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Structure and binding site of acetate on Pd(1 1 1) determined using density functional theory and low energy electron diffraction

Joanna James [a], Dilano K. Saldin [b], T. Zheng [c],
W.T. Tysoe [c], David S. Sholl [a,d,*]

[a] Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA
[b] Department of Physics and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA
[c] Department of Chemistry and Biochemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA
[d] National Energy Technology Laboratory, Pittsburgh, PA 15236, USA

Abstract

Acetate adsorbs on Pd(1 1 1) as a disordered overlayer. We have used a recently developed LEED *I–V* technique that allows the structure of disordered molecular overlayers to be examined to determine the structure of acetate adsorbed on Pd(1 1 1). Our experimental results are compared with plane-wave density functional theory calculations. The calculated and observed adsorption geometries are in excellent agreement.

Keywords: Density functional theory; Acetate; Low energy electron diffraction

1. Introduction

Accurate knowledge of the binding sites and orientation of molecules adsorbed on surfaces is an important component of any effort to describe heterogeneously catalyzed reactions with mechanistic detail. Within the context of molecular adsorption on well-defined surfaces, density functional theory (DFT) calculations have played a key role in the growing list of surface species whose structure is known. DFT has been used, for example, to describe complete reaction paths for reactions involving small molecules on metal surfaces [1,2] and to assess the structure of molecules on stepped and strained surfaces [1,3]. Increasingly, DFT is also being applied to more complex adsorbed species. Recent examples of this trend include studies of amino acids [4,5] and other multi-functional chiral species [6] adsorbed on metal surfaces.

Despite advances associated with theoretical calculations, experimental determination of the structures of adsorbed molecules remains vital. For the many surface species that form only disordered overlayers, experimental structure determination remains challenging. Synchrotron-based methods, such as photoelectron diffraction can be applied with great effect to these species, but the infrastructure requirements for this approach limit its routine use. We have recently introduced an alternative approach that relies on conventional low energy electron diffraction (LEED) to measure the structure of disordered overlayers [7–9]. The central idea in this approach is to interrogate the intensities of the substrate's (1 × 1) Bragg diffraction spots as they are modified by a disordered overlayer. We have recently used this technique to determine the structure of formate on Pd(1 1 1) and compared this structure with the predictions of DFT calculations [10]. The two techniques have structures for this adsorbate that were in excellent agreement with one another. Examples where we can assess the relative accuracy of these two distinct approaches are useful because, in order to apply our LEED approach to complex adsorbed species, such as amino acids, it will be necessary to use structures predicted by DFT as starting points to refine the experimental structure. That is,

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* Corresponding author. Tel.: +1 412 268 4207; fax: +1 412 268 7139.
E-mail address: sholl@andrew.cmu.edu (D.S. Sholl).

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we envision DFT as playing an integral role in the determination of complex structures with this experimental approach.

In this paper, we describe the structure of acetate, H_3CCOO, on Pd(1 1 1) determined using both plane-wave DFT calculations and the analysis of LEED patterns from the disordered acetate overlayer observed experimentally. Apart from our interest in exploring the relative accuracy of these two methods, acetate is of interest in several catalytic processes. Synthesis of oxygenates from syngas using group VIII transition metal catalysts involves formation of stable carboxylates [11–13]. Acetate has been proposed as an intermediate in palladium catalyzed synthesis of vinyl acetate [14–16]. The decomposition of acetates on several single crystal metal surfaces has been studied before [17–21], but little is known about the structure of acetate on these surfaces. On Cu(1 1 0), photoelectron diffraction has been applied [22] to show that acetate binds with oxygen above a Cu atom and the OCO plane oriented perpendicular to the surface with an OCO angle of 124°.

2. Methods

2.1. Theoretical methods

Plane-wave DFT calculations using the PW91 GGA functional were performed using the Vienna ab initio Simulation Package [23]. Pd(1 1 1) was represented by a slab four layers thick with the bottom two layers constrained and a vacuum spacing of 14 Å. All calculations used a (3×3) surface unit cell defined using the DFT-optimized Pd lattice constant of 3.96 Å. In each energy minimization calculation, all unconstrained atoms were relaxed until the force on each atom was less than 0.03 eV/Å and a $3 \times 3 \times 1$ k-point mesh was used. For each potential binding site that was examined, the initial structure of adsorbed acetate was estimated by using OCO bond lengths and angles obtained from our previous calculations [10] of formate on Pd(1 1 1) and placing the CH_3 group directly above the C atom in the OCO with bond lengths and angles taken from a gas phase calculation for the structure of acetic acid.

In order to experimentally determine the structure of a disordered acetate overlayer, *I–E* data from the clean surface was first analyzed by comparison with standard LEED calculations [24] to determine the incidence angle of the electrons relative to the surface. The *I–E* curves from the acetate-covered sample were then simulated for this angle of incidence by assuming an ordered overlayer of the smallest possible (1×1) periodicity with fractional occupancy of the same magnitude as the coverage Θ. The notion that a calculation involving only integer-order beams may be sufficiently accurate for practical calculations of the integer-order Bragg spots for large unit-cell overlayers may be regarded as a special case of the beam set neglect method [25,26]. The precision of the bond lengths was determined in standard way from the change in the Pendry R-factor [27] as a function of change in geometrical parameters.

