Nuclear Quantum Effects on Adsorption of H₂ and Isotopologues on Metal Ions

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Abstract

The nuclear quantum effects on the zero-point energy (ZPE), influencing adsorption of H₂ and isotopologues on metal ions, are examined using normal mode analysis of ab initio electronic structure results for complexes with 17 metal cations. The lightest metallic nuclei, Li and Be, are found to be the most 'quantum'. The largest selectivity in adsorption is predicted for Cu, Ni and Co ions. Analysis of the nuclear wavepacket dynamics on the ground state electronic potential energy surfaces (PES) performed for complexes of Li⁺ and Cu⁺² with H₂/D₂/HD. shows that the PES anharmonicity changes the ZPE by up to 9%.

1. Introduction

The fundamental understanding of the hydrogen/deuterium (H/D) interactions and dynamics is important for a wide range of applications – from neutron

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9 scattering [1] to proton transport through a proton exchange membrane of a fuel
10 cell to biomedical applications as a tracer element [2, 3] and, due to CH/CD
11 bond breaking properties, as a drug modifier [4]. For example, until recently it
12 was believed that the H/D isotope substitution had little effect on morphology
13 and optoelectronic properties. Yet as some experiments have shown, selective
14 deuteration of thiophene rings in poly(3-hexylthiophene) (P3HT) significantly
15 reduces its crystallinity. Similarly, selective deuteration of hexyl arms in P3HT
16 changes its optoelectronic properties without affecting its crystallinity [5, 6].
17 As another example, Jordan and co-workers [7, 8, 9] demonstrate that classical
18 simulations of H₂ interacting with Li-doped benzene yields more favorable H₂
19 binding and an incorrect temperature dependence of thermochemical properties
20 compared to the quantum simulations. NQE also play a role in dissociation of
21 H₂ on Au(111) surface [10].
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29 In this paper we study interactions of H/D with isolated metals centers en-
30 countered in porous materials such as MOFs and magnetic fusion devices used
31 for hydrogen isotope separation. In the latter type of material the plasma beam
32 containing hydrogen and deuterium ions erodes its containment walls, ultimately
33 incapacitating the device. Enriching the plasma-facing components with Li and
34 other low-Z metals in metallic and carbon-walled tokamaks can extend the per-
35 formance of magnetic fusion devices [11, 12]. The most common industrial
36 deuterium enrichment processes are the electrolysis, distillation, chemical ex-
37 change and Girdler-Sulfide process [13, 14]. These processes are straightforward
38 but extremely rare deuterium abundance makes its separation quite expensive.
39 It has been suggested by Beenakker et al. that hydrogen isotopologues can be
40 efficiently separated with nanoporous materials [15]. Beenakker et al. proposed
41 the Kinetic Quantum Sieving (KQS) method that occurs in the ultra-porous
42 materials. The KQS is the most pronounced when the difference between a
43 pore and molecular diameter is not much larger than the de Broglie wavelength
44 of a molecule. The quantum sieving method appears to be the most efficient
45 at relatively low temperature, nearly cryogenic, when the quantum effects are
46 the strongest. KQS method is only possible in the ultra-porous materials with
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the strict geometrical criteria and only few porous materials can satisfy its criteria [15, 16]. In a different separation mechanism, called Chemical Affinity Quantum Sieving (CAQS), strongly attractive centers of porous materials may adsorb preferentially heavy isotopologues due to their smaller ZPE, resulting in a stronger adsorption enthalpy [17, 18]. This method is maximized by strong adsorption centers, allowing high selectivity at temperatures of 100K and above. The approach is suitable for the rational design of porous materials for efficient hydrogen isotopologues separation. Specifically, metal-organic frameworks (MOFs) with open metal centers are examples of such materials.

