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Theoretical studies of the effect of hydrogen–hydrogen interactions on the structural and dynamical properties of metal/hydrogen clusters

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Using a combination of ground state, equilibrium, and dynamical Monte Carlo methods, we examine the role of hydrogen-hydrogen interactions on selected structural and time-dependent properties of hydrogen containing metal clusters. Equilibrium simulations include studies of the classical and quantum-mechanical geometries and energetics for embedded atom potential models of both the ground states and low-lying structural isomers of Ni₈H₂ and Pd₈H₂ clusters (4 ≤ n ≤ 9). In addition to these time-independent investigations, we utilize dynamical path integral methods to characterize the effects of hydrogen-hydrogen interactions on the hydrogen vibrational lineshapes in these systems. © 1998 American Institute of Physics. [S0021-9606(98)03606-X]

I. INTRODUCTION

Hydrogen/metal systems have been studied extensively owing to their theoretical and technological importance.1,2 A practical issue in addressing the equilibrium and dynamical properties of these systems is the role of hydrogen-hydrogen interactions. This is a concern since many experiments are performed at coverages where the effects of such interactions are significant. Such interactions are an issue, for example, in many surface diffusion measurements where hydrogen surface concentrations are typically above 5% of a monolayer.3

With their diverse phenomenology, cluster systems offer a noteworthy opportunity to address a variety of structural and dynamical problems. In previous work,4,5 for example, we have examined models of a single hydrogen atom in and on nickel and palladium clusters in order to explore the role of quantum-mechanical effects on the equilibrium structure and vibrational lineshapes.

In the present work, we extend our earlier studies by considering the properties of nickel and palladium clusters that contain two hydrogen atoms. In addition to the previously addressed classical/quantum-mechanical issues, we are particularly interested in the influence of hydrogen-hydrogen interactions on the equilibrium and dynamical properties of the clusters.

We emphasize at the outset that the investigations are based on a particular empirical model of the microscopic interactions. Rather than being definitive statements about specific materials, we therefore view the results as representative of the issues that are of concern in this class of physical systems. The results presented here are based on the EAM (embedded atom method). Although the EAM approach is based on an empirical parameterization of bulk data, previous research shows that the method is robust and yields at least qualitative predictions for cluster structures and binding energies.4,6 For example, the structures predicted using the EAM approach6 are consistent with those inferred by Parks et al. from N₂ adsorption data7 (with the exceptions of Ni₈ and Ni₁₄). Improved agreement (relative to EAM results) for sequential nickel binding energies9 can be obtained by using the more computationally demanding empirical CEM (corrected effective medium) model.8 It should be noted, however, that both methods predict a similar dependence of energies on cluster size and similar minimum energy structures. Finally, some insight into the quality of EAM predictions can be obtained by considering available first principles calculations.10 Such calculations predict, for example, the existence of two nearly degenerate isomers (a capped octahedron and a pentagonal bipyramid) for Ni₇ separated in energy by 0.35 eV. These results are consistent with both the isomeric structures and the associated energy difference (0.45 eV) predicted using EAM potentials.

In Sec. II we present and discuss the classical structure of the lowest energy configurations and low-lying isomers of metal/hydrogen clusters of the form MₙH₂. Here the metal, M, is either Ni or Pd and the number of metal atoms, n, ranges from 4–9. In Sec. III we consider quantum-mechanical effects on the structure of these clusters using both harmonic, zero-point analysis and diffusion Monte Carlo methods.11 In Secs. IV and V we examine the vibrational lineshape for hydrogen motion in these clusters. Section IV considers classical estimates that are obtained from the Fourier transform of autocorrelation function data calculated using conventional molecular dynamics methods.12 Analogous quantum mechanical vibrational lineshapes obtained from dynamical path integral methods13–16 are discussed in Sec. V. Finally, Sec. VI contains our concluding remarks.

II. OPTIMIZED CLASSICAL STRUCTURES

We begin by considering the stable structures of the MₙH₂ clusters. In these studies we are interested in both the global minimum (the classical lowest energy structure) and low-lying structural isomers. The embedded atom method
(EAM), described in detail elsewhere, is used in the present work. Present calculations utilize the same EAM parameter sets as our previous work for purposes of comparison.

