Quantum Nuclei at Weakly Bonded Interfaces: The Case of Cyclohexane on Rh(111)

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Abstract

The electronic properties of interfaces can depend on their isotopic constitution. One known case is that of cyclohexane physisorbed on Rh(111), in which isotope effects have been measured on the work function change and desorption energies. These effects can only be captured by calculations including nuclear quantum effects (NQE). In this paper, this interface is addressed employing dispersion-inclusive density-functional theory coupled to a quasi-harmonic (QH) approximation for NQE, as well as to fully anharmonic ab initio path integral molecular dynamics (PIMD). The QH approximation is able to capture that deuterated cyclohexane has a smaller adsorption energy and lies about 0.01 Å farther from the Rh(111) surface than its isotopologue, which can be correlated to the isotope effect in the work function change. An investigation of the validity of the QH approximation relying on PIMD simulations, leads to the conclusion that although this interface is highly impacted by anharmonic quantum fluctuations in the molecular layer and at bonding sites, these anharmonic contributions play a minor role when analysing isotope effects at low temperatures. Nevertheless, anharmonic quantum fluctuations cause an increase in the distance between the molecular layer and Rh(111), a consequent smaller overall work function change, and intricate changes in orbital hybridization.

I. INTRODUCTION

Usually, the electronic properties of interfaces do not strongly depend on the isotopic constitution of the atoms that compose them. This is because the electronic structure of different isotopes is the same and nuclei can typically be considered as classical particles, which means that an isotopic change cannot lead to a change in the (static) atomic structural properties of materials, and thus do not cause a change in the electronic structure. However, when the quantum nature of the nuclei makes itself more prominent, this ceases to be true. An isotopic change can lead to structural changes of the material and thus to a considerable change in the electronic structure. Such electron-phonon coupling effects can be captured to a great extent in the adiabatic limit [1]. In this case, electronic properties can be modified because of their dependence on the nuclear positions and the equilibrium distribution of nuclear fluctuations at any given temperature.

One known case to exhibit such isotopic effects is cyclohexane (C₆H₁₂) adsorbed on platinum-group metal surfaces. It was shown in a series of papers by Koitaya, Yoshinobu, and coworkers [2, 3], that the change of work function induced by adsorbed cyclohexane is different when considering C₆H₁₂ and fully deuterated C₆D₁₂. Based on work function measurements and previous calculation of alkanes on metal surfaces [4], it was suggested

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that deuterated molecules should lie farther from the surface. Also the desorption energy
differs significantly: that of C\textsubscript{6}H\textsubscript{12} on Rh(111) is 80-140 meV higher than that of C\textsubscript{6}D\textsubscript{12},
thus showing an inverse kinetic isotope effect. In these systems, such effects are of a certain
relevance because changes in the strength of the bond between hydrogen and metal and
between hydrogen and carbon impacts the dehydrogenation propensity of cyclohexane – a
molecule that often plays a central role in systems aiming at cheap high-density hydrogen
storage [5]. The availability of experimental data and the importance of these systems thus
make them an ideal ground to study the performance of different theoretical techniques in
a complex but well-defined environment.

The challenges for theory to tackle this problem stem from the necessity of capturing com-
plex electronic-structure changes, as well as the multidimensional atomic structure of quan-
tum nuclei. In particular, electron-phonon coupling needs to be included at least in an ap-
proximate fashion in order to relate nuclear fluctuations and electronic-structure variations.
Modelling these effects becomes more important as the field moves towards soft and hybrid
electronic materials, where electron-phonon coupling tends to be more pronounced [6, 7].
A common way to address such problems is to employ the harmonic approximation for the
nuclear vibrations on first-principles potential energy surfaces [8]. However, the validity of
this approximation in weakly bonded systems and interfaces, where anharmonic terms in
the potential energy surface are expected to play a role, is questionable.

Instead, a method capable of including NQE without relying on the harmonic approx-
imation is \textit{ab initio} path integral molecular dynamics (aiPIMD) [9]. Despite its immense
potential, a significant drawback of aiPIMD simulations is their high computational cost.
Therefore, in this work aiPIMD simulations are performed making use of a technique that
reduces the amount of replicas required for simulations of weakly-bonded interfaces [10].
These results are compared to harmonic and quasi-harmonic approximations. With these
simulations, we are able to explain the physical origin of the observed isotope effects on the
cyclohexane/Rh(111) interface and identify when a quasi-harmonic analysis of these effects
is valid. The capabilities and limitations of aiPIMD based on density-functional theory with
generalized gradient approximation functionals are further discussed for these cases.

II. RESULTS AND DISCUSSION

Experimental measurements conducted on the cyclohexane/Rh(111) interface have shown
that several aspects of the adsorption show a dependence on the coverage [2]. In particu-
lar, desorption competes with dehydrogenation at coverage values below 0.5. We therefore
built models for the different coverages, based on existing experimental data. On a clean
Rh(111) surface, experiment shows a high-order large commensurate (2\sqrt{79} \times 2\sqrt{79})R17.0°
pattern [11]. This system size would not be computationally tractable, given the amount
FIG. 1. The cyclohexane adsorption patterns considered in this work for modelling different coverages $\theta$. a) $\theta = 1$, $(2\sqrt{3} \times 2\sqrt{3}) R13.9^\circ$ unit cell. b) $\theta = 0.64$, $(3 \times 3)$ unit cell. c) $\theta = 0.46$, $(5 \times 5)$ unit cell. d) Coverage $\theta = 0.12$, $(7 \times 7)$ unit cell.

of \textit{ab initio} simulations necessary to investigate nuclear quantum effects in this system. A smaller commensurate structure that was also observed in experiment is a $(2\sqrt{3} \times 2\sqrt{3}) R13.9^\circ$ pattern [12], shown in figure 1a. This structure was taken as a reference for the full-coverage monolayer structure. The effective coverage for other structures derived from this one were calculated, and smaller unit cells for lower coverage were modelled. These models are shown in figure 1b-d. In the following, all calculations with the rev-vdW-DF2 [13] functional are performed with $\theta = 0.64$ (figure 1b), and the calculations with PBE+vdW$^\text{surf}$ [14, 15] functional (see Methods) are performed with $\theta = 0.46$ (figure 1c), unless explicitly stated otherwise.

A. Static results and the quasi-harmonic approximation

For the different coverages shown in figure 1, the adsorption energy $E_{\text{ads}}^{\text{pot}}$ per molecule was calculated as explained in Methods. The results employing the PBE+vdW$^\text{surf}$ functional are reported on the first column of figure 2b.

The harmonic free energy terms at a temperature of 150 K was added to the adsorption energy, as given by eq. 6. This temperature was chosen to satisfy several conditions. On one hand, the temperature should be below the temperature of desorption and dehydrogenation, which are both close to 200 K [2]. On the other hand, very low temperatures considerably
FIG. 2. a) The effect of the red shift in the C-H stretching modes on the adsorption energy, shown schematically. The difference in ZPE is between H and D is higher in vacuum than on surface, due to the different masses and the red-shift of the corresponding stretching mode upon binding.

b) Adsorption energies and harmonic free energies for different coverage values, calculated with the PBE+vdWsurf functional (light settings). The free energy is calculated for the temperature of 150 K and all energies are in meV. Experimental data from temperature programmed desorption (TPD) experiments from Ref. [2].

