First-principles approach to rotational-vibrational frequencies and infrared intensity for H$_2$ adsorbed in nanoporous materials

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The absorption sites and the low-lying rotational and vibrational (RV) energy states for H$_2$ adsorbed within a metal-organic framework are calculated via van der Waals density functional theory. The induced dipole due to bond stretching is found to be accurately given by a first-principles driven approximation using maximally-localized-Wannier-function analysis. The strengths and positions of lines in the complex spectra of RV transitions are in reasonable agreement with experiment, and in particular explain the experimentally mysteriously missing primary line for para hydrogen.

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Gas adsorption into nanoporous materials is of great interest for both fundamental science and applications. Molecular H$_2$ is challenging because it can vibrate, rotate, and translate quantum mechanically about its binding site due to its small mass. The vibration-rotation (RV) excitations induced by infrared (IR) absorption thus provide rich information [1]. However, determining the origin and strength of these lines is challenging because large unit cells are encountered in typical nanoporous structures, and the dynamic dipole is distributed over spatially remote parts of the structure. To determine the absorption intensity, a precisely tractable experimental quantity, one must only calculate the dipole, but also evaluate the quantum mechanical matrix element. An effective approximation scheme for doing this has not hitherto been found.

Here, we present such a scheme based on the combination of a self-consistent van der Waals density functional (vdW-DF) approach [2] with maximally-localized-Wannier-function (MLWF) analysis [3, 4] and apply it to H$_2$ adsorption in a prototypical metal-organic framework, MOF-5 [5]. Such materials have been extensively explored for hydrogen storage [6], gas separation, catalysis, and sensors [7]. We analyze the dynamical properties of the adsorbed H$_2$, finding results consistent with experiment. Importantly, we apply the MLWF analysis to calculate the induced dipole moment due to H$_2$ adsorption and bond stretching, decomposing the dipole into the contributions from both adsorbed dihydrogen and MOF. Monitoring the change in each Wannier center of the MOF structure upon H$_2$ adsorption provides an intuitive picture by breaking the H$_2$-sorbent interaction into individual components of the MOF structure, thus identifying the parts that directly interact with the dihydrogen. Such knowledge is important to optimize MOF structures for desired properties. In the present case, we use this information to calculate the dynamical dipole moment and its matrix element for H$_2$ vibrational transitions and RV transitions. We find that the IR intensity of the purely vibrational mode for para hydrogen is only about 2.5% of that for ortho hydrogen at the primary adsorption site, which agrees beautifully with the missing line in the experiment. [3]. A selection rule for RV transitions at the relevant site is also obtained and supported by the IR data.

The H$_2$ binding sites are efficiently determined by self-consistent vdW-DF calculations [2]. A series of total energy calculations for different bond lengths, orientations, and center-of-mass positions respectively are performed keeping the MOF atoms fixed at experimental positions [3]. The resulting potential energy surfaces are then used in the corresponding radial and rigid rotor Schrödinger equations respectively to extract the vibrational, rotational and translational frequencies [10, 11]. Anharmonic effects are fully included.

It has been shown that the sum of the Wannier-function centers is connected to the Berry phase theory of bulk polarization [3]. The dipole in the unit cell is given by $\mathbf{u} = e \sum_m Z_m \mathbf{R}_m - e \sum_n \mathbf{r}_n$, where $Z_m$ and $\mathbf{R}_m$ are the atomic number and position of the $m$th nuclei and $\mathbf{r}_n$ is the center of the $n$th Wannier function. Importantly, it is trivial to decompose the total dipole into components in various parts of the structure [3], which goes beyond the Berry-phase method. Thereby, we may use the change of Wannier center upon adsorption as a qualitative measure for understanding the H$_2$-MOF interaction and to determine the important parts of the MOF that directly interact with hydrogen.

There are four types of adsorption sites in this structure, as established experimentally [12] and theoretically [13], with reasonable agreement. We start with the positions determined by neutron scattering [12] and relax the H$_2$ with the vdW-DF approach, thereby confirming the positions of the four sites, named the cup, O3, O2, and benzene sites [12]. Fig. 1 shows the position of the cup site and a portion of the MOF-5 structure where there exists 3-fold rotation symmetry among the three benzene ring branches. The distance between the H$_2$ center-of-mass position and the oxygen atom passing...
through the rotation axis is about 4.2Å which is somewhat larger than the measured value of 3.8Å [12] due to a known vdW-DF overestimation of bond lengths [14]. Fig. 1 also shows the shift of the Wannier centers upon H₂ adsorption with respect to the bare MOF and the free H₂. See Supplemental Material for other sites [21]. These figures show that the Wannier centers associated with the π bonds in the benzene ring change significantly upon H₂ adsorption for all four adsorption sites, showing a clear and intuitive picture of the MOF components that interact directly with the adsorbed H₂.

Table I shows both the theoretical and experimental stretch frequency shifts of the adsorbed H₂ relative to free H₂. See text for zero point energies (not included in the binding energies E_B here).

| Site     | Theory (cm⁻¹) | Expr. (cm⁻¹) | Calculated E_B (kJ/mol) |
|----------|---------------|--------------|-------------------------|
| cup      | -23           | -27.5        | -11.1                   |
| O2       | -22           | -19.0        | -7.9                    |
| O3       | -13           | -17          | -7.8                    |
| benzene  | -15           | -              | -5.4                    |

The measured IR spectra also show some RV lines where both vibrational and rotational states change during a single transition. Usually inelastic neutron scattering is employed to study the H₂ rotational states and has been already applied to H₂ in MOF-5 [3, 4]. However, the low energy resolution limits detailed analysis. We therefore consider the RV measured with IR [3] for comparison with our rotational calculations. The left panel of Fig. 2 is the angular potential energy surface at the cup site. The coordinate system is chosen so that the origin is at the cup site and the Z axis is the 3-fold rotation axis (see Fig. S2 in Supplemental Material [7]). Fig. 2 shows that H₂ tends to lie in the XY plane and to be perpendicular to the rotation axis (Z). The energies for in-plane orientations are almost uniform. Therefore, the rotation is essentially two dimensional, as shown by the flattened ground-state angular wave function in the right panel of Fig. 2. Combining the stretch frequency and the rotational energies (see Supplemental Material), we obtain the RV frequencies. The results for the cup site are shown as S transitions in Table II where the frequency shifts are listed relative to the corresponding free H₂ values (see Supplemental Material for other sites). The magnitude of the shifts is consistent between theory and experiment, particularly for the leading peaks in each category that are most intense.