Using the EAM potential, we generate stable structures for $M_nH_2$ clusters using a combination of simplex methods and simulated annealing techniques. From two to four thousand random initial configurations are chosen for each cluster. The lowest energy structures plus the first few low-lying structural isomers for $Ni_nH_2$ so obtained are shown in Fig. 1.

In general, the global minima of nickel clusters with two hydrogen atoms have the same nickel atom topology as the corresponding monohydrides. The exception is the $Ni_8H_2$ cluster where two symmetrical octahedral sites are formed to accommodate the two hydrogen atoms rather than hydrogen binding outside the cluster with no octahedral sites. The strong repulsion between hydrogen atoms prevents the occupation of neighboring sites. As a consequence, within the EAM model the second hydrogen prefers binding outside if, as is the case in clusters with 5–7 nickel atoms, the available inside site places it in proximity to the other hydrogen atom. Since metal-metal bond distances in nickel clusters are smaller than in palladium clusters, nickel clusters often rearrange to form larger binding sites to accommodate hydrogen atoms. This can be seen from the global minimum structures of $Ni_9H_2$ and $Ni_{10}H_2$ clusters. EAM models of nickel clusters tend to form symmetric octahedral sites, if possible, to bind the two hydrogen atoms inside. The binding sites in analogous palladium clusters, however, are sufficiently large to accommodate hydrogen without rearrangement.

Most of the global minima of the EAM models of $Pd_nH_2$ clusters have the same geometry as the corresponding nickel clusters, as shown in Fig. 2. The exceptions is the $Pd_9H_2$ cluster where the two hydrogen atoms occupy two non-neighboring tetrahedral sites even though there is an octahedral site available in between. There exists a competition between larger binding sites and larger H-H distances in forming the stable structures. The larger lattice constant of palladium enables the cluster to accommodate hydrogen in its smaller tetrahedral binding sites. Hence, it seems that the H-H interaction is the primary factor in determining the classical structures, as can be seen from the lowest several isomers of the $Pd_9H_2$ cluster (cf. Fig. 2). The global minimum geometry of the $Ni_9H_2$ cluster with two symmetric octahedral sites appears as the fourth minimum of $Pd_9H_2$. The preference for the non-neighboring smaller binding site over the larger neighboring octahedral site may result from the nature of the H-H interaction. Christmann and co-workers have found that H-H interactions on Ni(111) are primarily repulsive up to second nearest neighbors. Based on the study of the experimental phase transition diagram, it is deduced that

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FIG. 1. Stable classical geometries of EAM models of $Ni_nH_2$ with $n = 4–9$.

FIG. 2. Stable classical geometries of EAM models of $Pd_nH_2$ with $n = 4–9$. 

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the third-neighbor interaction may be attractive.\textsuperscript{23,24} The physical origin of this long-distance interaction has been explored by Einstein and Schrieffer within a tight-binding model calculation.\textsuperscript{25}

There is a rearrangement of the structure of the Pd\textsubscript{7}H cluster structure upon the addition of a second hydrogen atom. The lowest potential energy minimum of Pd\textsubscript{7}H\textsubscript{2} has the same qualitative geometry for the palladium atoms as the quantum ground state of Pd-H.\textsuperscript{4,5} The structure is similar to the fcc (111) surface structure. This geometry is dominant in the lowest isomers for both Ni\textsubscript{7}H\textsubscript{2} and Pd\textsubscript{7}H\textsubscript{2} clusters. It is interesting to note the sequence of filling the binding site for the second hydrogen in these clusters. While the tetrahedral site is always occupied, the second hydrogen prefers to surface binding site and then the octahedral site in the Ni\textsubscript{7} cluster. In the corresponding palladium cluster, the filling sequence for the second hydrogen is the reverse (i.e. the octahedral site is preferred over the surface site).