The results for each coverage are summarized in the figure 2b, columns 2-7. The addition of the zero point energy and the temperature-dependent free energy terms, already in the harmonic approximation, lead to a different adsorption energy for C₆H₁₂ and C₆D₁₂. This is to be expected, because the C-H stretching modes associated with the CH groups that point to the surface of the adsorbed cyclohexane show a significant red shift of up to 300 cm⁻¹ in comparison to the gas phase, as shown in figure S1 in SI. Because of the difference in mass between the H and D atoms, such a red shift has a stronger impact on the ZPE of a CH vibration, compared to a CD one, as schematically shown in figure 2a. In both cases, the effect of ZPE increases the energy of adsorption (figure 2b, columns 2,3), and in the case of C₆H₁₂ this effect is stronger. When adding the full free energy contributions,
the translational and rotational entropic contributions of the gas-phase molecules work to decrease the adsorption free energy (figure 2b, columns 5,6). The magnitude of the isotope effect is not strongly affected by temperature and is about a factor two smaller than what is observed in experiment. We also observe that the difference between H/D adsorption energies becomes smaller at full coverage. It decreases from 37 meV for $\theta = 0.12$ down to 20 meV for $\theta = 1$. This fact can be explained because the red shift of surface-pointing C-H stretching modes decreases with increasing coverage, pointing to a weaker molecule-surface interaction (see SI, fig. S1). This confirms the weakening of the Rh-H bond with increasing coverage (and consequent strengthening of the C-H bond).

In order to gauge the reliability of these results, the impact of the exchange-correlation functional on the full adsorption profile of cyclohexane on Rh(111) was investigated. In Fig. 3(a), we show the adsorption curve with the PBE functional, the PBE+vdWsurf functional, the PBE functional with the recently proposed many-body dispersion method nl-MBD [16] and the non-local rev-vdW-DF2 [13] functional (see Methods for the details of calculations). Due to the high polarization of the Rh atoms, only many-body dispersion corrections connected to the polarizability functional described in Ref. [16] could be used to treat this system. VdW interactions are a fundamental piece of the molecule-surface interaction, as expected. Among the functionals that contain these interactions, the PBE+vdWsurf functional yields a larger adsorption energy and the molecules lie closer to the surface than when employing PBE+nl-MBD or the rev-vdW-DF2 functional. The latter functionals, which contain a better handling of the contribution of the polarizability of these systems to the van der Waals interactions, seem to better approach the experimental values. For further investigation, we employ light settings of the FHI-aims code and a comparison of the adsorption curve between tight and light settings is shown in figure S3 in SI. The shape of the potential along the desorption coordinate hints that anharmonic effects on this coordinate or others that couple with it could have an important effect on the adsorption properties of this system, and potentially on nuclear quantum effects.

In order to investigate the impact of nuclear quantum effects including anharmonicity at least on the desorption coordinate, harmonic phonons and the corresponding zero-point-energy contribution to the adsorption energy for the adsorbed C$_6$H(D)$_{12}$ at different distances to Rh surface were calculated. At each desired distance, we have fixed the surface and either the center of mass of the molecule (PBE+vdWsurf calculations) or positions of the carbon atoms (rev-vdW-DF2 calculations), and optimized the other degrees of freedom. See discussion in the SI regarding the inclusion of different vibrational modes in this ZPE correction. The quasi-harmonic ZPE-corrected energy of adsorption $E_{\text{ads}}^*$ was then calculated according to Eq. 7.

These values were calculated with the PBE+vdWsurf and with the rev-vdW-DF2 functionals, which represent the extremes in binding energies and binding distances within the
FIG. 3. a) Adsorption curves calculated with different exchange-correlation functionals and vdW corrections: PBE (dotted blue line), PBE +vdWsurf [15] (solid blue line), PBE+nl-MBD (solid red line), and rev-vdW-DF2 [13] (dashed green line). Calculations based on the PBE functional were performed with the unit cell of $\theta = 0.46$ and tight settings within the FHI-aims code. The calculation with rev-vdW-DF2 was performed on $\theta = 0.64$ with the Quantum-ESPRESSO code. Shaded areas show the experimental values of the adsorption energy of C$_6$H$_{12}$ (red) and C$_6$D$_{12}$ (grey) [2]. b), c) ZPE-corrected energy of adsorption for C$_6$H$_{12}$ (red) and C$_6$D$_{12}$ (black), calculated according to the eq. 7 with PBE + vdWsurf (light settings) (b) and rev-vdW-DF2 (c). Blue lines show the adsorption energy values calculated only with total energy differences. The calculation with rev-vdW-DF2 was performed with the STATE code. d) Work function change as a function of distance to surface. Vertical lines mark the equilibrium distances for classical nuclei (blue), C$_6$D$_{12}$ (black) and C$_6$H$_{12}$ (red).
functionals we have investigated. In addition, the PBE+vdWsurf is computationally cheaper to perform dynamical simulations, therefore we are interested in benchmarking its behaviour. The results are presented in Fig. 3b and c. The adsorption energies and distances obtained for C6H12 and C6D12 in this way are also summarized in table S2 in the SI. With this procedure, both functionals predict a deformation of the binding energy curve that is different for C6H12 and C6D12, such that C6H12 has a larger binding energy and adsorbs closer to the surface than C6D12. The H-D adsorption energy difference is 39 (36) meV for PBE + vdWsurf (rev-vdW-DF2) functional. These values follow the same trend as what was observed for the desorption energy from temperature programmed desorption experiments, but the isotope effect that we calculate is smaller than the one that was measured, which was of 84 ± 23 meV [2]. We have checked that adding finite temperature contributions in the harmonic approximation to these values, up to 150 K, does not appreciably change this calculated isotope effect (see SI, figure S4).

The adsorption of molecules on surfaces causes a change in the work function of the system, due to redistribution of charge on the surface and change in the surface dipole. In the case of a neutral, non-polar adsorbate like cyclohexane, this effect is typically attributed (i) to the so-called “pushback effect”, when molecules “push” the vacuum tail of the electron density of the metal back into a surface [17, 18], and (ii) to the polarization of the adsorbate induced by the mirror image charge formed in metal [19]. By analyzing electronic charge density differences, shown in figure 4, we observe the pushback effect but also the undeniable formation of H-bonds. To visualize this, the electronic densities were integrated over the directions parallel to the surface and projected it in the perpendicular direction (figure 4a). The total electronic density of the interface was compared with the sum of the electronic densities of the clean surface and the isolated adsorbate. We observe an electron depletion in the C-H bonds and accumulation in the H...Rh region, which is associated with H-Rh bond formation. It is accompanied by the pushback effect similar to what was reported by Bagus et al. for cyclohexane on a Cu(111) cluster [18]. In figure 4b, the redistribution of the electron density on a plane perpendicular to the surface, that crosses only carbon-carbon bonds, is shown. In this plane, the contribution of H-bonds is small, therefore the electron depletion that is present under the molecule can be attributed to a pushback effect. It is difficult to separate the role of H-bond formation and the pushback effect clearly. By investigating the spatial arrangement of the electronic density changes, we conclude that the contributions of these two effects are of comparable magnitudes (see SI, figures S5 and S6). Together, H-bonds and a pushback effect cause a 2.13 Debye per molecule decrease in the dipole moment of the interface, and the decrease of work function of 960 meV.