We also calculated the translational frequencies at the cup site associated with the motion of the whole H₂ against the adsorption site. The three translational frequencies, at 95, 108 and 133 cm⁻¹ respectively, are consistent with the value of 84 cm⁻¹ extracted from IR spectra [3]. They are also similar to that observed for H₂ in C₆₀ (110 cm⁻¹) [17]. The determination of the rotational and translational states gives the corresponding zero point energies of ~0.5 and 2 kJ/mol for H₂ at the cup site. The binding energy after corrections is therefore about 8.5 kJ/mol and somewhat larger than the measured adsorption enthalpy of ~5 kJ/mol [18, 19]. This overestimation by vdW-DF, also found in other MOF materials [10], is attributed to overestimation of the intermediate-range interactions [15].
H$_2$, while the corresponding para line is not observed. Since the orientational energy map only shows a small rotational barrier, the missing para-H$_2$ line cannot be explained by the assumption of a frozen H$_2$ orientation. Moreover, the local structure around this site has C$_{3v}$ symmetry. The rotational state of the para H$_2$ has the same symmetry as Z and transforms as A$_1$. Therefore the transitions between two A$_1$ states should be IR active, even though the X and Y components of the dipole give a vanishing contribution by symmetry.

To understand the unexpected missing para-H$_2$ line and to calculate the line weights in the more complex RV spectra, we evaluate the transition dipole integral explicitly. Assuming the electronic state remains in the ground state and the RV function is separable, one has

\[ I_{\alpha} = \langle \psi_{\text{MOF}}^{\dagger} | u_{\alpha} | \psi_{\text{MOF}} \rangle, \]

where \( u = \psi_{\text{MOF}}^R \psi_{\text{MOF}}^Z \psi_{\text{MOF}}^X \psi_{\text{MOF}}^Y \psi_{\text{MOF}}^Z \), \( \alpha = X, Y, Z \); the translational motion associated with H$_2$ center-of-mass is not included. The dipole is a function of the H$_2$ internuclear distance, R, and the bond orientation is defined by \( (\theta, \phi) \). It can be expanded as

\[ u_{\alpha}(R, \theta, \phi) = u_{\alpha}(R_0, \theta, \phi) + u'_{\alpha}(R, \theta, \phi) \Delta R \]

where \( R_0 \) is the equilibrium bond length, and \( u'_{\alpha} \) is the derivative of \( u_{\alpha} \) with respect to \( R \). Since the vibrational wave functions depend only on the inter-nuclear distance, the integral of the first term vanishes for transitions between different vibrational states due to orthogonality. We find

\[ I_{\alpha} = \langle \psi_{\text{MOF}}^{\dagger} | \Delta R \psi_{\text{MOF}}^R | \psi_{\text{MOF}}^{\dagger} | u_{\alpha} | \psi_{\text{MOF}} \rangle, \]

where \( | \psi_{\text{MOF}}^{\dagger} \rangle = | j m \rangle \) with \( j \) even (odd) for para (ortho) H$_2$, and similarly for \( | \psi_{\text{MOF}} \rangle \). The radial integral is a constant for both ortho and para H$_2$ and therefore unnecessary for understanding the missing line of para-H$_2$. The angular integral determines the relative intensity between them. We now need to evaluate this integral, for which \( u'_{\alpha}(R_0, \theta, \phi) \) remains to be calculated.

To perform ab initio calculations for \( u'_{\alpha} \) for every \( (\theta, \phi) \) is computationally expensive and impractical for this system. A possible approach is to compute the dipole from first principles for a few H$_2$ orientations and derive from them the dipole of all the other orientations. This becomes feasible if one can write the dipole as

\[
u_{\alpha} = \sum_i C_{i,\alpha} F_{i,\alpha}(\theta, \phi) \tag{1}\]

where \( F \) are some known functions and the summation needs to be run over only a few terms. This approach is appropriate if one realizes that H$_2$ and MOF are weakly interacting and the dipole induced on each other can be well described within a classical picture. First, MOF atoms produce an electric field \( \vec{E} \) which induces a dipole on H$_2$. At the cup site, the field is along Z due to the rotational symmetry so it can be easily shown that the induced dipole on H$_2$ is of the form in Eq. (1) by projecting the field perpendicular and parallel to the H$_2$ bond and calculating the corresponding dipole components. A second contribution to the total dipole of the system arises from the H$_2$ permanent quadrupole inducing a dipole on the MOF. The quadrupolar potential and the corresponding electric field at position \( \vec{r} \), depend on \( \vec{r} \), the H$_2$ quadrupole and the bond orientation, which are again of the form in Eq. (1). This field shifts the MOF charge density and induces a dipole. The total dipole on the MOF may be formally calculated by multiplying the electric field by the polarizability at the same position and integrating over the whole MOF. This procedure extends the classical picture of point charge into the continuous charge density regime. It cannot be performed in practice since the polarizability is not available. However, the final result for the dipole would be like the expression in Eq. (1), since the integration runs over the MOF space while \( (\theta, \phi) \) would be left unchanged. One can similarly add second-order corrections where the induced dipole on H$_2$ and MOF further produce dipole on each other. The final equation after this correction turns out to be quite simple for cup site absorption (see the Supplemental Material for derivation) and reads

\[
u_X^* = C_{11}^* \sin 2\theta \cos \phi - (C_{12}^* \cos 2\phi - C_{13}^* \sin 2\phi) \sin^2 \theta \\
u_Y^* = C_{11}^* \sin 2\theta \sin \phi + (C_{12}^* \sin 2\phi + C_{13}^* \cos 2\phi) \sin^2 \theta \tag{2}
\]

where \( s \) could be H$_2$, MOF, or the total system. The C coefficients depend on the H$_2$ quadrupole, polarizability and MOF geometry which are kept fixed during the vibrational transition. From Eq. (2) we see that only two orientations (each orientation gives three equations) are required to determine the five constants and correspondingly the dipole for any other orientations. To test this model, we calculate \( u'_Z \) for several H$_2$ orientations. Good linearity is obtained between \( u'_Z \) and \( \cos^2 \theta \) (see Fig. S7 in Supplemental Material), in agreement with our model. X and Y components are also consistent with our model (see Supplemental Material).