2.2. Experimental methods

LEED measurements were carried out in a doubly μ-metal shielded ultrahigh vacuum chamber operating at a base pressure of 5×10^{-11} Torr, and containing a Pd(1 1 1) single crystal as described previously [7]. The acetate species were formed by dosing 5 L of acetic acid (Aldrich, 99%) at 80 K and then heating briefly to 200 K resulting in the formation of a saturated overlayer, a procedure that has been shown previously to result in the formation of acetate species [28]. The sample was then allowed to cool to 80 K and the *I–E* curve collected.

3. Results and discussion

We used our DFT calculations to explore a range of possible high symmetry binding sites for acetate on Pd(1 1 1) in a manner very similar to our previous study of formate on the same surface [10]. We performed calculations in which the adsorbed molecule was initially placed centered over fcc, hcp, bridge and atop sites. In each case the OCO plane was initially placed normal to the surface and we explored several different orientations of this plane with respect to the surface. These initial states had the plane defined by the three H atoms in the terminal methyl group parallel to the surface. In each case, two independent calculations were performed that began with different rotations of this methyl group relative to the OCO group.

The calculations outlined above identified three stable adsorption sites for acetate on Pd(1 1 1); one with the OCO in bridge–fcc–atop positions, another with the OCO in bridge–hcp–atop positions and a third with the OCO in an atop–bridge–atop configuration. Not surprisingly, these are the same states that we identified previously for formate/Pd(1 1 1), and as with formate, it is the latter state that is more stable. To test for a tilt of the OCO plane with respect to the surface normal, the molecule was also placed at an angle of 20° with respect to the surface normal. The molecule was found to converge to an orientation perpendicular to the surface normal. Calculations exploring rotations of the terminal methyl group relative to the OCO group indicated that there is essentially no energy barrier for rotation of the methyl group in the plane of the surface.

The experimentally determined LEED *I–E* curves for acetate species on Pd(1 1 1) are shown as solid lines in Fig. 1. These were modeled by using the previously determined geometry of the formate species [10] to define the C–O and O–Pd distances and the orientation of the acetate plane. The C–C distance between the methyl group and the carboxylate carbon was taken at be a standard value