Within a MOF the metal is present in the cation form, which upon binding H_2 slightly elongates the HH bond [19], but does not promote its dissociation as metal surfaces do. Moreover, it has been shown experimentally that the choice of a metal center, not the organic linker, that mostly affects the uptake of hydrogen by MOFs [20]. Therefore, we use a simple model consisting of an isolated positively charged metal/ H_2 complex to analyze the NQE on selectivity of H_2/D_2 binding. (The relevance of such a model to hydrogen adsorption by porous materials is discussed for example in Ref. [21].) This choice of a minimal model (three atoms) enables us to assess small changes in the ZPE for a range of metal ions (from Li to Cu) within the same high quality electronic structure method and to perform quantum dynamics using high-level ab initio PES. The NQEs are examined for several metal ions binding H_2 and its isotopologues. The normal mode analysis is used to estimate NQE on adsorption selectivity for 17 metal centers as a function of temperature based on Langmuir isotherms (Section 2). The NQEs on the ground state including the anharmonicity of the PESs are estimated from the real-time quantum dynamics of Li^+H_2 on the spline-fitted analytical PES, and from the imaginary-time dynamics of $Cu^{+2}H_2$ on the PES interpolating ab initio data points (Section 3). Section 4 concludes.

2. Nuclear Quantum Effects for MH_2 : the normal mode analysis

The electronic structure of alkali and alkali-earth metal dihydride ions, such as LiH_2^+ , MgH_2^{2+} , and a few others has been rigorously studied in the context

of spectroscopy and mass-spectroscopic experiments. These studies were motivated by the relevance of the species to astrochemistry, by the fundamental question of ion-quadrupole interactions and by the opportunity of benchmarking theoretical and experimental rovibrational spectroscopy (Ref. [22] can serve as a mini-review on the topic). In particular, LiH_2^+ [23, 24] and AlH_2^+ [25] have been examined in great detail with the variety of theoretical methods including the high-level electronic structure studies with the CCSDT and IC-MRCI level and involving relativistic corrections [22]; subsequently, several analytical ground state electronic potential energy surfaces (PESs) have been constructed and used for extensive rovibrational calculations. One conclusion following from these state-of-the-art ab initio studies relevant to this work, is the need for a high level electronic structure method to describe these triatomic species. Our main interest is the NQE, specifically the change in the ZPE of the equilibrium complex upon single and double substitution of hydrogen atom with deuterium atom. This change in the ZPE is the leading factor which may affect the selectivity of adsorption of H_2 and isotopologues on open metal sites in porous materials, such as MOFs. Since the dominant NQE comes from the small difference ($20\text{-}30\text{ cm}^{-1}$) in the ZPEs of the isotopologues, our considerations in the choice of the electronic structure methods are (i) to have a high-accuracy PES near the equilibrium geometry, and (ii) sufficiently practical to study a wide range of metals, including transition metals, binding H_2 , and analyze the trends. (Future studies of MH_2 as part of MOF, expanding the system size, is an additional consideration.) Therefore, the Coupled-Cluster-Singles-Doubles (CCSD) with G3MP2Large basis [26] was chosen for the geometry optimization and vibrational frequency calculation for 17 metal ions binding H_2 and its isotopologues. The normal mode analysis is performed for MH_2 , MHD and MD_2 where M represents the following metal ions: $\text{M}=\{\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Be}^+, \text{Mg}^+, \text{Ca}^+, \text{Be}^{+2}, \text{Mg}^{+2}, \text{Ca}^{+2}, \text{B}^+, \text{Al}^+, \text{Co}^+, \text{Ni}^+, \text{Cu}^+, \text{Co}^{+2}, \text{Ni}^{+2}, \text{Cu}^{+2}\}$. For the transition metal centers Co, Ni and Cu several spin multiplicities have been considered and the lowest energy states selected [25, 23]. The electronic structure calculations have been performed using Q-Chem [27].