Regarding the equilibrium distance of absorption, there is an important effect that is observed. The adsorption distance of C6H12 is 3.349 (3.427) Å in PBE + vdWsurf (rev-vdW-DF2) calculations, and for C6D12, it is 3.362 (3.439) Å. The H-D equilibrium distance
difference is thus $\approx 0.01$ Å. Although apparently small, this adsorption distance difference has a measurable effect on the work function changes. The sensitivity of the work function change $\Delta \phi$ of the interface to the distance between the adsorbate and the metal surface is shown in figure 3d. We calculated it by shifting an adsorbate rigidly closer and farther from the slab with respect to the equilibrium position at the potential energy surface. Around the equilibrium distance, the work function depends almost linearly on the distance, and the slope is of 1.185 (1.205) eV/Å with the PBE+vdW$^{\text{surf}}$ (rev-vdW-DF2) functional. A change of adsorption distance as the one observed between the deuterated and normal cyclohexane (0.01 Å) would thus produce a $\Delta \phi$ of around 15 meV, which does not strongly depend on the functional. In experiment [2], the same qualitative trend was observed, but a larger isotope effect on $\Delta \phi$ was reported, namely of around 60 (80) meV at the coverage values of 0.46 (0.64).

### B. Validity of the quasi-harmonic analysis

The quasi-harmonic treatment and the relationship between the distance of the molecule to the surface and the work function change already provide a qualitative explanation about the electronic structure changes that take place upon isotopic substitution. At this point,
FIG. 5. a) A scheme of the spatially-localized ring polymer contraction (SL-RPC). The forces for a full ring polymer of \( P \) beads are approximated by a superposition of forces calculated for \( P \) beads at the molecular part, \( P' < P \) beads of the full system and a correction of \( P' \) beads at the molecular part. b,c) Anharmonicity measure \( \epsilon \) (see eq. 4) for individual Cartesian \( x \) and \( y \) components of atomic forces from the PIMD simulation of \( \text{C}_6\text{H}_{12} \) (red squares) compared to classical-nuclei MD (blue triangles), and difference in \( \epsilon \) between PIMD simulations of \( \text{C}_6\text{H}_{12} \) and \( \text{C}_6\text{D}_{12} \) (black crosses). All values calculated for \( \theta = 0.46 \) (two cyclohexane molecules in the unit cell) and at \( T = 150 \) K. \( \text{Rh}^{s1} \) and \( \text{Rh}^{s2} \) denote the 1st and the 2nd layers of the surface atoms. d) Anharmonicity measure \( \epsilon \) for the Cartesian \( z \) component of the forces. The distinct group of Rh atoms with highly anharmonic forces consists of atoms connected to cyclohexane via hydrogen bonds.

it is interesting to gauge the accuracy the quasi-harmonic approximation in these types of interfaces.

Path integral molecular dynamics (PIMD), a method which exploits the quantum-classical isomorphism between a quantum system and a classical ring polymer with infinite number of beads \( P \) \([9]\), can be employed in this context, in order to calculate static thermodynamic averages without relying on any harmonic ansatz. When performed on \textit{ab initio} potentials (aiPIMD), subsequent analysis can capture the coupling between quantum molecular vibrations and the electronic structure of a surface in the adiabatic limit, with full anharmonicity and full dimensionality.

However, given the need of a first-principles potential energy surface and the large system sizes involved, aiPIMD simulations of this sort are associated with a high simulation cost, because of the need of several replicas of the full system to obtain converged results (the
number of beads $P$, which controls the convergence of PIMD results to exact quantum
expectation values). In order to alleviate this cost, one can use the fact that the bonding
between molecules and a surface is relatively weak in the case of cyclohexane, to apply the
spatially-localized ring-polymer contraction (SL-RPC) [10]. The core idea of this contraction
is sketched in figure 6a. The potential energy (and the corresponding forces) of the full
system of $P$ beads is approximated as a superposition of $P$ replicas of the molecular part,
$P' \ll P$ replicas of the full system, and additional $P'$ of the molecular part with negative
sign, i.e.

$$V_P(q) \approx \frac{P}{P'} \sum_{k=1}^{P'} \left[ V_{\text{full}}(\tilde{q}^{(k)}_{\text{full}}) - V_{\text{mol}}(\tilde{q}^{(k)}_{\text{mol}}) \right]$$

$$+ \sum_{k=1}^{P} V_{\text{mol}}(q^{(k)}_{\text{mol}}),$$

where $\text{full}$ denotes the full system containing the surface and adsorbed molecules, and $\text{mol}$
denotes the adsorbate simulated in the same unit cell, but without the surface. $q^{(k)}$ are
Cartesian positions of beads, and $\tilde{q}^{(k)}_{\text{full}}$ are obtained by the Fourier interpolation of the full
$P$ beads ring polymer to the contracted $P'$-polymer.

This approximation, of course, does not come without errors. One can estimate the error
introduced by SL-RPC in a harmonic potential [10]

$$\delta E_{\text{RPC}} = E_{\text{RPC}} - E_{\text{P beads}} =$$

$$= \sum_{i=1}^{3N} \frac{k_B T}{2} \sum_{k=1}^{P'} \left[ \frac{\omega^2_{i,\text{mol}}}{\omega^2_k + \omega^2_{i,\text{mol}}} - \frac{\omega^2_{i,\text{full}}}{\omega^2_k + \omega^2_{i,\text{full}}} \right],$$

where $\{\omega_{i,\text{mol}}\}$ are normal modes of the isolated adsorbate, and $\{\omega_{i,\text{full}}\}$ are the corre-
sponding modes calculated by diagonalization of the part of Hessian matrix that describes
molecular displacements. Equation 2 is slightly different from eq. 9 in Ref. [10] because we
have not made the assumption of $\omega^2_{i,\text{mol}} - \omega^2_{i,\text{full}} \ll \omega^2_k + \omega^2_{i,\text{full}}$, as discussed in section 6
in the SI.

Similarly, one can estimate the error in a harmonic quantum free energy at finite tem-
peratures (see derivation in the SI) as,

$$\delta F_{\text{RPC}} = \frac{1}{2\beta} \sum_{i=1}^{3N} \sum_{k=1}^{P'} \ln \left(1 + \frac{\omega^2_{i,\text{full}} - \omega^2_{i,\text{mol}}}{\omega^2_k + \omega^2_{i,\text{mol}}} \right).$$

Such an estimate for a cyclohexane on Rh(111), when taking $P' = 1$ does not exceed
37 meV per molecule for the total potential energy and 79 meV/molecule for the total free
energy. When comparing H- and D-cyclohexane, one can rely on error cancellation. Then,
the error in potential energy difference is 19 meV/molecule, and in free energy difference
about 36 meV/molecule. It is thus clear that although this approximation is very useful, if quantitative results for this particular system are desired, a contraction to the centroid \((P' = 1)\) is not sufficient and we do not further pursue calculations of free energies at this level of approximation. It should, however, be sufficient to capture further important anharmonic effects if present.

Before analyzing the PIMD results, we study the anharmonic contributions to the forces in this system, separating them into classical finite temperature effects and nuclear quantum effects. For this purpose, we follow the lines of Ref. [20] and calculate an anharmonicity measure for different degrees of freedom. Because it is interesting to compare the difference between quantum and classical anharmonic contributions to different coordinates in the system, we calculate

\[
\epsilon(T)^{\text{CL/QM}} = \sqrt{\frac{\langle (F_{\text{DFT}}^{\text{CL/QM}} - F_{h}^{\text{CL/QM}})^2 \rangle_T}{\sigma_{F_{\text{DFT}}}^2(T)}},
\]

where \(F_{\text{DFT}}\) are the full DFT forces calculated, \(F_{h}\) are harmonic forces calculated for the same geometry and with the Hessian matrix obtained for the full system, \(\sigma^2\) is the variance, and \(\langle \ldots \rangle_T\) is the ensemble average at the temperature \(T\). The superscripts CL and QM denote a classical-nuclei (aiMD) and a quantum-nuclei (aiPIMD) simulations, respectively. In the latter case, we take the forces on the bead positions. We normalize both classical and quantum quantities by the respective PIMD variance of that quantity so that the difference \(\epsilon(T)^{\text{QM}} - \epsilon(T)^{\text{CL}}\) corresponds to a measure of the amount of “quantum anharmonicity”.