Table II summarizes our results for H$_2$ at the cup site. First we consider pure vibrations where rotational quantum numbers do not change (the Q lines in Table II). The angular integral \( \langle I_{\alpha}^Z \rangle \) for Q(0) (para) is much smaller than that for Q(1) (ortho), owing partly to the vanishing transition due to symmetry. This symmetry issue also applies to the \( |jm| = |10\rangle \rightarrow |10\rangle \) transition in Q(1) so that the integral is about 1/3 of that for the other two transitions of Q(1). Additionally, Fig. 2 shows that para H$_2$ has a larger probability to be oriented in XY plane, giving a smaller \( u'_Z \) upon bond stretching, while the |10\rangle state of ortho H$_2$ is \( p_z \) like and the H$_2$ bond is mainly perpendicular to XY plane. As a result, \( u'_Z \) for the para state is only about one quarter of that for the |10\rangle state (see Supplemental Material for the integral results of each component of \( u' \) for the Q transitions). To get the relative intensity between Q(0) and Q(1), we need to consider the population ratio between para and ortho hydrogen, which we took to be 1:3. Also, the calculated rotational
TABLE II: Theory vs. experiment [5] for RV transitions at the cup site. The frequency shift \( \Delta v \) (cm\(^{-1}\)) is relative to the corresponding free \( \text{H}_2 \) value. The theoretical intensity \([x I^2_\text{th}]\times 30K\) Boltzmann factor (times 3 for ortho) is normalized to 100 for the strongest line; strong (str), weak (wk), and absent (abs) describe the experimental intensity.

| \( m_i \) | \( m_f \) | Theory | \( \Delta v \) | Int. | Experiment | \( \Delta v \) | Int. |
|----------|----------|--------|-------------|------|------------|-------------|------|
| Q(0)     | ±1       | 0      | 0           | −23  | 2          | abs         |      |
| Q(1)     | ±1       | 0      | 0           | −23  | 97         | −27.5       | str  |
| Q*(1)    | ±1       | 0      | 22          | 9    | 39         | wk          |      |
| S(0)     | ±3       | 0      | −34         | 100  | −36.8      | str         |      |
|          | ±2       | 0      | −9          | 6    | −0.8       | wk          |      |
|          | ±1       | 0      | 6           | 9    | 21.6       | wk          |      |
| S(1)     | ±3       | 0      | −78         | 0    | abs        |              |      |
|          | ±2       | 0      | −53         | 3    | −61        | wk          |      |
|          | ±1       | 0      | −50         | ~0   | abs        |              |      |
|          | 0        | 0      | −33         | ~0   | abs        |              |      |

The calculated intensity close to those of the other two weak S(1) lines, after the 13% population weight is taken into account (Table II). Finally, we discuss the special Q*(1) line (\( |1\rangle, |±1\rangle \rightarrow |10\rangle \)) that is experimentally observed [3]. The calculated \( I^2_\text{th} \) of this transition is approximately equal to that for Q(0). However, the population between para and ortho hydrogen is \( \sim 1:3 \) which makes Q*(1) \( \sim 4 \) times stronger and observable. The calculated shift of 22 cm\(^{-1}\) is quite small compared to the experimental value of 39 cm\(^{-1}\). This is likely due to the neglect of rotation-translation coupling, which would probably lower the low rotational state even more and therefore increase the splitting between the \( m=0 \) and \( m=\pm 1 \) states.

In summary, we have proposed a method that provides an intuitive picture of \( \text{H}_2 \) interaction in complex environments. These techniques provide powerful tools for studying gas adsorption in general.

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energy of the \(|10\rangle \) state is about 5.5 meV higher than that for the \( m = \pm 1 \) states (see Supplemental Material). As such, its population is about 13% of that of the \( m = 1 \) or \( -1 \) state at the experimental temperature of 30K within a Boltzmann distribution approximation. We can therefore estimate that the vibrational intensity for para \( \text{H}_2 \) is about 2.5% of that for ortho \( \text{H}_2 \), hence agreeing with the IR measurement, where the para line was simply not observed [3].

Table II also shows the results for S lines in the IR spectrum, where \( \Delta j = 2 \). First a selection rule of \( \Delta m = \pm 2 \) is observed with small probabilities for other transitions. This table also predicts that there is one single strong line for each S(0) and S(1) at the experimental temperature 30K, with shifts of \( -44 \) and \( -34 \) cm\(^{-1}\) respectively, whereas the S(1) line at \( -53 \) cm\(^{-1}\) should be weak due to the low population of the \(|10\rangle \) state. More importantly, the strong line in each category exhibits the largest frequency relative to the free \( \text{H}_2 \) value. These results are in very good agreement with the IR measurements in Ref. [3] where a single strong S(0) line of \( -49.3 \) cm\(^{-1}\) and a strong S(1) line of \( -36.8 \) cm\(^{-1}\) are observed for \( \text{H}_2 \) at the cup site. A weak S(0) line at \( -6.8 \) cm\(^{-1}\) and two S(1) peaks at \( -0.8 \) and \( 21.6 \) cm\(^{-1}\) are also observed with intensities roughly one order of magnitude smaller than that of the corresponding strong line, consistent with our calculations. Furthermore, Table II shows that the calculated intensities of the two strong S lines and the Q(1) lines are comparable, which is also observed [2]. We also note a peak of \( \sim -61 \) cm\(^{-1}\) shift with an intensity similar to that of the S(1) at \( -0.8 \) cm\(^{-1}\) [2]. This peak might arise from the \(|10\rangle \rightarrow |3, \pm 2\rangle \) transitions with theo-

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Supplemental Material

Calculational methods

First-principles calculations based on van der Waals density functional theory were performed within the plane-wave implementation of the density functional theory in the ABINIT package [1], which we have adapted from the Siesta [2] code to incorporate the van der Waals interaction. We adopted Troullier-Martins pseudopotentials [3] with a gradient-corrected functional. An energy cutoff of 50 Ry and Gamma point sampling were used for total energy calculations.

Vibrational frequency

The four type of adsorption sites are shown in Fig. S1. To calculate the stretch frequency for H$_2$ at each of these four sites, we performed a series of calculations varying the bond length of H$_2$, with the center of H$_2$ and the host atoms fixed at their equilibrium positions. The resulting potential-energy curve was used in the Schrödinger equation to obtain the eigenvalues and excitation frequencies. A similar calculation was also carried out for isolated H$_2$ to obtain the frequency shift due to MOF-H$_2$ interaction. The \textit{ab initio} total energies vs H$_2$ internuclear distance were tabulated in Tables S3−S6 for H$_2$ at the four type of adsorption sites.

Rotational frequency

In order to calculate the rotational states, we first sample the solid angle to get the total energies. The spherical surface was sampled as follows: the polar angle were evenly divided into seven layers; and the azimuthal angle were then sampled by \{1,8,16,24,16,8,1\} number of points corresponding to each layer from pole to pole of the sphere. We next fit these potential energies with spherical harmonics

\[ V(\theta, \phi) = \sum_{lm} c_{lm} Y_{lm} \]  

which was then substituted into the rigid rotor equation and diagonalized for rotational energies. We found that fitting with $s$ and $d$ states gave results converged within 1 cm$^{-1}$. The fitted coefficients are shown in Table S2. The calculated rotational energy states are shown in Tables S8−S11.