The MH distances obtained with CCSD/G3MP2Large for the selected metals agree with the most advanced calculations of Ref. [22] reasonably well. For example, for cations of Li, Na, Be and Mg and for the dications of Be, Mg and Ca the agreement is within 0.02 Å ; for K⁺ the difference is 0.05 Å. A noticeable difference is found for Ca⁺: 3.38 Å in this work, while the range of values in Ref. [22] is [3.13, 3.33] Å. The red-shifts of the vibrational frequency of H₂ upon binding to Li⁺ and Al⁺ are 114 and 58 wavenumbers, respectively, in the CCSD/G3MP2Large calculation and they are 108 and 66 wavenumbers in Refs [23, 25]. The shifts are about 2.5% and 1.5% of the vibrational frequency of H₂ in free space) Overall, we deem CCSD/G3MP2Large adequate for the geometry optimization and normal mode analysis for our set of molecules yielding the ZPE changes for the H/D isotopologues.

To assess the importance of the quantum nature of the metal ions we have also computed the ZPE for the triatomics assuming unphysically large mass of the metal, $m_M = 10^6$ a.m.u. The optimal geometries of the triatomics and the ZPEs are summarized in Table 1. The equilibrium geometry is of C_{2v} (T-shape) symmetry: H₂ binds side-on to the metal center by donating the two σ -electrons to a vacant d-orbital of the metal as discovered by Kubas [19]. The main trends are shown in Figs 1–2. Binding of H₂ to the metal ion changes the ZPE which roughly correlates to the H-H distance as shown in Fig. 1. The vibrational frequency of H₂ stretch itself, listed in the last column of Table 1, also correlates with the bond length of H₂ in the triatomics: higher frequency correlates with shorter bond length. The change in the ZPE compared to the gas phase H₂ is in the range of 2.0 – 10 kJ/mol while the H-H is stretched up to 8% compared to the free space H₂ value. The ZPE computed for the triatomics with the infinitely heavy M is labeled as 'HH^M' in Table 1. The largest changes in the ZPE compared to the values with physical masses indicate more quantum 'character' of the metal ion. Not surprisingly, the lighter metal nuclei, namely Be⁺², Li⁺, Be⁺ (Fig. 2) are more quantum. The difference for these species is 0.736, 0.360 and 0.368 kJ/mol respectively. Smaller changes in the ZPE indicate less quantum 'character' of the metallic nuclei, such as the fourth row metals.

For example, the difference for Cu^{+2} is 0.096 kJ/mol. Overall, the energy range of the ZPE and of the change in the ZPE due to H/D substitution for our set of metal ions is within a factor of two from the similar quantities reported, for example, for H_2 adsorbing to Zn in MOF-5 [28] and lithium alanate [29].

The adsorption selectivity for a mixture of H_2 and D_2 gases is largely determined by the difference between the ZPE for MH_2 and MD_2 [30] for various metals,

$$\Delta = \text{ZPE}(\text{MH}_2) - \text{ZPE}(\text{MD}_2), \quad (1)$$

shown in Fig. A.1. The largest Δ is found for the transition metals (9.75-10.38 kJ/mol) followed by Li and Be metal centers (9.29-9.58 kJ/mol) which are also the most 'quantum' metal centers. The selectivity, defined as the ratio of the Langmuir isotherms [30, 31, 32] is computed as a function of temperature for four of the more selective (out of our set) metal ions, i.e., Li^+ , Cu^+ , Cu^{+2} and Co^+ shown in Fig. 3. Cu^{+2} and Li^+ will be studied in further detail in Section 3. Cu^+ and Co^+ show the largest adsorption selectivity (> 5) for D_2/H_2 at approximately 100K and for HD/H_2 at approximately 50K. These selectivities are computed as described in Supplementary material based on the normal mode frequencies. A more detailed dynamics study of the NQE is performed for one of the most quantum system, Li^+H_2 , and for one of the most 'selective' systems, Cu^{+2}H_2 .

3. Nuclear Quantum Effects in MH_2 : quantum dynamics

The importance of the PES anharmonicity on the ZPE of MH_2 species is assessed from the time-evolution of nuclear wavefunctions for two metal ions, namely, Li^+H_2 and Cu^{+2}H_2 and their H/D isotopologues. The choice of these species is guided by the normal modes analysis: Li^+H_2 has the second strongest (after Be ions) quantum character associated with the metal ion (~ 0.4 kJ/mol from Fig. 2), while the experimentally relevant Cu^{+2}H_2 exhibits one of the largest ZPE changes due to H/D substitution (~ 9.6 kJ/mol from Fig. A.1).