We show the results of this analysis for \(C_6H_{12}\) and \(C_6D_{12}\) in Fig. 5 (b-d), where the force components are resolved into the three Cartesian directions (all calculations with PBE+vdW\textsuperscript{surf}). Such an analysis shows, as expected, that anharmonic contributions are more pronounced in the adsorbate molecules, and the difference between quantum and classical anharmonic scores is really only pronounced on the molecular adsorbate. However, H-bonded sites on the top layer of the surface not only show a pronounced anharmonicity in the \(z\) direction, but also a considerable quantum component, no doubt caused by the nuclear quantum contributions to the H-bond. In fact, comparing the \(z\) component of the forces with the \(x\) and \(y\) components, the \(z\) anharmonic score is always higher for the top surface layer and the molecules. This supports the conclusion that most anharmonic effects lie on the out-of-plane motions of molecules, which are captured to a limited extent in the QH approximation. However, these calculations also show that the contribution of quantum anharmonicity on \(C_6H_{12}\) and \(C_6D_{12}\) is similar, suggesting that they could play a minor role for the evaluation of isotope effects in this potential energy surface.
FIG. 6. a) The distribution of distances from the Rh(111) surface to H/D atoms (solid lines) and C atoms (dashed lines). The red (black) lines show PIMD simulations of C₆H₁₂ (C₆D₁₂), and the blue lines represent MD simulations with classical nuclei. b) The distribution of ∆φ values for PIMD simulations of C₆H₁₂ (red), C₆D₁₂ (black) and classical MD simulation (blue). c) The species-projected electronic density of states in a single-point calculation (black), a classical-nuclei MD simulation (yellow), PIMD simulations for C₆H₁₂ (blue) and C₆D₁₂ (red). Peaks are broadened and shifted due to coupling with nuclear vibrations. Typical Kohn-Sham eigenstates are shown near the corresponding peaks. In all panels, T = 150 K.

C. Analysis of PIMD results

From the aiMD and aiPIMD simulations (PBE+vdWsurf) we could directly estimate structural properties of the classical and quantum C₆H₁₂ and C₆D₁₂ on Rh(111) at 150 K. In addition, we could capture changes in the electronic structure including full electron-phonon coupling at the adiabatic limit, by averaging the desired electronic quantities of interest over the trajectories. The only drawback, as we will see below, is that even with the SL-RPC technique, statistically converging the quite small energy differences and structural changes observed upon deuteration is a very challenging task in this system, that could not be totally fulfilled with the amount of simulations we were able to perform for each of the systems (see Methods). Each force evaluation containing the full interface with the model θ = 0.46...
(FHI-aims program, light settings) amounts, on average, to 3.1 minutes when parallelized over 240 cores (Intel Xeon Gold 6148 Skylake processors, COBRA supercomputer). This cost renders these simulations computationally expensive even without considering nuclear quantum effects.

The results are summarized in figure 6a-c. In panel a, we show the distribution of the distance from the adsorbate atoms to the top layer of the Rh(111) surface. As expected, a more localized position distribution is observed for C$_6$D$_{12}$ than for C$_6$H$_{12}$, and it is even more localized for classical-nuclei cyclohexane. The inset in panel a shows that C$_6$H$_{12}$ can reach closer to the surface than C$_6$D$_{12}$ and classical-nuclei cyclohexane, but it was not possible to resolve differences on the average position $h_{\text{COM}}$ to an accuracy of 0.01 Å.

In figure 6b, the distribution of work function values at 150 K is shown. Again, C$_6$H$_{12}$ presents a broader distribution than C$_6$D$_{12}$ and classical-nuclei MD. The distributions are shifted with respect to each other, and their mean values $\langle \Delta \phi \rangle$ are ordered so that $\langle \Delta \phi \rangle_H < \langle \Delta \phi \rangle_D < \langle \Delta \phi \rangle_{\text{Classical}}$. The resulting values for $\langle \Delta \phi \rangle$ are $-928 \pm 16$ meV for C$_6$H$_{12}$, $-917 \pm 12$ meV for C$_6$D$_{12}$, and $-903 \pm 5$ meV for classical-nuclei cyclohexane. The H/D difference is $11 \pm 20$ meV. Compared to the QH approximation, the aiMD and aiPIMD simulations predict the molecules to lie farther away from the surface ($h_{\text{COM}} = 3.42 \pm 0.01$ Å) by around $0.06 \pm 0.01$ Å (see estimation of $h_{\text{COM}}$ within the QH approximation including temperature effects in fig. S3). Accordingly, the aiPIMD simulations predict a considerably smaller overall work function change. This is a consequence of taking into account anharmonic contributions at a temperature of 150 K (we note that the rigid “out of plane” vibrations of the adsorbates lie around 80-130 cm$^{-1}$, thus having components that are thermally activated at 150 K). This is also consistent with the high anharmonic score of the forces in the $z$ direction, especially at H-bonded sites. Statistically converging the differences between C$_6$H$_{12}$ and C$_6$D$_{12}$ would require a considerable computational effort. However, with the current uncertainty intervals, it is possible to conclude that the isotope effects from the PIMD simulations cannot differ largely from the QH results, confirming that anharmonic contributions play a minor role for these effects in this potential energy surface.

The aiPIMD simulations additionally give access to the electron density of states renormalized by the quantum fluctuations of the molecules. We project the total electronic density of states on the atomic species averaged over several snapshots of the simulations in figure 6c, compared to the static result. There is a pronounced broadening of the peaks only on the adsorbate (for both quantum and classical nuclei), and this broadening is much more pronounced when considering quantum nuclei. We note that it is not clear if one can assign any physical interpretation to such broadening of Kohn-Sham single-particle orbitals. Nevertheless, this effect is caused by the dependence of these ground-state orbital energies on nuclear configurations and the interplay of this dependence with the distribution of nuclear configurations. In addition, there are considerable energy shifts due to this electron-phonon
interaction in levels associated with $sp^3$ orbitals. Since $sp^3$ orbitals are responsible for C-H bonding, we tentatively correlate these shifts with the interplay of ZPE and anharmonicity, which effectively changes bond-lengths and thus the electronic structure in this system. The semilocal/nonlocal functionals we employ are not able to provide a quantitative level alignment of this interface, even if they can predict the HOMO level reasonably well because of the cancellation of the self-interaction error and the missing image-potential effect [21, 22]. Even though a much higher level of theory (e.g. many-body perturbation theory) would be desirable for a quantitative comparison with UPS experiments conducted at this interface [12], the magnitude of changes that we observe in the Kohn-Sham electronic density of states highlights the importance of taking nuclear fluctuations into account when analysing the electronic spectra of such interfaces.

III. CONCLUSIONS

In summary, we have studied isotope and anharmonic effects on the cyclohexane/Rh(111) interface by means of DFT calculations coupled to harmonic lattice dynamics, aiMD, and aiPIMD.

Employing a QH approximation, in which the harmonic ZPE contributions were calculated with the molecule fixed at different distances from the surface, it could be shown that the binding energy of $C_6D_{12}$ is smaller than $C_6H_{12}$ and that $C_6D_{12}$ lies 0.01 Å farther from the surface than $C_6H_{12}$, in qualitative agreement with the isotope effects previously observed experimentally [2] at the same interface. By showing that the work-function change of the interface is very sensitive to the molecule-surface distance, this geometrical isotope effect could be correlated with the isotope-induced change in the work function, thus confirming the hypothesis that Koitaya, Yoshinobu and coworkers proposed [3], based on experimental observations. Finally, these simulations also showed that the electronic-density rearrangement at the interface is impacted by both H-bond formation and the pushback effect and that the inclusion of van der Waals contributions, especially those that can capture well the polarizability of metallic atoms, improve energetics and adsorption distances in these systems.