It is interesting to study the expansion of the cluster upon the incorporation of hydrogen. The comparison of the global minimum of Pd\textsubscript{7}H\textsubscript{2} and the second minimum of Pd\textsubscript{7}H shows that the second hydrogen occupies a tetrahedral site, enlarges that site by about 5\% in linear dimension, and also expands the original octahedral site by 2\% through H-H repulsion. Since the equilibrium lattice position of an interstitial hydrogen atom requires that the electron density be as low as possible, the expansion in the tetrahedral site is much larger than in the octahedral site. It should also be noted that when hydrogen moves from an octahedral site to a surface site (second minimum), there is an expansion in the octahedral site instead of a contraction. The interlayer distance (i.e., the distance between the two three-fold planes) increases from 2.154 to 2.159 Å. In the EAM formalism, the outermost metal layer embeds itself into a higher electron density by moving toward the second layer, thus lowering the energy. When hydrogen appears on the surface, this contraction is reduced thus expanding the octahedral site. For the nickel cluster, the expansion upon the addition of a hydrogen atom to the octahedral site corresponds to an expansion of 1.1\% in the octahedral site and 6\% in the tetrahedral site. The movement of hydrogen from an octahedral site to the surface site induces an expansion of 0.14\% in the octahedral site. As is mentioned, the equilibrium structures are obtained using simplex method and confirmed by simulated annealing method. Repeated minimizations show that the resulting structures are consistent within a precision of 1 meV in the energy and 10\textsuperscript{-4} Å in the bond length.

### III. QUANTUM GROUND STATE STRUCTURE AND ENERGY

The quantum ground state energy and structure are determined by using the DMC (diffusion quantum Monte Carlo) method. The present results utilize Ceperley’s algorithm\textsuperscript{11} with a different sampling procedure. All the at-

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**TABLE I. Normal mode frequencies (in cm\textsuperscript{-1}) for hydrogen vibration in selected clusters.** $I_0$, $I_1$, \ldots refer to the lowest isomer, the second lowest isomer, etc.

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oms are moved simultaneously instead of just one atom in each Monte Carlo step. The trial function is of the form:

$$\phi_T = \prod_{i<j} e^{-\frac{1}{2} \sum_{i<j} \varphi_{ij}(r_{ij})}$$

(1)

where \( \varphi_{ij} \) is given by

$$\varphi_{ij} = \begin{cases} e^{-d_{ij}(r_{ij} - c_{ij})^2} & \text{if } M-M \\ e^{-d_{ij}(r_{ij} + c_{ij})^2} & \text{if } M-H \ or \ H-H \end{cases}$$

(2)

In Eq. (2) \( M \) refers to the metal atom and \( H \) refers to hydrogen atom. The parameters \( \alpha, d_{ij} \) and \( c_{ij} \) are optimized by minimizing the variance in the local energy. The numerical values used for these parameters are: \( \alpha = 0, d_{MH} = 0.00198 \text{ Bohr}^{-1} \), \( d_{HH} = 0.0001 \text{ Bohr}^{-1} \), \( d_{MM} = 0.00002 \text{ Bohr}^{-2} \), \( c_{MH} = 1 \text{ Bohr}^{-1} \), \( c_{HH} = 0.6 \text{ Bohr}^{-1} \), \( c_{MM} = 4.6 \text{ Bohr} \).

The calculations are divided into about 150 blocks of 2000 iterations. The number of random walkers is maintained at approximately 1000 by random duplication or elimination. The optimized classical potential energy minima are used as the initial distribution. The wave-functions are obtained by weighting each final DMC configuration by \( 1/\phi_T \), which give the probability distributions for the atoms. The resulting distribution is well localized at positions representing the atoms of physical systems. The quantum ground state structures are constructed by positioning each atom at the center of mass of the density corresponding to each atom. The structures obtained in general reflect the classical global potential energy minima, with the exception of the Ni$_5$H$_2$, Ni$_7$H$_2$, and Pd$_9$H$_2$ clusters. Figure 3 shows the quantum ground state structures and the corresponding classical global minimum structure for these three clusters. The quantum ground state structure for the nickel atoms for both Ni$_5$H$_2$ and Ni$_7$H$_2$ have the same qualitative geometry as classical global minimum, but with different hydrogen binding sites. The common feature is that the hydrogen binding in a tetrahedral site moves out to the surface site. For Ni$_5$H$_2$, where only tetrahedral sites are available for inside binding, the quantum ground state has the structure of the classical second minimum with two hydrogen atoms binding on surface sites. For Ni$_7$H$_2$, the quantum ground state resembles the third classical minimum with one hydrogen in an octahedral site and the other on the surface of the tetrahedral site. The small tetrahedral site is not lowest in energy when the contribution from the zero-point motion of the hydrogen atom is included, and the outside binding is preferred as a result. The outside binding also lowers the energy by reducing the repulsive interaction between the hydrogens. For the Pd$_9$H$_2$ cluster, the quantum ground state resembles the geometry of the fourth classical minimum with the hydrogens binding inside the two octahedral sites. Therefore, the larger binding site becomes the most important factor in determining the quantum ground state minimum structure owing to the zero-point motion.