Wannier function approach for dipole moment and IR intensity

The Wannier functions were calculated with the Wannier90 code [4] embedded in ABINIT and the Brillouin zone was sampled by a 2x2x2 Monkhorst-Pack grid. The Wannier centers for the bare MOF were first calculated and used as initial guess for the H$_2$ loaded system. The change of MOF Wannier centers upon H$_2$ adsorption was obtained from

\[ \delta \mathbf{r}_n = \mathbf{r}_{n}^{MOF+H_2} - \mathbf{r}_{n}^{MOF} \]  

where $\mathbf{r}_n$ is the center of the $n$-th Wannier function. Fig. S3−S5 show these changes for the O2, O3 and benzene sites while the cup site is given in the main text.

To calculate the IR intensity, one first needs to get the derivative of the dipole with respect to the normal coordinates corresponding to H$_2$ stretch vibration. We used the H$_2$ internuclear distance as an approximation for the stretching normal coordinates and the derivative was approximate by the finite difference. To reduce the numerical errors, the bond stretching should be sufficiently large, but still in the linear regime. We found that a stretch of 0.05Å from equilibrium bond length was appropriate, as shown in Fig. S6.
The total induced dipole of the system can be approximated by a sum of four terms.

\[ u = u_0^{H_2} + u_0^{MOF} + u_1^{MOF} + u_1^{H_2} \]  

(S3)

The first term on the right-hand side is the induced dipole on \( H_2 \) due to interactions with MOF atoms. The second term is the induced dipole on MOF atoms due to \( H_2 \) quadrupole. The third term is the induced dipole on MOF due to \( u_0^{H_2} \) and the fourth term is the induced dipole on \( H_2 \) due to \( u_0^{MOF} \). These last two terms are second order corrections. We now derive the expressions for the four terms for cup site adsorption.

\[ u_0^{H_2} \]

Due to the 3-fold symmetry, the electric field \((\vec{E})\) at cup site due to MOF atoms is along the rotation axis, i.e. \( Z \). For \( H_2 \) with its bond oriented along \((\theta, \phi)\), the projected fields along and perpendicular to the bond are

\[ E_\parallel = E \cos \theta \]
\[ E_\perp = E \sin \theta \]  

(S4a)  

(S4b)

and the corresponding induced dipole is

\[ u_\parallel = E \alpha_\parallel \cos \theta \]
\[ u_\perp = E \alpha_\perp \sin \theta \]  

(S5a)  

(S5b)

where \( \alpha_\parallel \) and \( \alpha_\perp \) are the \( H_2 \) polarizability along and perpendicular to the bond. In Cartesian coordinates, this gives

\[ u_0^{H_2}_X = E(\alpha_\parallel - \alpha_\perp) \sin \theta \cos \theta \cos \phi \]  

(S6a)

\[ u_0^{H_2}_Y = E(\alpha_\parallel - \alpha_\perp) \sin \theta \cos \theta \sin \phi \]  

(S6b)

\[ u_0^{H_2}_Z = E(\alpha_\parallel \cos^2 \theta + \alpha_\perp \sin^2 \theta) \]  

(S6c)

\[ u_0^{MOF} \]

Hydrogen molecule has permanent quadrupole. The tensor is \( Q_{zz} = -2Q_{xx} = -2Q_{yy} = Q \). For \( H_2 \) at origin with orientation of \((\theta, \phi)\), the quadrupole potential at position \( P_1(X,Y,Z) \) is

\[ V(r) = \frac{3Q}{2r^5} \tilde{Z}^2 - \frac{Q}{2r^3} \]  

(S7)

where \( r = (X^2 + Y^2 + Z^2)^{1/2} \) and \( \tilde{Z} = X \sin \theta \cos \phi + Y \sin \theta \sin \phi + Z \cos \theta \). The electric field of this potential is

\[ E_{0X}(r) = \frac{3Q}{2r^7}\left\{-2r^2 \sin \theta \cos \phi \tilde{Z} + 5X \tilde{Z}^2\right\} - \frac{3Q}{2r^5}X \]  

(S8a)

\[ E_{0Y}(r) = \frac{3Q}{2r^7}\left\{-2r^2 \sin \theta \sin \phi \tilde{Z} + 5Y \tilde{Z}^2\right\} - \frac{3Q}{2r^5}Y \]  

(S8b)

\[ E_{0Z}(r) = \frac{3Q}{2r^7}\left\{-2r^2 \sin \theta \cos \phi \tilde{Z} + 5Z \tilde{Z}^2\right\} - \frac{3Q}{2r^5}Z \]  

(S8c)

The MOF charge density will be shifted by this field and thus leads to induced dipole. To calculate this induced dipole on MOF, one may view that there is an electron at position \( P_1 \) with partial charge which is equal to the charge density at \( P_1 \). This charge has a certain polarizability. The total induced dipole can then be formally calculated by multiplying the electric field by the corresponding polarizability and then integrating over the whole MOF space. This procedure is somewhat an extension of the classical point charge into the continuous charge density regime. Assuming the polarizability is isotropic, the final result will have the same dependence on \((\theta, \phi)\) as electric field since the integration runs over \((X,Y,Z)\) while \((\theta, \phi)\) will be left unchanged. In other words, we will have an equation of the form in Eq. (5) in the main text. Note that the isotropic assumption is not critical here except in making the final
Due to the 3-fold rotation symmetry, there are three equivalent points with equal polarizability in MOF. Taking advantage of this symmetry, the sum of the electric fields at the three positions is

\[ E_{0X} = \frac{9Q}{4r^2} \left\{ (3r^2 - 5Z^2) Z \sin 2\theta \cos \phi - \frac{5}{2} (3XY^2 - X^3) \sin^2 \theta \cos 2\phi + \frac{5}{2} (3X^2Y - Y^3) \sin^2 \theta \sin 2\phi \right\} \]  
(S9a)

\[ E_{0Y} = \frac{9Q}{4r^2} \left\{ (3r^2 - 5Z^2) Z \sin 2\theta \sin \phi + \frac{5}{2} (3X^2Y - Y^3) \sin^2 \theta \cos 2\phi + \frac{5}{2} (3XY^2 - X^3) \sin^2 \theta \sin 2\phi \right\} \]  
(S9b)

\[ E_{0Z} = \frac{9Q}{4} \frac{(5Z^2 - 3r^2)Z}{r^2} (3 \cos^2 \theta - 1) \]  
(S9c)