The reliability of the QH approximation was assessed by estimating the degree of anharmonicity the nuclear motions at a temperature of 150 K. Anharmonic contributions to the forces are particularly pronounced at H-bonded sites on the surface and on the degrees of freedom belonging to the adsorbates. In these cases, in particular, the difference between classical and quantum anharmonic contributions is also large, meaning that techniques like PIMD are necessary to describe structural aspects and related electron-phonon interactions in these systems. However, the quantum anharmonic contributions to $C_6H_{12}$ and $C_6D_{12}$ are very similar for coordinates parallel to the surface, and thus play a minor role when address-
ing isotope effects. This explains why the QH approximation fares well for these quantities in these solid-state systems at lower temperatures.

Indeed, in the aiPIMD simulations, the pronounced anharmonic character of certain degrees of freedom in the direction perpendicular to the surface plane cause the equilibrium distance of the adsorbates to be around 0.06 Å farther from the surface than the QH approximation would predict. This is accompanied by considerably smaller work function changes. However, as expected due to the small contribution of anharmonic effects beyond the QH approximation and within the statistical error bars, the observed isotope effects on this system (distance to surface, adsorption energy and work function change) do not differ significantly from the QH case. Finally, the effect of electron-phonon coupling on the electronic density of states in the adiabatic limit causes a pronounced shift (and broadening) of Kohn Sham levels related to the CH bond.

Although we obtain excellent qualitative agreement with experiment and are able to provide an atomistic view on the origins of the isotope effects measured in this interface, quantitative agreement on the magnitude of the isotope effect on the work-function change and on the adsorption energy remains elusive. We are left with the conclusion that this disagreement is likely coming from slightly different conditions in experiment or the remaining approximations that were employed in this work, namely, the DFT functional and the SL-RPC approximation. We suggest that the functional would be the largest source of remaining errors, given the known drawbacks that functionals based on generalized gradient approximations present for adsorbates on metallic surfaces [23]. This motivates the training of fitted (or machine-learned) potentials on a higher level of theory, for example employing functionals that, beyond grasping many-body dispersion interactions, also mitigate the self-interaction error and capture long-range screening [24, 25]. Such potentials would both decrease the cost related to statistical sampling and increase the (quantitative) predictive power of these simulations.

IV. METHODS

Electronic structure calculations with FHI-aims: Energies and forces are calculated using density-functional theory (DFT) with the PBE exchange-correlation (XC) functional [26]. The calculations were done with the all-electron FHI-aims code, which uses numerical atom-centered orbitals [27] as basis sets. The FHI-aims package contains predetermined settings for numerical parameters and basis sets, which are aimed at different accuracy levels. “Light” settings were used for PIMD and phonon calculations, and “tight” settings were used for potential energy curves and electron density rearrangement.

An important component for the description of interfaces are dispersion interactions. For the molecule-surface interactions, we employed the pairwise Tkatchenko-Scheffler van
der Waals correction, modified in order to capture a collective response of a surface in the Lifshitz-Zaremba-Kohn form [15]. The parameters for Rh are reported in Ref. [28]. The van der Waals interaction between Rh atoms was not included.

We considered 4 Rh(111) layers in all FHI-aims calculations. The 2 bottom layers of the slab are fixed in the bulk geometry. The bulk geometry was calculated for the single-atom FCC unit cell using 16x16x16 k-point grid. The resulting lattice constant of 3.83 Å is in good agreement with the experimental value of 3.80 Å [29]. The surface was aligned perpendicular to the z axis. In order to isolate the system from its periodic replicas in the z direction, a dipole correction [30] and vacuum layer of 30 Å in both directions were applied.

Vibrational analysis was performed by a modified version of the Phonopy code coupled to FHI-aims [31, 32], which allowed to build the Hessian only for the molecular adsorbate and to account for a surface as a rigid environment. This approximation is well justified because the coupling between Rh atoms and the molecules is very weak, and this weak coupling is concentrated in the low-frequency modes of the adsorbates, which behave very similarly for H- and D-cyclohexane and thus do not impact isotope effects. We set atomic displacements to 0.01 Å for finite difference calculations.

**Quantum Espresso and STATE calculations:** Calculations were carried out with the rev-vdW-DF2 exchange-correlation functional [13, 33] as implemented in the Quantum Espresso (QE) [34, 35] and STATE [4, 36] packages. QE was used for the adsorption site search and the calculation of the adsorption energy curve, and STATE was used for calculations of vibrational spectra, adsorption energy curves with and without zero-point-energy correction, and the work function as functions of the molecule-surface distance. For these calculations, a Rh(111) (3×3) surface with 5 metal layers with a vacuum equivalent to eight monolayer (19.77 Å) is considered. The slab was constructed using the lattice constant optimized with rev-vdW-DF2 of 3.80 (3.81) Å for QE (STATE) calculations. The molecule was put on one side of the slab and the effective screening medium method was used to eliminate the artificial electrostatic interaction with the neighboring slabs [37, 38]. Projector augmented wave [39] potentials from the pslibrary 1.0.0 [40] and a plane-wave basis set with a cutoff energy of 80 (640) Ry were used for wave functions (charge density) in the QE calculation. Ultrasoft pseudopotentials [41] and a plane-wave basis sets with a cutoff energy of 49 (625) Ry for wave functions (charge density) were used in STATE calculations. A 6 × 6 (4 × 4) k-point grid was used in QE (STATE) calculations. Harmonic vibrational frequencies were calculated by using the Wilson’s GF method and finite difference method as implemented in the STATE package [42]. Atoms were displaced along the vibrational eigenmodes and the magnitude of the displacement was determined self-consistently.

**Adsorption energies and free energies:** The adsorption energies per molecule were calculated with

\[
E_{\text{ads}}^{\text{pot}} = (E_{s+m}^{\text{pot}} - E_s^{\text{pot}})/N_{\text{mol}} - E_m^{\text{pot}},
\] (5)
where \( E_{pot}^{s+m} \) is the total energy at the potential energy surface of a slab with molecules adsorbed, \( E_{pot}^{s} \) is the total energy of a clean surface relaxed with 2 bottom layers fixed in bulk position, \( E_{pot}^{m} \) is the total energy of a molecule relaxed in vacuum, and \( N_{mol} \) is the number of molecules in a unit cell. A similar expression can be written for a free energy of adsorption.

The harmonic vibrational free energy was calculated as

\[
F_{vib} = \sum_{i=1}^{N_{modes}} \left[ \frac{\hbar \omega_i}{2} + k_B T \ln \left( 1 - \exp^{-\frac{\hbar \omega_i}{k_B T}} \right) \right] + \\
+\text{[if gas phase]} \left( F_{trans} + F_{rot} \right),
\]

where \( N_{modes} = 3N - 3 \) when the free energy of a clean surface is calculated (\( N \) is the number of atoms in a unit cell), \( N_{modes} = 3N - 3N_s \) (\( N_s \) is the number of surface atoms in a unit cell) when the free energy of molecules adsorbed on surface is calculated, and \( 3N_m - 6 \) (\( N_m \) is the number of atoms in a molecule), when the free energy of an isolated molecule is calculated. Rotational and translational contributions were added for the free molecule according to the rigid-body and ideal gas textbook expressions [43]. The expression above only takes into account vibrations at the \( \Gamma \) point of the unit cell. Because we focus mostly on molecular vibrations in this work, this approximation does not introduce large errors in the calculated free energy differences. For the translational term, we took a pressure of \( 10^{-8} \) Pa, which is close to the reported experimental conditions [2].

