Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Vacancy diffusion in palladium hydrides

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Figure 1 shows the optimized lattice parameters as a function of hydrogen content. The lattice parameters follow a linear relationship with hydrogen content according to Vegard's law.

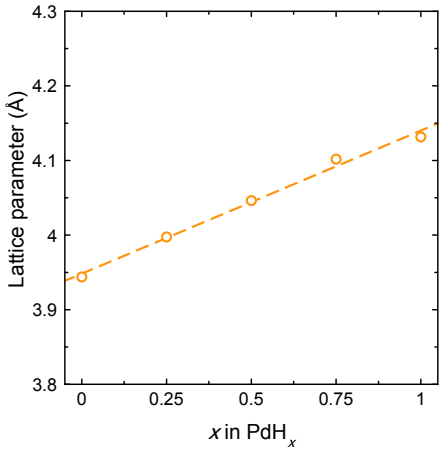

Figure 1: Optimized lattice parameters as a function of H content and linear fit. The disordered structures, $PdH_{0.25}$, $PdH_{0.5}$ and $PdH_{0.75}$, were modeled as special quasirandom structures.

Vacancy formation was sampled at five different sites along a <1 1 0> path in the disordered systems ($0.25 \leq x \leq 0.75$) as summarized in Table 1. These sites were considered representative of the local structure surrounding the vacancy due to the high symmetry of the structure. However, lattice dynamics beyond the nearest neighbor were not equally captured. Table 2 shows the vacancy migration enthalpies between the considered vacancy sites.

Table 1: Vacancy formation enthalpies and number of hydrogen atoms adjacent to the vacancy at sites denoted 1-5 along the migration paths in PdH_x.

Material	ΔH^f (eV) / *n*					
	1	2	3	4	5	Average
Pd	1.13 / 0	1.13 / 0	–	–	–	1.13
$PdH_{0.25}$	0.98 / 1	0.86 / 2	1.02 / 1	1.00 / 1	1.20 / 0	1.01±0.12
$PdH_{0.5}$	1.21 / 1	1.01 / 2	0.96 / 3	0.96 / 3	0.92 / 4	1.01±0.11
$PdH_{0.75}$	0.76 / 4	0.64 / 4	0.92 / 4	0.87 / 3	0.68 / 6	0.77±0.12
PdH	0.39 / 6	0.40 / 6	–	–	–	0.39

Table 2: Vacancy migration enthalpies in PdH_x along the sites defined in Table 1 and number of hydrogen adjacent to the migration Pd atom (n_{TS}), denoted Hnn in Fig. 1.

Material	ΔH^m (eV) / n_{TS}				
	1→2	2→3	3→4	4→5	Average
Pd	0.95 / 0	–	–	–	0.95
$PdH_{0.25}$	0.85 / 1	0.87 / 0	0.77 / 0	0.88 / 0	0.84±0.05
$PdH_{0.5}$	0.78 / 0	0.93 / 1	0.87 / 1	1.00 / 2	0.90±0.09
$PdH_{0.75}$	0.80 / 1	1.16 / 2	0.84 / 0	0.88 / 2	0.92±0.16
PdH	0.79 / 2	–	–	–	0.79

Two different configurations were considered for calculating $^{\Delta S^{\,f}_{vib}}$ for the disordered systems. The number of hydrogen atoms associated with the vacancy in these configurations were 1&2, 2&3, and 4&5 in $PdH_{0.25}$, $PdH_{0.5}$ and $PdH_{0.75}$, respectively. These configurations were considered sufficient due the minor standard deviations in $\exp\left(\Delta S^{\,f}_{vib}/k_B\right)$: 0.35, 0.31 and 0.026, for $PdH_{0.25}$, $PdH_{0.5}$ and $PdH_{0.75}$, respectively. The vibrational entropies of palladium and hydrogen in bulk and adjacent to vacancies are shown together with $^{\Delta S^{\,f}_{vib}}$ in Figure 2.