Table I lists the hydrogen normal mode frequencies for selected clusters. The corresponding harmonic energies and classical potential energies are listed in Table II. DMC calculations show that zero-point energy effects can reorder the energy of isomers. The reordering can be easily predicted from a normal mode analysis of the lowest closely lying isomers, as can be seen from Table II. If the zero-point energy is included, the global minimum energy of Ni$_5$H$_2$ is increased from \(-27.308 \) to \(-26.018 \text{ eV} \), the second minimum is increased from \(-27.292 \) to \(-26.062 \text{ eV} \), and the third minimum has a ground state energy of \(-26.089 \text{ eV} \). Hence, a normal mode analysis predicts (correctly) that the third isomer should be the quantum ground state structure.

Table III lists the ground state energies calculated from the normal mode approximation and DMC. A normal mode analysis in general gives a good approximation, which indicates that the anharmonic effects at zero temperature are small.

As mentioned previously, the quantum-mechanical ground state structures and the classical minimum energy configurations differ for the Ni$_5$H$_2$ and Pd$_9$H$_2$ clusters. Interestingly, this is not the case for the corresponding deuterium compounds. Diffusion Monte Carlo calculations reveal that both the mono- and deuteride clusters share common quantum and classical minimum energy topologies. For purposes of comparison with the results listed in Table III, these diffusion Monte Carlo calculations produce estimates of

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**TABLE II.** The classical EAM ground state energies (CM) and the zero-point corrected ground state energies (NM) for the clusters in Table I (units are eV).

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<td>-29.870</td>
<td>-30.937</td>
<td>-29.736</td>
</tr>
<tr>
<td>Ni$_7$H$_2$</td>
<td>-34.445</td>
<td>-33.257</td>
<td>-34.329</td>
<td>-33.079</td>
</tr>
<tr>
<td>Pd$_5$H$_2$</td>
<td>-19.062</td>
<td>-18.110</td>
<td>-18.875</td>
<td>-17.912</td>
</tr>
<tr>
<td>Pd$_5$H$_2$</td>
<td>-22.166</td>
<td>-21.252</td>
<td>-22.068</td>
<td>-21.074</td>
</tr>
<tr>
<td>Pd$_5$H$_2$</td>
<td>-25.253</td>
<td>-24.194</td>
<td>-25.149</td>
<td>-24.011</td>
</tr>
<tr>
<td>Pd$_5$H$_2$</td>
<td>-31.294</td>
<td>-30.178</td>
<td>-31.286</td>
<td>-30.155</td>
</tr>
</tbody>
</table>

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TABLE III. Summary of EAM zero point (NM) and diffusion Monte Carlo (DMC) estimates of the ground state energies of M₇H₂ metal/hydrogen clusters. The structural isomer used for the harmonic estimates is that corresponding to the previous structure found for the DMC ground state. The error bars listed are one standard deviation.

<table>
<thead>
<tr>
<th>No. metal atoms</th>
<th>Nickel E₀ (eV)</th>
<th>Palladium E₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harmonic</td>
<td>DMC</td>
<td>Harmonic</td>
</tr>
<tr>
<td>4</td>
<td>−15.903</td>
<td>−15.94 ± 0.03</td>
</tr>
<tr>
<td>5</td>
<td>−19.150</td>
<td>−19.19 ± 0.02</td>
</tr>
<tr>
<td>6</td>
<td>−23.020</td>
<td>−23.05 ± 0.02</td>
</tr>
<tr>
<td>7</td>
<td>−26.228</td>
<td>−26.23 ± 0.02</td>
</tr>
<tr>
<td>8</td>
<td>−29.870</td>
<td>−29.86 ± 0.03</td>
</tr>
<tr>
<td>9</td>
<td>−33.257</td>
<td>−33.24 ± 0.02</td>
</tr>
<tr>
<td>10</td>
<td>−37.007</td>
<td>−36.98 ± 0.03</td>
</tr>
</tbody>
</table>

the −26.442 and −30.472 eV for the Ni₇D₂ and Pd₉D₂ clusters, respectively.