The quasi-harmonic ZPE-corrected energy of adsorption \( E^*_{ads} \) was calculated as a difference between the energy at the equilibrium distance and at 10 Å away from the surface, which is considered to be far enough to remove all molecule-surface interaction,

\[
E^*_{ads}(h_{COM}) = \left( E_{pot}^{s+m}(h_{COM}) + \sum_{i=1}^{3N_m-6} \frac{\hbar \omega_i}{2}(h_{COM}) \right) - \\
- \left( E_{pot}^{s+m} + \sum_{i=1}^{3N_m-6} \frac{\hbar \omega_i}{2} \right)_{h_{COM}=10Å},
\]

where \( h_{COM} \) denotes the distance from the center of mass of the adsorbate to the Rh surface. Although \( E^*_{ads} \) is not a true adsorption energy, this procedure compensates spurious interactions that might appear in a particular simulation cell. For the ZPE contribution, we include either \( (3N_m - 3) \) or \( 3N_m \) molecular vibrations in PBE + vdWsurf or rev-vdW-DF2 calculations, respectively (see SI).

**Ab initio molecular dynamics:** AiMD and aiPIMD simulations were carried out by connecting FHI-aims to the i-PI code [44]. For classical-nuclei MD, a timestep of 1 fs was used. For a PIMD, a smaller timestep of 0.5 fs was employed to handle high-frequency vibrations of a ring polymer.
In order to accelerate sampling in the NVT ensemble, we applied a colored-noise generalized Langevin thermostat (GLE)\cite{45, 46} to the classical-nuclei aiMD simulations. For the aiPIMD simulations, the PIGLET thermostat was used \cite{47}. This approach preserves quantum distribution and gives a fast convergence of observables with respect to the number of replicas. The parameters for the thermostats are: 8 attached degrees of freedom (denoted as $s$ in the paper \cite{46}), the frequency range for a centroid is 0.32-3200 cm$^{-1}$ for C$_6$H$_{12}$ and 0.23-2300 cm$^{-1}$ for C$_6$D$_{12}$. The $A$ and $C$ matrices (as defined in \cite{46}) are parameterized for $\hbar \omega/k_B T = 50$ using the GLE4MD library \cite{48}. We observed convergence with around 12 beads for the adsorbate atoms (H) at 150 K within this setup. We have calculated 6 independent trajectories of total length of 11 ps for C$_6$H$_{12}$, 5 trajectories of total length of 25 ps for C$_6$D$_{12}$, and 5 trajectories of total length of 97 ps for classical-nuclei cyclohexane. The thermalization time is not included in the numbers provided.

The effect of nuclear fluctuations on electronic observables (work function, electronic density of states, etc.) were calculated as the average of single-point calculations from aiPIMD trajectories through the following general expression

$$\langle A \rangle = \frac{1}{Z} \text{Tr} \left[ \hat{A} e^{-\frac{\hat{H}}{k_B T}} \right] \overset{\text{ergodicity, PIMD sampling}}{=} \frac{1}{PN_s} \sum_{i}^{N_t} \sum_{k}^{P} A (q^{(k)}(t_i)) , \tag{8}$$

where $A$ is any position-dependent observable, $Z$ is the partition function, $\hat{q}$ is a position operator, $\hat{H}$ is the Hamiltonian, $P$ is the number of beads of a ring polymer, $N_t$ is a number of snapshots from a PIMD trajectory, and $q^{(k)}$ is a position vector for a bead $k$. The snapshots from the PIMD trajectory were picked so that they are statistically independent. The criterion for independence is an autocorrelation time of the property $A$. In our PIMD calculations, the autocorrelation time is 30 fs for a velocity, 300 fs for a work function and 600 fs for the z-coordinate of the center of mass of a molecule. For classical nuclei simulations, the same expression was used with $P = 1$.

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Supplemental information
Quantum Nuclei at Weakly Bonded Interfaces: The Case of Cyclohexane on Rh(111)

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I. COVERAGE DEPENDENCE OF VIBRATIONAL SPECTRUM

Vibrational density of states (vDOS) shows the role of coverage in adsorption energy. We show in figure S1 vDOS for the adsorption patterns considered in this work. The key feature is a red shift in the stretching vibrations of the CH groups pointing to the surface (denoted as (I) in figure S1b). This red shift decreases with the increase of coverage. It means that surface-molecule interaction becomes weaker. At highest coverage $\theta = 1$ there is multiple splitting of CH stretching frequencies. It is an evidence that cyclohexane adsorption sites become highly nonequivalent because of molecule-molecule interactions. We also note a blue shift in stretching vibrations of CH groups of type (III) and slight red shift in groups (II) and (IV).

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FIG. S1.  

a) ZPE levels when a red shift appears in the vibrations of adsorbed molecules. The adsorption energy of C\textsubscript{6}H\textsubscript{12} is therefore expected to be higher than that of C\textsubscript{6}D\textsubscript{12}. 
b) Different CH groups for a cyclohexane adsorbed on a surface. 
c) The vibrational spectra of CH stretching modes of cyclohexane in vacuum (black) and on a Rh(111) surface with coverage \(\theta = 0.12\) (red), \(\theta = 0.46\) (blue), \(\theta = 0.64\) (green) and \(\theta = 1\) (ochre). The grey arrows assign peaks to the CH groups given in (b). As the red shift in CH stretching modes decreases, the H/D difference in the adsorption energy decreases also. At the full coverage (\(\theta = 1\)), the intermolecular interaction is so strong that single adsorption sites become highly non-equivalent, which is reflected in multiple peak splitting in the range between 2540 and 3040 cm\textsuperscript{-1}.
II. COMMENSURATE ADSORPTION PATTERNS

Potential energies of adsorption $E_{\text{pot}}^{\text{ads}}$ for the systems discussed in the paper are provided in the table S1. In addition to “production” calculations made with Light settings of the FHI-aims, we provide reference calculations made with Tight settings. Additionally to the structures discussed in the manuscript, we show another structure, namely $(2.64 \times 2.64)R19.1^\circ$, which has coverage $\theta = 0.84$ compared to the reference structure (figure S2). This structure was observed in experiments [1], but not on a clean Rh surface. Instead, a Rh surface was covered by a small concentration of hydrogen ($\theta_H = 0.1 - 0.2$). We note that this structure has an adsorption energy very similar to the $\theta = 1$ structure, but we have not done a further investigation.

FIG. S2. A $(2.64 \times 2.64)R19.1^\circ$ adsorption pattern with coverage $\theta = 0.84$. The black parallelogram shows a unit cell.