M	Geometry			ZPE [kJ/mol]					ν [cm ⁻¹]
	MH [Å]	HH [Å]	$\angle$ HHM°	HH	HD	DD	HH ^M	Δ^M	HH
Li ⁺	2.037	0.751	79.38	32.56	28.24	23.26	32.20	0.360	4297.32
Na ⁺	2.424	0.747	81.13	31.16	26.95	22.10	30.32	0.088	4336.52
K ⁺	2.948	0.745	82.74	29.71	25.70	21.04	29.67	0.033	4372.29
Be ⁺	1.838	0.768	77.95	32.48	28.15	23.22	32.11	0.368	4077.98
Mg ⁺	2.665	0.749	81.92	29.48	25.51	20.89	29.43	0.192	4308.54
Ca ⁺	3.381	0.745	83.67	28.42	24.60	20.11	28.41	0.079	4367.59
Be ⁺²	1.620	0.815	75.44	34.38	29.85	24.80	33.63	0.745	3555.79
Mg ⁺²	2.045	0.776	79.07	33.09	28.61	23.54	32.89	0.192	3969.72
Ca ⁺²	2.463	0.758	81.15	31.92	27.59	22.63	31.84	0.079	4195.14
B ⁺	2.353	0.753	80.79	30.13	26.09	21.42	29.97	0.159	4241.78
Al ⁺	3.076	0.746	83.04	29.18	25.25	20.67	29.14	0.038	4353.14
Co ⁺²	1.889	0.796	77.86	33.51	28.91	23.77	33.41	0.092	3727.22
Ni ⁺²	1.841	0.801	77.44	33.81	29.17	23.99	33.70	0.092	3674.04
Cu ⁺²	1.795	0.812	76.93	33.66	29.02	23.88	33.55	0.079	3550.11
Co ⁺	1.743	0.783	77.02	35.66	30.76	25.30	35.57	0.096	3812.05
Ni ⁺	1.736	0.781	77.00	35.73	30.82	25.34	35.64	0.105	3848.18
Cu ⁺	1.774	0.776	77.37	34.72	29.96	24.62	34.64	0.105	3941.30
H ₂ ^{gas}		0.742		26.38	22.85	18.66			4411.39

Table 1: Geometry and ZPE for MH₂ triatomics and H/D isotopologues obtained at the CCSD/G3MP2Large theory level. The last ZPE column (HH^M) is the value for an infinitely heavy M. The column Δ^M lists the difference in ZPE of MH₂ for the standard isotope mass of M and for the infinitely heavy M. The last column contains the vibrational frequency of H₂ bound to the metal ion in wavenumbers. The data in the last row is for the diatomic gas phase (free space) H₂ and isotopologues.

Figure 1: The ZPE of MH_2 ions relative to the ZPE of the H_2 molecule as a function of the HH distance. The vertical lines match the metal ions of the legend.

Figure 2: Assessing the QM character of the metallic nuclei: the difference Δ^M of the ZPE of MH_2 species with the ZPE computed for an infinitely heavy metal ion as a function of the ZPE. The vertical lines match the metal ions of the legend.

Figure 3: Adsorption selectivity as a function of temperature for the 1:1 mixture of D_2/H_2 adsorbed on Co^+ (black, solid line), Cu^+ (red dash), Cu^{++} (green dot-dash) and Li^+ (blue circle/solid line). The same for the 1:1 mixture of HD/H_2 is shown on the inset.

3.1. Li^+H_2

Given that Li^+H_2 is a four electron system, its electronic PES is obtained using a high level ab initio method, CCSD/G3MP2Large. The electronic energies are computed on a grid of 21×21 positions of the metal ion for 6 values of the HH distance. The center-of-mass of H_2 is at the origin of the Cartesian coordinates, the positions of Li^+ span the grid with the spacing of $0.2 a_0$; the values of HH distance are $r = \{0.9, 1.1, 1.3, 1.4, 1.5, 1.7\} a_0$. The ab initio energy values are used to construct an analytical spline-fitted PES on which real-time quantum dynamics is performed.