IV. CLASSICAL VIBRATIONAL SPECTRUM

This section considers the finite temperature classical power spectra, I(ω), for the hydrogen atoms in M₇H₂ clusters. Because it provides a particularly convenient model of the fcc (111) surface structure, we focus attention in what follows on the Pd₇H₂ cluster. While the details of the results vary, the methods discussed below apply equally to other systems. Power spectra are calculated from the expression

\[ I(\omega) = 2 \int_0^\infty C(t) \cos(\omega t) dt, \]  

where \( C(t) \) is the classical position or velocity autocorrelation function. The final spectra are smoothed from \( I(\omega) \) through

\[ I(\omega') = \int d\omega I(\omega) \exp\left(-\frac{1}{2} \left( \frac{\omega' - \omega}{\delta\omega} \right)^2 \right), \]  

where \( \delta\omega \) specifies the degree of smoothing. A value of \( \delta\omega = 5 \text{ cm}^{-1} \) is used in most of our calculation. Molecular dynamics methods \(^{12} \) are used to calculate \( C(t) \). Relatively long trajectories (80000 time steps of 30 au in duration) are utilized to determine the time correlation functions involved. To prevent rotation of the clusters, initial velocities are set to zero and a body-fixed coordinate system is used. Initial configurations are generated from equilibrium Monte Carlo snapshots of the system at a specified “temperature” \( T \). Because the initial kinetic temperature is taken to be zero, the effective cluster temperature is thus, within a simple harmonic model, roughly equal to \( T/2 \).

Figures 4(a) and 4(b) show MD (molecular dynamics) spectra for Pd₇H₂ and Pd₉H₂ at a temperature of \( T=10 \text{ K} \). The sharp spectral features indicate that the motion at these temperatures is effectively harmonic. This is confirmed by noting that the peaks in Fig. 4 are in excellent agreement with the normal mode frequencies listed in Table I.

The lowest energy structure of Pd₇H₂ has \( C_{₃v} \) local symmetry for both hydrogens. Local hydrogen vibrational modes are thus doubly degenerate \( E \) modes or singly degenerate \( A \) states. For example, the local modes of the octahedral hydrogen in Pd₇H₂ have at 2488 cm⁻¹ \( (E \text{ state}) \) and 1518 cm⁻¹ \( (A \text{ state}) \) while the corresponding tetrahedral hydrogen local modes are at 2341 cm⁻¹ \( (E \text{ state}) \) and 3260cm⁻¹ \( (A \text{ state}) \), respectively. From Table II, we see that the normal modes of the Pd₇H₂ system contain recognizable signatures of these local mode frequencies. The splitting seen in the \( E \)-states is relatively small, an indication that the absorbate-absorbate interactions are not severe. Another indication that the mo-

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FIG. 4. The classical power spectra obtained from the velocity autocorrelation functions: (a) Pd₇H₂ at \( T=10 \text{ K} \). (b) Pd₉H₂ at \( T=10 \text{ K} \). (c) The tetrahedral hydrogen in Pd₇H₂ at \( T=10 \text{ K} \). (d) The octahedral hydrogen in Pd₇H₂ at \( T=10 \text{ K} \). (e) Pd₇H₂ at \( T=100 \text{ K} \). (f) Pd₉H₂ at \( T=700 \text{ K} \).
tion of the individual hydrogen atoms contain components of
the system’s normal modes can be seen in Figs. 4(c) and
4(d). For example, in addition to features that can be attrib-
uted to its local modes, the power spectrum of the octahedral
hydrogen contains a peak at 2340 cm$^{-1}$ arising from cou-
pling to the tetrahedral hydrogen’s local E-mode. The spec-
trum for tetrahedral hydrogen [Fig. 4(d)] similarly reflects
the E-modes of the octahedral hydrogen.

As the temperature increases, the large non-linearities in
potential energy between atoms become important and an-
harmonic effects start to play a role in the vibrational spec-
trum. Figure 4(e) presents the spectrum of Pd$_7$H$_2$ at $T$
= 100 K. A comparison with Fig. 4(a) shows that the higher
temperature peaks are broadened and shifted to lower fre-
quencies relative to the low temperature spectrum. The clus-
ter at 100 K does not isomerize during the course of the
simulation trajectory. The peaks in the vibrational spectrum
thus correspond to relatively well defined normal modes of
the lowest energy isomer. As the temperature is increased
and the cluster begins to visit higher energy isomeric struc-
tures, well defined sharp features of the spectrum are lost
[see Fig. 4(f)]. For comparison, the low temperature classical
spectrum of Pd$_7$D$_2$ is shown in Fig. 5.

