crown-4 during the TPD experiment.

This geometry allows the 12-crown-4 coverage to be estimated. An approximate Van der Waals' diameter for 12-crown-4 is 9.75 Å which yields an approximate circular area of 74.6 Å<sup>2</sup>. The area of an exposed palladium atom on the (1 1 1) face of palladium is 6.54 Å<sup>2</sup> yielding an approximate coverage of 0.088 monolayers. This value is in reasonable agreement with the 12-crown-4 coverage measured above and is in accord with the conclusion that the crown ether adsorbs with its molecular plane parallel to the (1 1 1) surface as suggested by infrared spectroscopy.

In the proposed C<sub>4v</sub> adsorption geometry, the H–C–H planes of all of the CH<sub>2</sub> groups are oriented close to perpendicular to the palladium surface. Assuming that the methylene groups have local C<sub>2v</sub> symmetry, the scissor mode has A<sub>1</sub>, the wag B<sub>1</sub>, the twist A<sub>2</sub> and the rock B<sub>2</sub> symmetry. In the case that the methylene groups are oriented with the H–C–H plane perpendicular to the surface, only modes that transform as a vector oriented along the *y* direction (in the H–C–H plane) will be infrared active on the surface; both the *x* and *z* vectors are parallel to the surface in this configuration. The presence of a relatively intense feature at 1024 cm<sup>-1</sup>, assigned to a CH<sub>2</sub> rocking mode (Table 1), is therefore consistent with the proposed adsorption geometry.

As the exposure increases to 5 L, an additional feature appears at 1150 cm<sup>-1</sup> with perhaps smaller peaks at ~920, 1250 and 1450 cm<sup>-1</sup>. As noted above, some second-layer adsorption appears to take place at these exposures so that these additional features are likely to be associated with adsorption of 12-crown-4 into the second layer. A 12-crown-4 exposure of 14 L at 80 K leads to the condensation of second and subsequent layers and a multiplicity of features that can be assigned to molecular 12-crown-4 (see Table 1).

Heating to 250 K, where the TPD data indicate that the multilayer has desorbed (Figs. 2 and 3), removes these peaks in accord with this assignment. The infrared spectrum at this temperature consists of features at 848, 1145, 1306, 1685 and 1730 cm<sup>-1</sup>. As discussed above, the features at 1730 and 1685 cm<sup>-1</sup> are assigned to the presence of crown ether decomposition products. In this case, the 1145 cm<sup>-1</sup> C–O–C mode of E symmetry is also



evident. This may suggest that the plane of the crown ether is now slightly tilted on the surface or that the molecule is distorted.

Further heating to 350 K removes all of the crown ether modes and yields two features at 1860 and 1444  $\text{cm}^{-1}$ . The 1860  $\text{cm}^{-1}$  mode is due to CO adsorbed on the surface which desorbs molecularly in a broad feature between 350 and 450 K (Fig. 2) [56]. The peak at 1333  $\text{cm}^{-1}$  is characteristic of an ethylidyne species ( $\text{CH}_3\text{-C}\equiv$ ) on Pd(1 1 1) [59] so that CO and ethylidyne are the final surface thermal decomposition products of the adsorbed crown ether.

## 5. Conclusions

12-crown-4 adsorbs at 80 K on Pd(1 1 1) via the oxygen lone pairs with the molecular plane oriented parallel to the surface. The overlayer saturates at an exposure of 11 L with coverage of  $0.073 \pm 0.008$  monolayers, consistent with this adsorption geometry. The overlayer thermally decomposes, via aldehyde intermediates at above  $\sim 250$  K. Small amounts of aldehyde and ethylene are detected in TPD. The final surface thermal decomposition products found by annealing to  $\sim 350$  K are adsorbed CO and ethylidyne species.

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