In dynamics the three nuclei are treated as QM particles described in the Jacobi coordinates (R, r, θ) of a triatomic molecule ABC [33]. The molecule is treated as non-rotating (zero total angular momentum). Labeling the two hydrogen atoms as A and B and the metal ion as C, r is the distance between A and B, $r = |\vec{R}_B - \vec{R}_A|$; the mass conjugate to r is the reduced mass of the diatomic μ , $\mu = m_A m_B / (m_A + m_B)$. R is the distance between the atom C

and the center of mass of the AB fragment; the mass conjugate to R is denoted M , $M = (m_A + m_B)m_C/(m_A + m_B + m_C)$. θ is the angle between the vectors r and R . Subtracting the center-of-mass motion and fixing the total angular momentum to zero ($J = 0$), the three-dimensional Hamiltonian is [33]

$$\hat{H} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2} \left(\frac{1}{MR^2} + \frac{1}{\mu r^2} \right) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + V(R, r, \theta). \quad (2)$$

The distances R and r are treated on an equidistant grid. The Discrete Variable Representation (Gauss-Legendre quadrature) is used for angle θ [34]. The wavefunction is evolved in real time using the split operator propagator and Fast Fourier Transform [35, 36]. The grid and propagation parameters are given in Table 2.

The ground state energy and a few low-lying excited energy levels are obtained from the Fourier transform of the time autocorrelation function $C(t)$ of a wavefunction ψ_0 , $C(t) = \langle \psi_0 | \psi_t \rangle$. The initial wavefunction ψ_0 is defined as a product of real Gaussian functions in the distances $q = \{R, r\}$,

$$g(q) = \exp(-\alpha_q(q - q_0)^2), \quad (3)$$

and θ the angular function,

$$\psi_0(R, r, \theta) = \mathcal{N} g(R) g(r) \sin^2 \theta. \quad (4)$$

$\mathcal{N}$ is the normalization constant. The angular dependence is introduced into Eq. (4) to ensure that the initial wavefunction overlaps with the first few excited states.

The normal mode vibrational analysis of the CCSD/G3MP2Large calculation yields three vibrational modes shown in Fig. A.2: the relative diatomic-metal translational mode of frequency 477.51 cm^{-1} ; the diatomic rotational mode of frequency 669.54 cm^{-1} ; the diatomic vibrational mode of frequency 4297.32 cm^{-1} . The modes are sketched in Fig. A.2. The lowest transition frequencies obtained from the Fourier transform of the autocorrelation function are listed in Table 3. Apparently the low excitation states do not involve excitation of the diatomic vibrational mode.

Real-time dynamics of Li^+H_2										
N_t	dt	α_R	α_r	R_0	r_0	N_θ	R_{min}	r_{min}	dR	dr
30000	2.0	12	12	3.8	1.40	60	2.0	0.6	0.03	0.014
Imaginary-time dynamics of Cu^{+2}H_2										
N_t	dt	α_x	α_y	x_0	y_0	k	x_{min}	y_{min}	dx	dy
5000	0.05	6	2	1.53	0	0.02	0	-1.575	0.025	0.025

Table 2: Dynamics simulation parameters (in atomic units) for MH_2 systems. N_t is the number of time-steps and dt is the time-increment in atomic units. The linear coordinates R and r are represented by 128 equidistant grid points each. Li^+H_2 : N_θ is the number of the angle DVR points; R_{min} and r_{min} are the left grid boundaries; $\alpha_r = 14, 16 \text{ a}_0^{-2}$ for HD and D_2 , respectively. Cu^{+2}H_2 : k is the force constant of the harmonic potential, V_z , added to the z -coordinate; x_{min} and y_{min} are the left grid boundaries; the grid and wavepacket parameters for the z -coordinate are the same for y ; the time-step and the width parameters are rescaled by the appropriate isotope mass for HD and DD.