V. QUANTUM VIBRATIONAL SPECTRA

In this section we utilize dynamical path integral methods$^{14–16,26,27}$ to compute the quantum-mechanical vibra-
tional lineshapes for Pd$_7$H$_2$ system. Readers interested in the
details of the method are referred to the review paper by
Jarrell and Gubernatis.$^{13}$ Briefly summarized, the method uti-
lizes maximum entropy methods to stabilize the inversion of
imaginary time correlation function data to produce the de-
sired spectral lineshapes. The required imaginary time input
data are computed using established equilibrium path integ-
ral methods.$^{28,29}$

In the present work, Fourier path integral methods are
used to calculate the mean-square displacement, $R^2(\tau)$, for
hydrogen atoms in the cluster.$^{14}$ This function represents the
mean-square displacement between points on the equilibrium
quantum-mechanical paths of the hydrogen atoms separated
in imaginary time equal to $\tau$. Specifically, $R^2(\tau)$ is given by

$$R^2(\tau) = \langle |r(i\tau') - r(i(\tau + \tau'))|^2 \rangle$$

$$= 2[D(0) - D(\tau)],$$

where $D(\tau)$ is the position-position autocorrelation function,

$$D(\tau) = \langle r(-i\tau) r(0) \rangle.$$  

$R^2(\tau)$ is related to the vibrational spectrum, $I(\omega)$, through
the expression

$$R^2(\tau) = \int_0^\infty \left( 1 - \frac{e^{-\beta\hbar\omega/2} + e^{\beta\hbar\omega/2}}{e^{\beta\hbar\omega/2} + e^{-\beta\hbar\omega/2}} \right) A(\omega) d\omega,$$

where $A(\omega) = (1 + \exp(-\beta\hbar\omega))I(\omega)$. $R^2(\tau)$ is periodic in 0
$\leqslant \tau \leqslant \beta\hbar$. This interval is divided into 80 equal-spaced
points for numerical calculation. Using input data for $R^2(\tau)$
computed from equilibrium path integral methods, Eq. (8) is
solved for $A(\omega)$ [and hence $I(\omega)$] using maximum entropy
methods$^{30–33}$ to regularize the inversion.$^{22}$

In the present path integral calculations, the Monte Carlo
data are blocked every 50 steps to break serial correlation.
Each block data is averaged over 20 configurations. The
Monte Carlo steps are continued until the maximum entropy
inversion produces a converged spectrum. All the cluster at-
oms are quantized in the calculation. To rule out the effect of
cluster rotations, a body-fixed coordinate system is used with
the “z-direction” taken to be perpendicular to the plane
formed by the three “surface” atoms in the cluster. As dis-
cussed earlier, a perfect $C_{3v}$ cluster symmetry would lead to
a symmetric $A_1$ and a doubly degenerate $E$ state. Fluctua-
tions in the cluster’s geometry can be expected to break this
perfect symmetry.
Maximum entropy inversion results for $T=100$ K are presented in Fig. 6 for tetrahedral and octahedral hydrogens, respectively. As in the case of Pd$_7$H cluster, the hydrogen motion in the clusters is coupled with the Pd atoms. Consequently, the hydrogen spectra contain low-frequency palladium phonon side-bands. From both Figs. 6(a) and 6(b), we see that the degenerate $E$-mode is split, an indication that finite temperature cluster fluctuations are disrupting the perfect $C_{3v}$ ground state symmetry.

Compared with the octahedral hydrogen spectrum for the Pd-H cluster, the octahedral hydrogen spectrum in Pd$_7$H$_2$ shows three significant differences:

- the parallel vibrational modes are broadened;
- the peaks are shifted to higher frequencies, particularly the $E$-mode features;
- there is a weak feature at about 3600 cm$^{-1}$.