Since we do PIMD and QH simulations with Light settings of FHI-aims, we provide a comparison of adsorption energy curve between Light and Tight settings in figure S3. The difference in binding energy is 58 meV.
TABLE S1. Adsorption energy for different adsorption patterns, calculated with PBE+vdWsurf by FHI-aims code with *Light* and *Tight* settings.

| θ      | Adsorption Pattern | *E*_{ads} (eV/molecule) |
|--------|--------------------|--------------------------|
| 1 (2√3 × 2√3) R13.9° | 9 molecules, 4 Rh layers | Light, 2x2x1 k-points | 1.023 |
|        |                    | Tight, only Γ-point      | 1.002 |
|        |                    | Tight, 3x3x1 k-points    | 0.979 |
| 0.84 (2.64 × 2.64) R19.1° | 7 molecules, 4 Rh layers | Tight, only Γ-point      | 1.020 |
|        |                    | Tight, 3x3x1 k-points    | 0.976 |
| 0.64   | 3x3 slab with 1 molecule | Light, 4x4x1 k-points   | 0.946 |
| 0.46   | 5x5 slab with 2 molecules | Light, 2x2x1 k-points   | 0.953 |
|        |                    | Tight, 2x2x1 k-points    | 0.912 |
| 0.12   | 7x7 slab with 1 molecule | Light, 2x2x1 k-points   | 0.945 |

FIG. S3. Adsorption curves calculated with PBE+vdWsurf [2] functional with *Tight* (solid blue line) and *Light* (dashed black line) settings of FHI-aims. Calculations were performed with the unit cell of θ = 0.46. Shaded areas show the experimental values of the adsorption energy of C₆H₁₂ (red) and C₆D₁₂ (grey), obtained by temperature programmed desorption [3].
For calculation of a ZPE corrected adsorption curves, two different procedures were used in FHI-aims and STATE calculations (PBE + vdWsurf and rev-vdW-DF2, respectively). In FHI-aims setup, we include only \((3N_m - 3)\) molecular vibrations, where \(N_m\) is the number of atoms in a molecule. The rest 3 lowest-frequency modes (0 to 55 cm\(^{-1}\) depending on distance to surface) correspond to the hindered translations of a rigid molecule. They have completely classical behavior and high entropy, and they are populated at very low temperatures. There is no evidence that these modes behave differently for normal/deuterated cyclohexane, except the obvious effect of mass, which can be safely neglected. However, these 3 rigid-molecule modes give relatively high mobility to molecules. It raises a question of applicability of the harmonic approximation when the molecule deviates far away from its equilibrium position.

As mentioned in the text, we include only ZPE correction and neglect finite temperature corrections. Here, we show this contribution as dashed lines in figures S4a,b. We calculate the effect of 150 K temperature on the harmonic free energy of all \((3N_m - 3)\) vibrations that we consider in figure S4b, and the same only for the \((3N_m - 6)\) intramolecular modes fig. S4b. Clearly, temperature effects are concentrated in the rigid-molecule modes, and these effects are negligibly small in the intramolecular vibrations. \(h_{\text{COM}}\) when including \((3N_m - 3)\) modes is 3.349 (3.365) Å for H and 3.362 (3.380) Å for D at the temperature of 0 (150) K.

![FIG. S4. The effect of temperature on the harmonic free energy of cyclohexane (red) and D-cyclohexane (black) with and without inclusion of hindered rigid rotation modes (a and b, respectively). Solid lines show ZPE-corrected potential energy, dashed lines add finite temperature corrections at the temperature of 150 K. The curves are aligned to the reference value at distance of 10 Å. Calculations are done with PBE + vdWsurf functional.](image-url)
IV. ELECTRON DENSITY REARRANGEMENT

In order to better illustrate the distribution of charges near the molecules, we show multiple slices of the electron density difference between the full system (surface+molecules) and the superposition of an isolated adsorbate and a clean surface (figures S5, S6). In these pictures, shades of blue mean electron depletion upon adsorption, and shades of red mean electron accumulation.

FIG. S5. A difference between the electron density of a surface with molecules adsorbed and the sum of isolated surface and isolated molecules, measured at different y,z slices along x coordinate. Red color denotes electron density accumulation, and blue denotes depletion.
FIG. S6. A difference between the electron density of a surface with molecules adsorbed and the sum of isolated surface and isolated molecules, measured at different x,y slices along z coordinate. Red color denotes electron density accumulation, and blue denotes depletion.

V. THERMODYNAMIC INTEGRATION

Beyond the harmonic approximation, we don’t have an analytical expression for the free energy of adsorption. But the difference between C₆H₁₂ and C₆D₁₂ in PIMD simulations can be estimated by thermodynamic integration, following the procedure proposed in [4].

\[ \Delta F_{H-D} = (\langle K_D \rangle \sqrt{m_D} + \langle K_H \rangle \sqrt{m_H}) \ast \left( \frac{1}{\sqrt{m_H}} - \frac{1}{\sqrt{m_D}} \right), \]

with \( \langle K \rangle \) is average kinetic energy, and \( m_H, m_D \) are the atomic masses of hydrogen and deuterium, respectively. We calculate \( \Delta F_{H-D} \) for adsorbed molecules and for a gas phase,
and, subtracting them, we obtain the difference of the free energy of adsorption. The result is given in the table S2. We found that this procedure has insufficient accuracy and is unable to resolve the H/D difference. The calculated value of $\Delta F_{H-D}^{\text{ads}}$ is $6 \pm 8$ meV. The result is therefore inconclusive and very approximate (integral approximation by its end points and insufficient statistical sampling).

|                         | PBE + vdWsurf, $\theta = 0.46$ | rev-vdw-DF2, $\theta = 0.64$ |
|-------------------------|---------------------------------|--------------------------------|
|                         | C$_6$H$_{12}$ | C$_6$D$_{12}$ | no ZPE | C$_6$H$_{12}$ | C$_6$D$_{12}$ | no ZPE |
| ZPE-corrected $E_{\text{ads}}^*$ (meV) | 1091 | 1052 | 959* | 876 | 840 | 818 |
| QH $h_{\text{COM}}$ (Å) | 3.349 | 3.362 | 3.385 | 3.427 | 3.439 | 3.471 |
| QH $\Delta \phi$ (meV) | -1015 | -999 | -963 | -1205 | -1190 | -1151 |
| PIMD $\Delta F_{\text{ads}}$ (therm. int.) | $E_{\text{ads}}^{C_6H_{12}} - E_{\text{ads}}^{C_6D_{12}} = 6 \pm 8$ meV | - | - | - |
| PIMD $h_{\text{COM}}$ (Å) | $3.41 \pm 0.01$ | $3.42 \pm 0.01$ | $3.416 \pm 0.007$ | - | - | - |
| PIMD $\Delta \phi$ (meV) | $-928 \pm 16$ | $-917 \pm 12$ | $-903 \pm 5$ | - | - | - |

TABLE S2. The results of quasi-harmonic calculation: the adsorption energy, the equilibrium distance between molecules and the surface, and the work function change for C$_6$H$_{12}$ and C$_6$D$_{12}$. *The value here is slightly different from the $E_{\text{ads}}^{\text{pot}}$ in the figure 2b in the manuscript because of the different calculation procedure, see the text. The PIMD value obtained by the thermodynamic integration is not reliable.

VI. ESTIMATE OF THE ERROR OF SL-RPC IN POTENTIAL ENERGY

Our expression 2 in the manuscript can be rewritten as

$$
\frac{k_B T}{2} \sum_{\nu} \sum_k \left[ \frac{\omega_{\nu,\text{mol}}}{\omega_k^2 + \omega_{\nu,\text{full}}^2 + \Delta} - \frac{\omega_{\nu,\text{full}}^2}{\omega_k^2 + \omega_{\nu,\text{full}}^2} \right],
$$

where $\Delta = \omega_{\nu,\text{mol}}^2 - \omega_{\nu,\text{full}}^2$. Since $\Delta$ is much smaller than $\omega_k^2 + \omega_{\nu,\text{full}}^2$, it can be omitted, and we immediately get eq. 9 from the Ref. [5]. It is a reasonable approximation of one fraction, which gives an error of not more than 10% in practical cases. However, two fractions have quite close values, therefore the difference between them can be even smaller than the error introduced by omitting the $\Delta$. This fact leads to a significant overestimation of the error, if the eq. 9 from [5] is used.
VII. ESTIMATE OF THE ERROR OF SL-RPC IN FREE ENERGY

Assuming a system to be harmonic, the Hamiltonian of a ring polymer with $P$ beads in “physical” normal modes can be written as

$$H = K + \sum_{\nu=1}^{3N} \sum_{k=1}^{P} \left[ \frac{m_{\nu}\omega_{\nu}^2}{2} \left( q_{\nu}^{(k)} - q_{\nu}^{(k+1)} \right)^2 + \frac{m_{\nu}\omega_{\nu}^2}{2} q_{\nu}^{(k)2} \right].$$  \hspace{1cm} (3)

Here $K$ is a kinetic energy, $\nu$ denotes normal modes (NMs) of a physical system, $m_{\nu}$ is an effective mass associated with the normal mode $\nu$. Note that here, $k$ stands for a bead index – in contrast to the following equations, where it will enumerate normal modes of a free ring polymer.