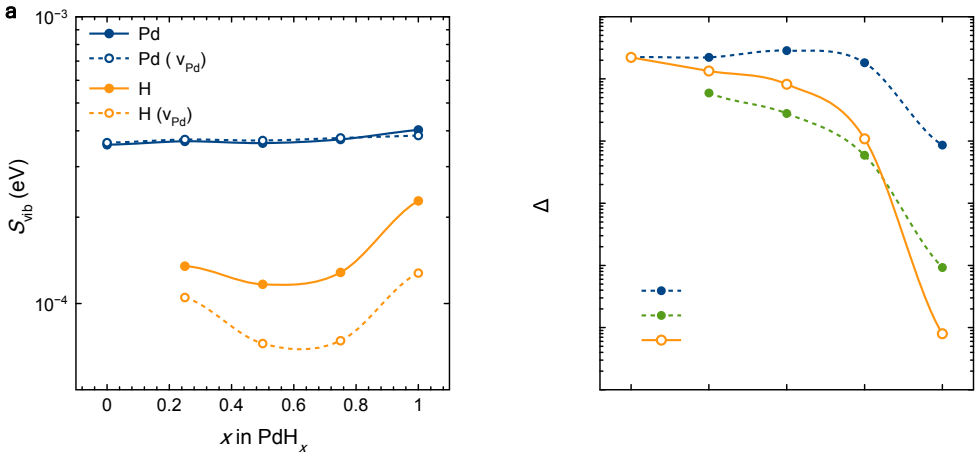

Figure 2: Vibrational entropies of Pd and H atoms in the bulk and adjacent to vacancies at 298 K (a), and the corresponding contribution from ΔS_{vib}^{f} to the pre-exponential.

The effective frequencies ν^* were calculated for one configuration per composition, as summarized in Table 3.

Table 3: Effective frequencies ν^* and the contributions from the migrating Pd atom (Pd_{TS}), the four nearest neighbor Pd atoms at the transition state (Pd_{nn}), and from the seven additional Pd atoms adjacent to vacancies at the transition state compared to the initial/final state (v_{Pd}, incl. standard deviation from two calculations).

Material	ν^*	**Contributions to** ν^*		
		Pd_{TS}	Pd_{nn}	v_{Pd}
Pd	1.76 THz	2.84 THz	0.38	1.61
$PdH_{0.25}$	0.48 THz	4.49 THz	0.07	1.57±0.07
$PdH_{0.5}$	0.63 THz	4.88 THz	0.07	1.98±0.86
$PdH_{0.75}$	0.56 THz	4.40 THz	0.09	1.46±0.59
PdH	0.53 THz	4.31 THz	0.05	0.23

Figure 3 shows the potential profiles of Pd and H obtained by the finite displacement method with 4 displacements in each cartesian direction for each species. The step size of the displacements was 0.015 Å for palladium. Step sizes up to 0.05 Å were required for hydrogen in order to avoid that the changes in energy were negligible. Figure 4 shows similar potential profiles with asymmetric profiles in $PdH_{0.5}$.