The induced dipole on MOF is therefore given by

\[ u_{0X}^{MOF} = C_{01}^{MOF} \sin 2\theta \cos \phi - C_{02}^{MOF} \sin^2 \theta \cos 2\phi + C_{03}^{MOF} \sin^2 \theta \sin 2\phi \]  
(S10a)

\[ u_{0Y}^{MOF} = C_{01}^{MOF} \sin 2\theta \sin \phi + C_{02}^{MOF} \sin^2 \theta \cos 2\phi + C_{03}^{MOF} \sin^2 \theta \sin 2\phi \]  
(S10b)

\[ u_{0Z}^{MOF} = C_{04}^{MOF} (3 \cos^2 \theta - 1) \]  
(S10c)

where

\[ C_{01}^{MOF} = \int \frac{9Q}{4r^2} (3r^2 - 5Z^2) Z \alpha^{MOF} (r) \, dr \]  
(S11a)

\[ C_{02}^{MOF} = \int \frac{9Q}{4r^2} \frac{5}{2} (3XY^2 - X^3) \alpha^{MOF} (r) \, dr \]  
(S11b)

\[ C_{03}^{MOF} = \int \frac{9Q}{4r^2} \frac{5}{2} (3X^2Y - Y^3) \alpha^{MOF} (r) \, dr \]  
(S11c)

\[ C_{04}^{MOF} = \int \frac{9Q}{4r^2} (5Z^2 - 3r^2) Z \alpha^{MOF} (r) \, dr \]  
(S11d)

and the integration runs over the 1/3 irreducible region of MOF, as a result of the 3-fold rotation symmetry.

2\textsuperscript{nd}-order corrections: \( u_1^{MOF} \) and \( u_1^{H_2} \)

The induced dipole on H\(_2\) and MOF, \( u_0^{H_2} \) and \( u_0^{MOF} \), further induces dipole on each other and produces second order corrections. For \( u_0^{H_2} \), it gives electric field at \( P_1(X,Y,Z) \)

\[ E_{1X} (r) = \frac{1}{r^3} \left( -3u_{0X}^{H_2} + 3u_0^{H_2} \cdot rX \right) \]  
(S12a)

\[ E_{1Y} (r) = \frac{1}{r^3} \left( -3u_{0Y}^{H_2} + 3u_0^{H_2} \cdot rY \right) \]  
(S12b)

\[ E_{1Z} (r) = \frac{1}{r^3} \left( -3u_{0Z}^{H_2} + 3u_0^{H_2} \cdot rZ \right) \]  
(S12c)

Similar to the derivation of \( u_0^{MOF} \), one obtains

\[ u_{1X}^{MOF} = C_{11}^{MOF} \sin 2\theta \cos \phi - C_{12}^{MOF} \sin^2 \theta \cos 2\phi + C_{13}^{MOF} \sin^2 \theta \sin 2\phi \]  
(S13a)

\[ u_{1Y}^{MOF} = C_{11}^{MOF} \sin 2\theta \sin \phi + C_{12}^{MOF} \sin^2 \theta \cos 2\phi + C_{13}^{MOF} \sin^2 \theta \sin 2\phi \]  
(S13b)

\[ u_{1Z}^{MOF} = C_{14}^{MOF} \cos^2 \theta + C_{15}^{MOF} \]  
(S13c)
where

$$C_{11}^{\text{MOF}} = \int \left\{ 9Q \left( \frac{3Z}{r^5} \frac{5Z^3}{r^7} \right) + 3E \left( \frac{1}{r^3} \frac{3Z^2}{r^5} \right) \left( \alpha_\parallel - \alpha_\perp \right) \right\} \mathbf{a}^{\text{MOF}}(r) \, dr$$

(S14a)

$$C_{12}^{\text{MOF}} = \int \left\{ \frac{45Q}{8r^7} \left( 3XY^2 - X^3 \right) \right\} \mathbf{a}^{\text{MOF}}(r) \, dr$$

(S14b)

$$C_{13}^{\text{MOF}} = \int \left\{ \frac{45Q}{8r^7} \left( 3X^2Y - Y^3 \right) \right\} \mathbf{a}^{\text{MOF}}(r) \, dr$$

(S14c)

$$C_{14}^{\text{MOF}} = \int \left\{ \frac{27Q}{4} \left( \frac{3Z^2}{r^5} \frac{5Z^3}{r^7} \right) - 3E \left( \frac{1}{r^3} \frac{3Z^2}{r^5} \right) \left( \alpha_\parallel - \alpha_\perp \right) \right\} \mathbf{a}^{\text{MOF}}(r) \, dr$$

(S14d)

$$C_{15}^{\text{MOF}} = \int \left\{ \frac{9Q}{4} \left( \frac{3Z}{r^5} \frac{5Z^3}{r^7} \right) - 3E \left( \frac{1}{r^3} \frac{3Z^2}{r^5} \right) \alpha_\perp \right\} \mathbf{a}^{\text{MOF}}(r) \, dr$$

(S14e)

and the integration again runs over 1/3 of the MOF region.

Now let us look at the second-order correction on H$_2$, $\mathbf{u}_1^{H_2}$. The hydrogen quadrupole generates electric field at P$_1$ as given by Eq. (S9). With the help of the partial charge and local polarizability concept, this field produces a local dipole $\mathbf{u}_0^{\text{MOF}}(r) = \mathbf{a}^{\text{MOF}}(r) \mathbf{E}_0(r)$ where $\mathbf{E}_0(r)$ is given in Eq. (S8) and $\mathbf{a}^{\text{MOF}}(r)$ is assumed to be isotropic. The electric field back at H$_2$ due to this local dipole is

$$E_{1X}^{H_2} = -\frac{r}{r^5} \left\{ E_{OX}^{\text{MOF}}(r^2 - 3X^2) - 3E_{0Y}^{\text{MOF}}XY - 3E_{0Z}^{\text{MOF}}XZ \right\}$$

(S15a)

$$E_{1Y}^{H_2} = -\frac{r}{r^5} \left\{ E_{OY}^{\text{MOF}}(r^2 - 3Y^2) - 3E_{0X}^{\text{MOF}}XY - 3E_{0Z}^{\text{MOF}}YZ \right\}$$

(S15b)

$$E_{1Z}^{H_2} = -\frac{r}{r^5} \left\{ E_{OZ}^{\text{MOF}}(r^2 - 3Z^2) - 3E_{0X}^{\text{MOF}}XZ - 3E_{0Y}^{\text{MOF}}YZ \right\}$$

(S15c)

Inserting Eq. (S9) into Eq. (S15), adding together the three rotationally equivalent points and integrating over the 1/3 MOF region, one finally obtains

$$\tilde{E}_{1X}^{H_2} = C_{11}^{H_2} \sin \theta \cos \phi - C_{12}^{H_2} \sin^2 \theta \cos 2\phi + C_{13}^{H_2} \sin^2 \theta \sin 2\phi$$

(S16a)

$$\tilde{E}_{1Y}^{H_2} = C_{11}^{H_2} \sin \theta \sin \phi + C_{12}^{H_2} \sin^2 \theta \sin 2\phi + C_{13}^{H_2} \sin^2 \theta \cos 2\phi$$