Expanding the spring-terms and rearranging the summation over $k$ (also making use of periodicity of a ring polymer $q^{(P+1)} = q^{(1)}$), one can rewrite a Hamiltonian as following:

$$H = K + \sum_{\nu=1}^{3N} \sum_{k=1}^{P} \left[ \frac{m_{\nu}\omega_{\nu}^2}{2} \left( 2q_{\nu}^{(k)2} - q_{\nu}^{(k)} q_{\nu}^{(k+1)} - q_{\nu}^{(k)} q_{\nu}^{(k-1)} \right) + \frac{m_{\nu}\omega_{\nu}^2}{2} q_{\nu}^{(k)2} \right].$$  \hspace{1cm} (4)

Then, the spring terms can be written in a matrix form (bold below means $P$-dimensional vectors $\{q^j\}, j \in [1, \ldots, P]$ and corresponding square matrices)

$$V_{spring} = \sum_{\nu=1}^{3N} \frac{m_{\nu}\omega_{\nu}^2}{2} q_{\nu}^\top A q_{\nu},$$  \hspace{1cm} (5)

$$A = \begin{bmatrix} 2 & -1 & 0 & \ldots & -1 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & \ldots \\ \ldots & 0 & \ldots \\ -1 & -1 & 2 \end{bmatrix}$$  \hspace{1cm} (6)

We diagonalize the $A$ matrix by performing a normal mode transformation $C$:

$$A = C\tilde{A}C^\top.$$  \hspace{1cm} (7)

$$\tilde{q}_{\nu} = C q_{\nu}$$  \hspace{1cm} (8)

The matrix $C$ is unitary, therefore the transformation to the normal modes of a free ring polymer doesn’t change the physical potential term

$$\frac{m_{\nu}\omega_{\nu}^2}{2} q_{\nu}^2 = \frac{m_{\nu}\omega_{\nu}^2}{2} \tilde{q}_{\nu}^\top C^{-1\top} C^{-1} \tilde{q}_{\nu} = \frac{m_{\nu}\omega_{\nu}^2}{2} \tilde{q}_{\nu}^2.$$  \hspace{1cm} (9)
The Hamiltonian in the “double normal-mode” representation (i.e. the normal modes of a physical system and the normal modes of a free ring polymer) reads as

\[
H = K + \sum_{\nu=1}^{3N} \sum_{k=0}^{P-1} m_\nu \left( \frac{\omega_k^2 + \omega_{\nu,full}^2}{2} \right) \bar{q}_\nu^{(k)}^2, 
\]

(10)

where \( k \) denotes NMs of a free ring polymer. Here and below, \( full \) index stands for the “expensive” potential energy surface which describes all interactions in a system, while \( mol \) stands for the “cheap” one. In case of spatially-localized contraction, a “cheap” potential describes only interactions within an adsorbate.

**Contraction procedure.** Given a ring polymer of \( P \) beads, one can contract it to a lower dimensionality. Many useful expressions can be found in [6]. Equations 21-22 from [6], rewritten in our notation:

\[
q^{(j')}_{\nu} = \sum_{j=1}^{P'} \left( T_{P'}^P \right)_{j'j} q^{(j)}_{\nu},
\]

(12)

where

\[
\left( T_{P'}^P \right)_{j'j} = \frac{1}{P} \sum_{k=-P'/2}^{P'/2} C_{j'k}^P \bar{C}_{j^*k}^P
\]

(13)

is a contraction matrix from \((P \times 3N)\) to \((P' \times 3N)\)-dimensional space. It performs transformation \( C^P \) to a Fourier space, there it truncates the high-order coefficients and transforms back to a lower-dimensional real space by \( C^{P'} \). Similarly, we define an expansion matrix \( T_{P'}^P \) from \((P' \times 3N)\) to \((P \times 3N)\)-dimensional space. The expansion procedure is a reverse of a contraction with only difference: instead of truncating Fourier series, we have to expand it from \( P' \) to \( P \) terms. Since we don’t have these coefficients, we set them to be zero. It can be shown that the potential energies of the \( P \)- and \( P' \)-ring polymers are related as

\[
\sum_{k=1}^{3N} V(q^{(k)}_1, ..., q^{(k)}_{3N}) \approx \frac{P}{P'} \sum_{j=1}^{P'} V(q'^{(j)}_1, ..., q'^{(j)}_{3N}),
\]

(14)

with respect to the accuracy of contraction.

The Hamiltonian after the SL-RPC is applied:

\[
H = K + \sum_{\nu=1}^{3N} \left[ \sum_{k=0}^{P'-1} m_\nu \left( \frac{\omega_k^2 + \omega_{\nu,full}^2}{2} \right) \bar{q}_\nu^{(k)}^2 + \sum_{k=P'}^{P'-1} m_\nu \left( \frac{\omega_k^2 + \omega_{\nu,mol}^2}{2} \right) \bar{q}_\nu^{(k)}^2 \right].
\]

(15)

Then, the partition function of this system is

\[
Q = \prod_{\nu=1}^{3N} \left[ \prod_{k=0}^{P'-1} \frac{1}{\beta P \hbar \sqrt{\omega_k^2 + \omega_{\nu,full}^2}} \prod_{k=P'}^{P'-1} \frac{1}{\beta P \hbar \sqrt{\omega_k^2 + \omega_{\nu,mol}^2}} \right].
\]

(16)
The free energy of a (single) physical system:

\[
F = -\frac{1}{\beta} \ln(Q) = -\frac{1}{\beta} \sum_{\nu=1}^{3N} \left[ - \sum_{k=0}^{P'-1} \ln(\beta_P h \sqrt{\omega_k^2 + \omega_{\nu,full}^2}) \right] = 3NP \ln(\beta_P h) + \frac{1}{2\beta} \sum_{\nu=1}^{3N} \left[ \sum_{k=0}^{P'-1} \ln(\omega_k^2 + \omega_{\nu,full}^2) + \sum_{k=P'}^{P-1} \ln(\omega_k^2 + \omega_{\nu,mol}^2) \right].
\]

The free energy difference between SL-RPC and \( P \) beads calculated with full potential:

\[
\delta F = (F^{\text{RPC}} - F^{\text{P beads}}) = \frac{1}{2\beta} \sum_{\nu=1}^{3N} \sum_{k=P'}^{P-1} \ln \left( \frac{\omega_k^2 + \omega_{\nu,mol}^2}{\omega_k^2 + \omega_{\nu,full}^2} \right) = \frac{1}{2\beta} \sum_{\nu=1}^{3N} \sum_{k=P'}^{P-1} \ln \left( 1 + \frac{\omega_{\nu,mol}^2 - \omega_{\nu,full}^2}{\omega_k^2 + \omega_{\nu,full}^2} \right).
\]

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