The first two changes are consequences of the dynamical coupling between the two hydrogens and of an increase in the magnitude of the shape fluctuations in the Pd$_7$H$_2$ system relative to Pd$_7$H. Quench studies of the “inherent structures” of the Pd$_7$, Pd$_7$H, and Pd$_7$H$_2$ systems reveal that adding hydrogen to the parent cluster increases the number of low-lying structural isomers, and, in a related fashion, lowers the energy barriers that separate these isomers. The general “softening” of the cluster substrate upon the addition of hydrogen produces shape fluctuations for the dihydride system that are greater than those in the mono-hydride. This increase in shape fluctuations provides a plausible mechanism for the observed spectral broadening. While it is not the principal topic of the current discussion, we also note that this mechanism also provides a possible mechanism to rationalize the “hydrogen induced mobility” reported elsewhere. The larger shift and broadening seen in the $E$-modes indicate a stronger coupling of these modes. This is in line with the classical results discussed in Sec. IV. We note that surface experiments have reported similar spectral shifts and broadening with increasing hydrogen coverage.

The weak feature at 3600 cm$^{-1}$ is likely either an overtone of the octahedral local $A$-mode or an indication of coupling to the high-frequency, tetrahedral local $A$-mode. While we have not attempted to do so here, this matter could be resolved by calculations in which the tetrahedral hydrogen in Pd$_7$H$_2$ were replaced with deuterium.

For both octahedral and tetrahedral hydrogen, the calculated frequencies are lower than the corresponding normal mode frequencies. The magnitude of the anharmonic shifts for the octahedral (tetrahedral) hydrogen are 23% and 8% (16% and 8%) for the $E$ and $A$-modes, respectively. This compares with anharmonic shifts of 17% and 3% for the octahedral hydrogen in Pd$_7$H.

**VI. CONCLUSION**

Hydrogen-hydrogen interactions play a significant role in a variety of metal/hydrogen systems. In an effort to characterize this role more fully, we have begun a series of cluster and bulk investigations of these materials.

In this paper, we have examined the role of hydrogen-hydrogen interactions on the equilibrium and dynamical properties of embedded atom potential models of Ni$_n$H$_2$ and Pd$_n$H$_2$ clusters ($4 \leq n \leq 9$). Structural as well as isotopic isomers have been considered to permit a comparison with previous, monohydride findings.

Maximum entropy, dynamical path integral methods have been used in the present work to compute hydrogen vibrational lineshapes. These studies, along with earlier cluster and surface investigations, illustrate the value of such methods in assessing the significance of anharmonic and quantum-mechanical effects in these finite-temperature, many-body systems.

Within the embedded atom model, we find that the distribution of dihydride clusters of nickel and palladium reflect a variety of competing effects. In general, the classical global minima of the dihydride nickel clusters studied have the same qualitative geometries for the nickel atoms as the corresponding monohydrides. An exception is the Ni$_9$H$_2$ cluster where hydrogen-hydrogen repulsion induces a structural change. The classical global minimum energy structures of the dihydride palladium clusters mirror those of nickel with the exception of the Pd$_9$H$_2$ system where the effects of the larger palladium-palladium bond length play a significant role.

As was the case in previous studies, we have found examples (Ni$_n$H$_2$, Ni$_n$H$_2$, and Pd$_n$H$_2$) where the quantum-mechanical ground state structures differ from the corresponding classical predictions. In these cases the common feature is that the zero-point motion of hydrogen induces a preference for moving hydrogen out of smaller, tetrahedral positions to either surface or larger, octahedral locations. We note that in each of these examples, simple zero-point corrections to the classical isomer energies properly predict the ground state structures found in more elaborate, diffusion Monte Carlo investigations.
In addition to specific results for various systems, the present studies have suggested what may be a general molecular mechanism for what has been termed hydrogen induced mobility.\(^{35}\)

Hydrogen-hydrogen interactions have also been studied using the EAM potential for hydrogen adsorbed on Pd(111)\(^{38,39}\) and Ni(111).\(^{40}\) Good agreement between the theoretically predicted and experimentally observed phase diagrams was found. These studies also suggested that the hydrogen-hydrogen potential of mean force is primarily repulsive up to second nearest neighbors, while the third-neighbor interaction may be attractive. Although this potential was not explicitly calculated in the present study, the predicted cluster binding sites of hydrogen would appear to be consistent with earlier surface findings. Differences between the classical and quantum minimum energy cluster structures suggest that zero-point effects tend to weaken these repulsive hydrogen-hydrogen interactions.

Finally, it is important to emphasize that the present studies are based on a particular model of the microscopic interactions involved. Consistent with our intended purposes, such studies are broadly useful for testing theoretical methods and identifying qualitative trends. Their quantitative merit concerning specific predictions for particular systems awaits further study.

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