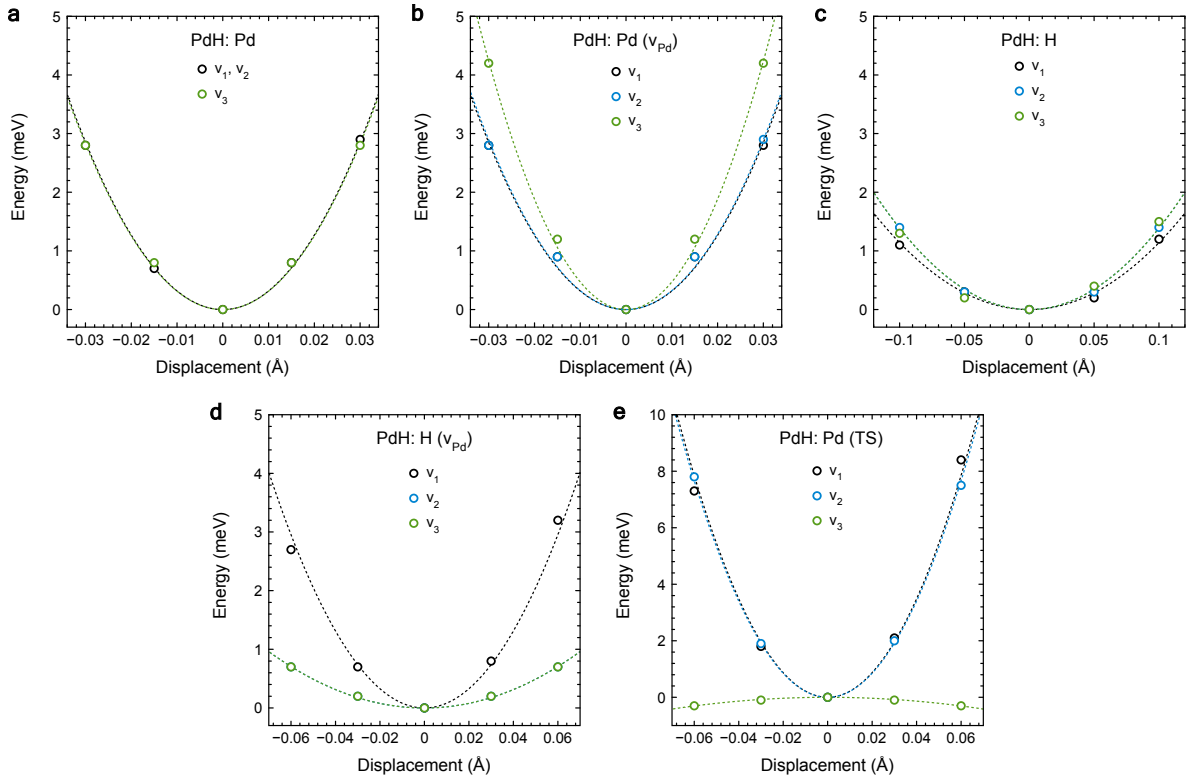

Figure 3: Potential profiles from finite displacement calculations in PdH: (a) Pd, (b) Pd adjacent to a Pd vacancy, (c) H, (d) H adjacent to vacancy, and (e) Pd at the transition state. Lines are fits according to the harmonic approximation.

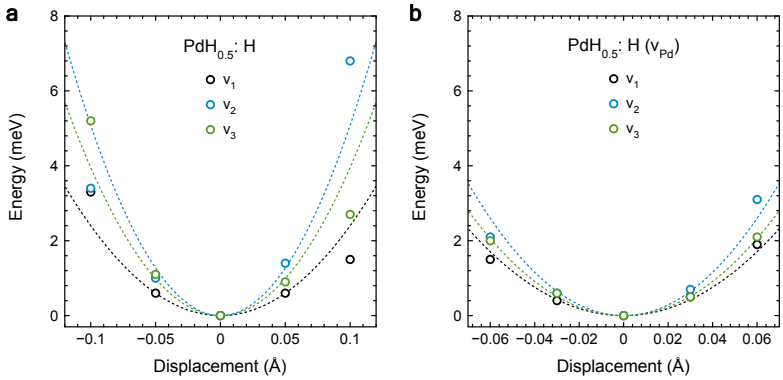

Figure 4: Potential profiles from finite displacement calculations in $PdH_{0.5}$: (a) H, (b) H adjacent to a Pd vacancy. Lines are fits according to the harmonic approximation.

The vibrational frequencies of palladium and hydrogen atoms in the bulk and adjacent to monovacancies are summarized in Table 4.

Table 4: Vibrational frequencies and zero-point energies of Pd and H in bulk and adjacent to a Pd vacancy (v_{Pd}) in PdH_x.

Material	**Atom**	ν_j **(cm^{-1})**			**ZPE (meV)**
		j=1	j=2	j=3	
PdH	Pd	124.1	123.4	113.5	22.4
	Pd (v_{Pd})	149.3	128.9	111.7	24.2
	H	257.3	256.6	228.3	46.0
	H (v_{Pd})	662.4	323.3	322.7	81.1
$PdH_{0.75}$	H	467.5	417.0	319.3	74.6
	H (v_{Pd})	710.5	545.1	428.7	104.4
$PdH_{0.5}$	H	510.7	441.3	334.8	79.8
	H (v_{Pd})	634.6	543.3	475.9	102.5
$PdH_{0.25}$	H	415.4	405.2	329.6	71.3
	H (v_{Pd})	477.1	438.2	426.1	83.2
Pd	Pd	143.9	143.9	143.8	26.8
	Pd (v_{Pd})	151.4	148.0	124.1	26.3