The anharmonicity can be measured using the difference between two lowest excitation transitions

$$\eta = \frac{\omega_{10} - \omega_{21}}{\omega_{10}}$$

Here $\omega_{mn} = (E_m - E_n)/\hbar$ is the transition frequency between states m and n . For the harmonic system $\eta = 0$. Labeling the relative translational mode as T and the diatomic's rotational mode as R , the analysis of the spectrum gives $\eta_T = 6.8\%$ and $\eta_R = 7.5\%$. The estimate for the H_2 vibration, based on the Morse-potential fit to the energy of the H_2 stretch, is $\eta_V = 10\%$. (The parameters of the Morse fitting potential are listed in Table A.1.)

Transition frequency [cm^{-1}]	Transition	Normal mode frequency [cm^{-1}]
514.8	T: $ 0\rangle \rightarrow 1\rangle$	477.51
479.6	T: $ 1\rangle \rightarrow 2\rangle$	
737.0	R: $ 0\rangle \rightarrow 1\rangle$	669.54
682.0	R: $ 1\rangle \rightarrow 2\rangle$	

Table 3: The transition frequencies and corresponding excitation energies of Li^+H_2 . T labels the relative translation of the diatomic and metal; R labels the rotations of the diatomic. (Translation and rotation are coupled.)

3.2. Cu^{+2}H_2

To assess the effect of the H/D isotope substitution on the ZPE for Cu^{+2} (27 electrons) as the metal center using the ab initio method comparable to that used for Li^+ , we simplified the vibrational model of MH_2 to reduce the cost of

constructing the PES. We use a 'translationally adiabatic' description: Cu^{+2} is fixed at the equilibrium distance from the center-of-mass of the H_2 fragment. This is equivalent to freezing R in the Hamiltonian given by Eq. (2). Then, the quantum protons or deuterons are described by a vector $\vec{r} = \vec{R}_B - \vec{R}_A$ in the Cartesian space $\vec{r} = (x, y, z)$, characterizing rotation and vibration of the diatomic. Since all three atoms are described in the (x, y) plane, the coordinate z is redundant. However, we use a three-dimensional set up for this system, sketched in Fig. A.3 in order to have a general framework suitable for studies of MH_2 inside a MOF or other porous material. A molecular environment will break the cylindrical symmetry of the PES with respect to rotation along the x -axis. A more rigorous three-dimensional body-fixed Cartesian Hamiltonian [37] will be considered in the future. For a fixed R our nuclear Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y) + V_c(z), \quad (5)$$

where μ is the reduced mass of the diatomic AB. The z -motion separates from the (x, y) and its contribution to the ZPE is subtracted from the ZPE of Eq. (5).

The separation of the translational motion of H_2 significantly reduces the cost of ab initio calculations, since the PES becomes two-dimensional, $V = V(x, y)$. $V(x, y)$ is obtained from a six-point two-dimensional interpolation of the electronic energy values computed on the (x, y) grid $x = [-1.5, 1.5] a_0$, $dx = 0.1 a_0$ and the same for y . The ab initio data are computed using CCSD with the 6-31G* basis for H and G3Large basis for Cu. The ZPE of the Morse potential describing metal-diatomic stretch (Table A.1) is added to the final energy to account for the isotope effect in this mode approximately.

The split-operator/Fast Fourier Transform propagation in imaginary time gives estimates of the ZPE [38] for Cu^{+2}H_2 and its isotopologues. To accelerate convergence of the imaginary time dynamics [39] we have added a simple 'confining' quadratic potential $V_c = kz^2/2$ ($k = 0.02 \text{ E}_h a_0^{-2}$). The parameters of the