(S16b)

$$\tilde{E}_{1Z}^{H_2} = C_{14}^{H_2} \cos^2 \theta + C_{15}^{H_2}$$

(S16c)

where

$$C_{11}^{H_2} = \int \frac{9\mathbf{a}^{\text{MOF}}(r)QZ}{2r^{28}} \left( \frac{33}{16} - \frac{Z^2}{8r^2} - \frac{15Z^4}{16r^4} - \frac{5X^2Y^2}{4r^4} \right) \, dr$$

(S17a)

$$C_{12}^{H_2} = \int \frac{9\mathbf{a}^{\text{MOF}}(r)Q(3Y^2 - X^2)X}{2r^{28}} \, dr$$

(S17b)

$$C_{13}^{H_2} = \int \frac{9\mathbf{a}^{\text{MOF}}(r)Q(3X^2 - Y^2)Y}{2r^{28}} \, dr$$

(S17c)

$$C_{14}^{H_2} = \int \frac{9\mathbf{a}^{\text{MOF}}(r)QZ}{2r^{28}} \left( \frac{9}{8} \frac{15Z^4}{16r^4} + \frac{5X^2Y^2}{4r^4} \right) \, dr$$

(S17d)

$$C_{15}^{H_2} = \int \frac{9\mathbf{a}^{\text{MOF}}(r)QZ}{2r^{28}} \left( \frac{57}{16} \frac{37Z^2}{8r^2} - \frac{15Z^4}{16r^4} - \frac{5X^2Y^2}{4r^4} \right) \, dr$$

(S17e)

and the integral is over the 1/3 of the MOF space. Considering the anisotropy of the polarizability of H$_2$, we have

$$\mathbf{u}_1^{H_2} = \left[ \alpha_\parallel + (\alpha_\parallel - \alpha_\perp) \begin{pmatrix} \sin^2 \theta \cos^2 \phi & \sin^2 \theta \sin \phi \cos \phi & \sin \theta \cos \theta \cos \phi \\ \sin^2 \theta \sin \phi \cos \phi & \sin^2 \theta \sin^2 \phi & \sin \theta \cos \theta \sin \phi \\ \sin \theta \cos \theta \cos \phi & \sin \theta \cos \theta \sin \phi & \cos^2 \theta \end{pmatrix} \right] \tilde{E}_1^{H_2}$$

(S18)

The anisotropic term impose a small correction to the first term inside the bracket. For simplicity, we neglect the second term so that $\mathbf{u}_1^{H_2}$ and $\tilde{E}_1^{H_2}$ have a simple linear relationship. In particular, they have the same form of dependence on $(\theta, \phi)$ as given in Eq. (S16).
From Eq. (S6), (S10), (S13) and (S16), we conclude that the following equations hold

\[ u_X^s = C_1^s \sin 2\theta \cos \phi - (C_2^s \cos 2\phi - C_3^s \sin 2\phi) \sin^2 \theta \]  \hspace{1cm} (S19a)

\[ u_Y^s = C_1^s \sin 2\theta \sin \phi + (C_2^s \sin 2\phi + C_3^s \cos 2\phi) \sin^2 \theta \]  \hspace{1cm} (S19b)

\[ u_Z^s = C_4^s \cos^2 \theta + C_5^s \]  \hspace{1cm} (S19c)

where \( s \) denotes the system and could be \( \text{H}_2 \), MOF or the total. To determine the coefficients \( C \)'s, we calculated the dipole and the derivative of the dipole with respect to \( \text{H}_2 \) internuclear distance with Wannier function approach for five hydrogen orientations. The Z components of the obtained values were used to fit \( C_4 \) and \( C_5 \) in Eq. (S19c). As shown in Fig. S7, good linearity is obtained in agreement with our model.

To compute \( C_1 \), \( C_2 \) and \( C_3 \), we pick three \textit{ab initio} calculated value, \( u'_x/u'_y \) of orientation 4 and \( u'_z \) of orientation 5, to solve a 3\times3 linear equation for the coefficients. To check the values obtained, we substitute them back into Eq. (S19a) and (S19b) for other orientations and compare with the \textit{ab initio} results. The comparison are shown in Table S12 and S13. Consistent results are obtained generally while we do see some deviations on the induced dipole on \( \text{H}_2 \), which may be due to the neglect of the anisotropy in Eq. (S18). However, the absolute magnitude of these deviations are quite small (< 10%) compared to the total value which is the sum of the induced dipole on MOF and on \( \text{H}_2 \).
FIG. S1: Illustration of H₂ adsorption sites in MOF-5 unit cell (top) and primitive cell (bottom). MOF-5 has FCC structure with lattice constant of 25.89 Å [6]. The primitive cell has 106 atoms. The H atoms on benzene rings are omitted for clarity.
FIG. S2: Illustration of the MOF frame of reference. Origin is at the cup adsorption sites and Z is along the $<111>$ direction of cubic crystal lattice shown in Fig. S1. It is also the 3-fold rotation axis.
FIG. S3: Illustration of the O2 adsorption site and the change of Wannier centers due to H2 adsorption compared to bare MOF and free H2. The vector lengths are enlarged by 1200.
FIG. S4: Illustration of the O3 adsorption site and the change of Wannier centers due to H\textsubscript{2} adsorption compared to bare MOF and free H\textsubscript{2}. The vector lengths are enlarged by 1200.
FIG. S5: Illustration of the benzene adsorption site and the change of Wannier centers due to H$_2$ adsorption compared to bare MOF and free H$_2$. The vector lengths are enlarged by 1200.
FIG. S6: $\delta u$ as a function of $H_2$ internuclear distance. $u_0$ is the dipole at equilibrium distance.
TABLE S3: Calculated total energy vs H$_2$ internuclear distance at cup site

| R (a.u.) | E (a.u.) |
|---------|---------|
| 0.63258 | -1147.23459646 |
| 0.70817 | -1147.34182739 |
| 0.78376 | -1147.41767267 |
| 0.85935 | -1147.47155388 |
| 0.93494 | -1147.50972612 |
| 1.01052 | -1147.53646724 |
| 1.08611 | -1147.55478553 |
| 1.16170 | -1147.56683964 |
| 1.23729 | -1147.57419775 |
| 1.31288 | -1147.57801104 |
| 1.38847 | -1147.57913028 |
| 1.48297 | -1147.57768502 |
| 1.57745 | -1147.57390705 |
| 1.67194 | -1147.56843515 |
| 1.76642 | -1147.56176098 |
| 1.86091 | -1147.55423624 |
| 1.95540 | -1147.54614531 |
| 2.04988 | -1147.53771266 |
| 2.14437 | -1147.52910151 |
| 2.23886 | -1147.52044322 |
| 2.33334 | -1147.51183591 |
TABLE S4: Calculated total energy vs H$_2$ internuclear distance at O2 site