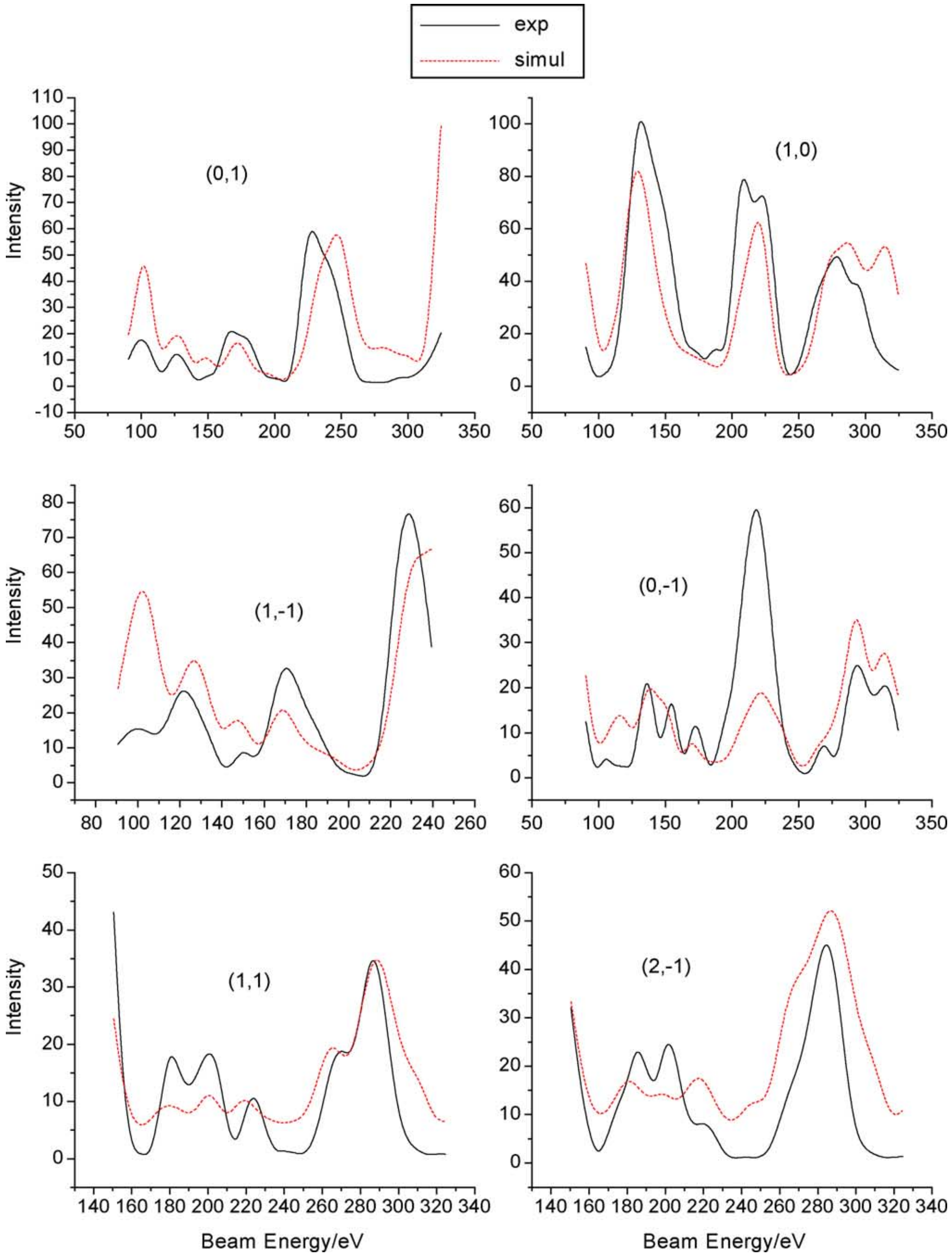

Fig. 1. Experimentally determined intensity vs. energy (*I–E*) curve for 5 L of acetic acid adsorbed on Pd(1 1 1) at 170 K and heated to 200 K to form the acetate species (solid line). Shown also plotted on this curve is the calculated *I–E* curve for the best-fit structure depicted in Fig. 2.

of 1.54 Å. These structural data were input directly into the Tensor LEED program, which converged well to yield a final Pendry R-factor of 0.29 with only very small changes to the input bond lengths. The resulting theoretical *I–E* curves (dashed lines) are compared with the experimental results in Fig. 1.

The experimental and theoretical values of the geometrical parameters are compared in Table 1, where clearly the agreement between the two sets of data is extremely good. In this case, the experimental errors were determined in a

Table 1
Comparison of selected bond distances and angles for acetate/Pd(1 1 1) as determined by DFT and LEED

	Acetate/Pd(1 1 1) from LEED	Acetate/Pd(1 1 1) from DFT
d(O–Pd) (Å)	2.12 ± 0.06	2.12
Angle of OCO plane to surface (°)	90 ± 2	90
OCO angle (°)	128 ± 3	127
d(C–O) (Å)	1.26 ± 0.07	1.28
d(C–C) (Å)	1.48 ± 0.04	1.51

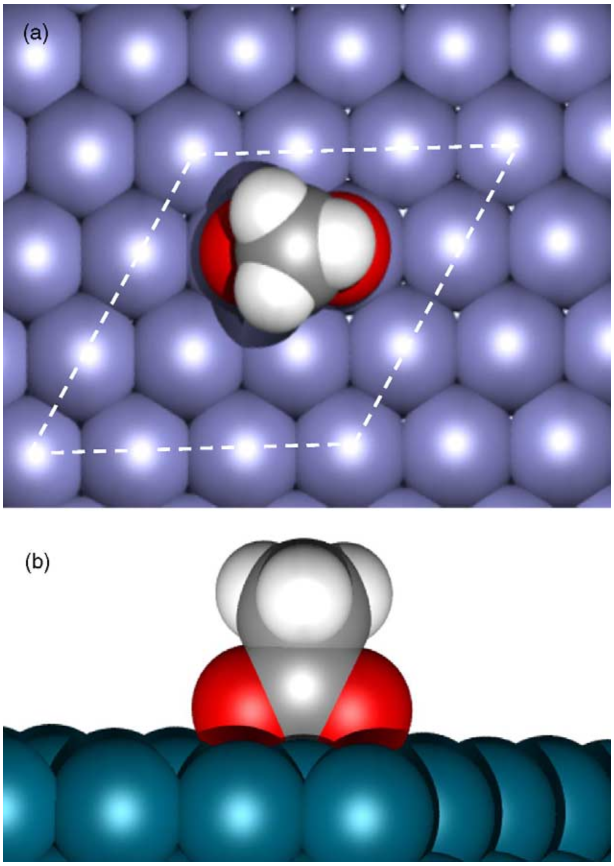

Fig. 2. (a) Top and (b) side view of the geometry of acetate on Pd(1 1 1) as determined from DFT calculations. In part (a), the dotted lines indicate the unit cell that was used for the calculations.

standard way from the change in Pendry R-factor with change in structural parameter. The final structure of the acetate species on Pd(1 1 1) is depicted in Fig. 2. The good agreement between the experimental and calculated geometries for both formate [10] and acetate species indicates that DFT calculation yields precise geometries and can be used to provide input geometries for more complex adsorbates.

4. Conclusions

The geometry of a disordered overlayer of acetate species on Pd(1 1 1) was determined from the LEED *I–E* curve and compared with results of density functional theory. The theoretically measured geometry is in excellent agreement with experiment where the theoretical values lie well within experimental error in all cases. This indicates that DFT can be effectively used to provide input geometries to LEED structural determinations in the case of more complex adsorbate geometries.

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