dynamics and of the initial wavefunction,

$$\psi_0 = \mathcal{N}g(x)g(y)g(z), \quad (6)$$

are listed in Table 2. The normal mode analysis underestimates the ZPE of the the rotational and vibrational modes by about 8% for D₂; the anharmonic character of the potential is clearly seen in the contour plots of the ground state wavefunctions shown for H₂ and D₂ in Fig. 4. Localization of the ground state wavefunctions of different isotopes leads to a slight shortening of approximately 0.6% and 1.3% of the average HD and DD bonds compared to the HH bond. The bond length dispersion, defined as $\sigma_{xy} = (\langle R_{xy}^2 \rangle - \langle R_{xy} \rangle^2)^{1/2}$, is smaller by about 7% and 17% for MHD and MD₂ species compared to MH₂ as shown in Table 4. The latter trend follows the normal modes estimate (assumption of the Gaussian ground state wavefunction) of the effect, which for HD and DD gives the change of 7.45% and 18.9%.

Figure 4: The density maps of the ground state wavefunction for H₂ and D₂ bound to Cu⁺². The deviation from the oval shapes illustrates the anharmonicity of the PES; the change in the wavefunction localization highlighted by the contour, plotted for the isodensity values of 0.1.

4. Conclusions

We have examined the nuclear isotope effect of H₂ and isotopologues binding to selected metal ions (M). A high quality electronic structure method is needed to describe the triatomic MH₂ given the weak binding (23.43 kJ/mol for Li⁺H₂) and large M-H₂ distances (3.07 Å for Al⁺H₂) for many triatomics. According to the normal mode analysis performed at CCSD/G3MP2Large level, the largest

The zero-point energies for AB-Cu ⁺²						
AB	E_0 [E _h]	E_0	E_0^{nm}	E_0^{tran}	ZPE	ZPE ^{nm}
HH	0.01001	26.28	26.28	6.23	32.51	33.56
HD	0.00893	23.47	22.76	5.10	28.58	28.95
DD	0.00764	20.08	18.58	4.44	24.52	23.81

Bond length for AB-Cu ⁺²						
AB	R_{AB} [Å]	ΔR_{AB} [%]	σ_{AB} [Å]	$\Delta\sigma_{AB}$ [%]	R_{ACu} [Å]	σ_{ACu} [Å]
HH	0.836	0	0.098	0	1.80	0.088
HD	0.831	0.62	0.091	7.3	1.80	0.082
DD	0.825	1.34	0.082	16.7	1.80	0.074

Table 4: ZPE obtained from the wavefunction energy decaying to the ground state for Cu⁺²H₂ and isotopologues (in kJ/mol unless noted otherwise). E_0^{nm} is the energy of H₂ rotation and vibration, scaled by the reduced masses for HD and D₂. E_0^{tran} is the ground state energy of the translational mode from the fit of PES to the Morse oscillator. ZPE is the total zero-point energy estimated from the dynamics. The last column, ZPE^{nm}, lists the normal modes values (CCSD/G3Large method). The bond lengths R and their dispersion σ , $\sigma = \sqrt{\langle R^2 \rangle - \langle R \rangle^2}$, are given in Angstrom. The bond lengths of the minimum energy configuration (CCSD/G3Large method) are $R_{HH} = 0.80\text{\AA}$ and $R_{HCu} = 1.79\text{\AA}$.

effect associated with the ZPE of the triatomics and the gas phase diatomics and, thus, the largest selectivity in adsorption of the diatomics is predicted for +1 and +2 ions of Cu, Co and Ni. The most quantum character of the metal ion affecting the ZPE is found for the lightest metals Li and Be. The normal modes ZPE computed with the physical and infinite masses differ by about 2%. Thus, most metallic nuclei can be treated as classical particles. The dynamics study performed on the fitted/interpolated surfaces for the 'most quantum' and 'most selective' ions, Li⁺ and Cu⁺² include the anharmonicities of the PES. The effect of anharmonicity changes the ZPEs and excitation energies by up to 9%, suggesting that the description of such systems beyond the normal modes is desirable. The Cartesian space description of the diatomic bound to the metal ion, used in this work and improved by using three-dimensional body-fixed Hamiltonian [37] can be extended to MH₂ systems embedded in a metal-organic-framework or other porous molecular environment. Other extensions of this study may include excited translational/rotational states of H₂.

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