| R (a.u.) | E (a.u.)  |
|---------|----------|
| 0.63142 | -1147.23167787 |
| 0.70701 | -1147.33946050 |
| 0.78259 | -1147.41567703 |
| 0.85818 | -1147.46981324 |
| 0.93377 | -1147.50816182 |
| 1.00936 | -1147.53502878 |
| 1.08495 | -1147.55343531 |
| 1.16054 | -1147.56555111 |
| 1.23613 | -1147.57295236 |
| 1.31172 | -1147.57679567 |
| 1.38731 | -1147.57793396 |
| 1.48182 | -1147.57650225 |
| 1.57630 | -1147.57273083 |
| 1.67079 | -1147.56726718 |
| 1.76528 | -1147.56059280 |
| 1.85976 | -1147.55307608 |
| 1.95425 | -1147.54499838 |
| 2.04873 | -1147.53657940 |
| 2.14322 | -1147.52798691 |
| 2.23771 | -1147.51934958 |
| 2.33219 | -1147.51076491 |
| R (a.u.) | E (a.u.)       |
|---------|---------------|
| 0.63117 | -1147.23131641|
| 0.70676 | -1147.33921650|
| 0.78235 | -1147.41551509|
| 0.85794 | -1147.46970566|
| 0.93353 | -1147.50809162|
| 1.00912 | -1147.53498512|
| 1.08471 | -1147.55340776|
| 1.16030 | -1147.56553250|
| 1.23589 | -1147.57293612|
| 1.31147 | -1147.57677507|
| 1.38705 | -1147.57790325|
| 1.48153 | -1147.57645368|
| 1.57601 | -1147.57265607|
| 1.67050 | -1147.56716130|
| 1.76499 | -1147.56045531|
| 1.85947 | -1147.55290340|
| 1.95396 | -1147.54478993|
| 2.04845 | -1147.53633172|
| 2.14293 | -1147.52769561|
| 2.23742 | -1147.51900844|
| 2.33191 | -1147.51036692|
| R (a.u.) | E (a.u.)       |
|---------|---------------|
| 0.63097 | -1147.23028851 |
| 0.70656 | -1147.33826702 |
| 0.78215 | -1147.41460791 |
| 0.85774 | -1147.46882070 |
| 0.93333 | -1147.50721490 |
| 1.00891 | -1147.53410287 |
| 1.08450 | -1147.55251525 |
| 1.16009 | -1147.56462548 |
| 1.23568 | -1147.57201447 |
| 1.31127 | -1147.57584010 |
| 1.38686 | -1147.57695620 |
| 1.48135 | -1147.57549948 |
| 1.57583 | -1147.57170006 |
| 1.67032 | -1147.56620858 |
| 1.76480 | -1147.55950504 |
| 1.85929 | -1147.55195560 |
| 1.95378 | -1147.54384388 |
| 2.04826 | -1147.53538984 |
| 2.14275 | -1147.52676285 |
| 2.23724 | -1147.51809406 |
TABLE S7: Expansion coefficients (meV) of orientational potential energy surface in the basis of spherical harmonics. The equilibrium energy is set to be zero.

| site   |  $s$  | $d_{z^2}$ | $d_{xz}$ | $d_{yz}$ | $d_{x^2-y^2}$ |
|--------|------|-----------|----------|----------|---------------|
| cup    | 17.0 | 0.06      | 8.45     | 8.41     | 8.55          | -0.006        |
| O2     | 25.0 | -3.74     | -6.36    | -6.90    | -5.76         | -4.88         |
| O3     | 7.73 | 0.27      | -2.43    | -2.39    | -2.38         | 0             |
| benzene| 1.46 | -0.52     | 0        | 0.27     | 0             | 0.80          |
TABLE S8: Rotational eigen energies (meV) at cup site

| State # | Energy  | $E_i - E_j$ | $i$ | $m$ |
|---------|---------|-------------|-----|-----|
| 1       | 4.428   |             | 0   | 0   |
| 2       | 17.498  | 13.070      | -1  |     |
| 3       | 17.555  | 13.127      | 1   | 1   |
| 4       | 23.014  | 18.586      |     | 0   |
| 5       | 46.197  | 41.769      | -2  |     |
| 6       | 46.197  | 41.769      | 2   |     |
| 7       | 50.094  | 45.666      | 2   | -1  |
| 8       | 50.135  | 45.707      | 1   |     |
| 9       | 51.781  | 47.353      |     | 0   |
| 10      | 89.88   | 85.452      | -3  |     |
| 11      | 89.88   | 85.452      |     | 3   |
| 12      | 92.934  | 88.506      | -2  |     |
| 13      | 92.934  | 88.506      | 3   | 2   |
| 14      | 94.856  | 90.428      | -1  |     |
| 15      | 94.894  | 90.466      | 1   |     |
| 16      | 95.552  | 91.124      |     | 0   |
TABLE S9: Rotational eigen energies (meV) at O2 site

| State # | Energy  | Ei-E1  |
|---------|---------|--------|
| 1       | 6.76    |        |
| 2       | 18.614  | 11.854 |
| 3       | 22.306  | 15.546 |
| 4       | 24.03   | 17.270 |
| 5       | 49.036  | 42.276 |
| 6       | 49.39   | 42.630 |
| 7       | 50.619  | 43.859 |
| 8       | 53.265  | 46.505 |
| 9       | 53.439  | 46.679 |
| 10      | 93.026  | 86.266 |
| 11      | 93.146  | 86.386 |
| 12      | 94.315  | 87.555 |
| 13      | 95.211  | 88.451 |
| 14      | 95.488  | 88.728 |
| 15      | 97.788  | 91.028 |
| 16      | 97.801  | 91.041 |
TABLE S10: Rotational eigen energies (meV) at O3 site

| State # | Energy | $E_i - E_0$ | $l$ | $m$ |
|---------|--------|-------------|-----|-----|
| 1       | 2.148  | 0           | 0   | 0   |
| 2       | 15.815 | 13.667      | 0   | 0   |
| 3       | 17.356 | 15.208      | 1   | -1  |
| 4       | 17.434 | 15.286      | 1   | 0   |
| 5       | 45.551 | 43.483      | 0   | 0   |
| 6       | 45.869 | 43.721      | -1  | 0   |
| 7       | 45.924 | 43.776      | 2   | 1   |
| 8       | 47.026 | 44.878      | -2  | 0   |
| 9       | 47.027 | 44.879      | 2   | 0   |
| 10      | 89.685 | 87.537      | 0   | 0   |
| 11      | 89.831 | 87.683      | -1  | 0   |
| 12      | 89.884 | 87.736      | 1   | 0   |
| 13      | 90.375 | 88.227      | 3   | -2  |
| 14      | 90.377 | 88.229      | 2   | 0   |
| 15      | 91.253 | 89.105      | -3  | 0   |
| 16      | 91.253 | 89.105      | 3   | 0   |
| State # | Energy (meV) | $E_i - E_0$ (meV) |
|--------|--------------|-------------------|
| 1      | 0.409        |                   |
| 2      | 14.929       | 14.520            |
| 3      | 15.051       | 14.642            |
| 4      | 15.35        | 14.941            |
| 5      | 44.332       | 43.923            |
| 6      | 44.339       | 43.930            |
| 7      | 44.553       | 44.144            |
| 8      | 44.64        | 44.231            |
| 9      | 44.691       | 44.282            |
| 10     | 88.408       | 87.999            |
| 11     | 88.409       | 88.000            |
| 12     | 88.595       | 88.186            |
| 13     | 88.611       | 88.202            |
| 14     | 88.693       | 88.284            |
| 15     | 88.773       | 88.364            |
| 16     | 88.787       | 88.378            |
FIG. S7: $\partial u_Z / \partial R$ vs $\cos^2 \theta$ for the induced dipole on H$_2$ and MOF. $u'_Z$ was calculated as the difference between the dipole moments at equilibrium bond length and a stretch of 0.05Å.
TABLE S12: Comparison of \((\delta u_X, \delta u_Y)\) on MOF due to H\(_2\) bond stretching of 0.05\AA\ between the \textit{ab initio} and the fitted values

| orientation | \(\theta\)(degree) | \(\phi\)(degree) | \(\delta u_X\) | \(\delta u_Y\) | \(\delta u_X\) | \(\delta u_Y\) |
|-------------|-------------------|-----------------|---------------|---------------|---------------|---------------|
| 1           | 99.650            | -95.723         | 5.69E-04      | 9.44E-04      | 5.69E-04      | 9.634E-04     |
| 2           | 87.054            | -6.190          | -4.864E-04    | -8.400E-04    | -5.178E-04    | -8.720E-04    |
| 3           | 10.097            | 112.811         | -5.760E-05    | -1.008E-04    | -5.172E-05    | -9.052E-05    |
| 4           | 54.741            | -98.278         | 2.774E-04     | 2.464E-04     | --            | --            |
| 5           | 42.937            | -16.295         | 2.640E-04     | -6.126E-04    | --            | -5.754E-04    |

TABLE S13: comparison of \((\delta u_X, \delta u_Y)\) on H\(_2\) due to bond stretching of 0.05\AA\ between the \textit{ab initio} and the fitted values

| orientation | \(\theta\)(degree) | \(\phi\)(degree) | \(\delta u_X\) | \(\delta u_Y\) | \(\delta u_X\) | \(\delta u_Y\) |
|-------------|-------------------|-----------------|---------------|---------------|---------------|---------------|
| 1           | 99.650            | -95.723         | -1.631E-05    | -4.322E-05    | -2.286E-05    | -6.552E-05    |
| 2           | 87.054            | -6.190          | 1.562E-05     | 2.220E-05     | 1.340E-05     | 4.522E-05     |
| 3           | 10.097            | 112.811         | 1.338E-05     | 3.052E-05     | 9.392E-06     | 2.030E-05     |
| 4           | 54.741            | -98.278         | -2.190E-06    | 3.340E-05     | --            | --            |
| 5           | 42.937            | -16.295         | -6.386E-05    | 3.326E-05     | --            | 4.184E-05     |
TABLE S14: Theory vs experiment (Ref.5) for RV frequency shifts (cm$^{-1}$) of adsorbed H$_2$ relative to free H$_2$. The vibrational transition is from the ground state to the 1st excited state ($v=0 \rightarrow v=1$).

| site | S(0) (para) ($j=0 \rightarrow j=2$) | S(1) (ortho) ($j=1 \rightarrow j=3$) |
|------|----------------------------------|----------------------------------|
| O2   | Th. | -37, -34, -24, -3, -1 | -15, -14, -4, 3, 5, 24, 24 |
|      | Ex. | -36.7, -27.3, -24.3, -7.4 | -12.9 |
| O3   | Th. | -19, -16, -7 | -10, -9, -4, 3 |

TABLE S15: Angular integral $\langle j m | \mathbf{u}' | j m \rangle$ for H$_2$ at cup site. The energy of the $|00\rangle$ is set as reference. The units for $\mathbf{u}'$ is $10^{-3}$e.

| jm   | $u'_x$  | $u'_y$  | $u'_z$  | $u'' (\times 10^{-5} e^2)$ | $E$ (meV) |
|------|--------|--------|--------|---------------------------|----------|
| 00   | -0.009 | 0.02   | -2.23  | 5.0                       | 0        |
| 11   | -2.38  | 7.69   | -1.41  | 66.7                      | 13.1     |
| 10   | 2.36   | -7.67  | -1.40  | 66.4                      | 13.2     |
| 01   | 0.003  | 0.01   | -4.67  | 21.8                      | 18.6     |
TABLE S16: Theoretical predictions and experimental data for $v = 0 \rightarrow v = 1$ transitions of H$_2$ at the cup site. The frequency shift $\Delta v$ (cm$^{-1}$) is relative to the corresponding free H$_2$ value and the angular integral given by $I^2_A = |\langle j_f m_f | \mathbf{u} | j_i m_i \rangle|^2 (10^{-6} \text{e}^3)$. The rotational energy (meV) $E^\text{rot}$ of the $|00\rangle$ state is set as a reference. The theoretical intensity is calculated from $I^2_A$ weighted by the 30K Boltzmann factor and the spin ratio of 1:3 between para and ortho H$_2$. The strongest line is normalized to 100.

| $m_i$ | $m_f$ | $E^\text{rot}$ | $\Delta v$ | $I^2_A$ | Intensity $\Delta v$ | Intensity |
|------|------|---------------|----------|--------|----------------------|---------|
| Q(0)($j_i=0 \rightarrow j_f=0$) | 0 | 0 | 0 | -23 | 5 | 2 | absent |
| Q(1)($j_i=1 \rightarrow j_f=1$) | ±1 | ±1 | 13.1 | -23 | 66 | 97 | -27.5 | strong |
| Q*(1)($j_i=1 \rightarrow j_f=1$) | ±1 | 0 | 13.1 | 22 | 6 | 9 | 39 | weak |
| S(0) ($j_i=0 \rightarrow j_f=2$) | 0 | ±1 | 13.1 | -12 | 10 | 5 | -6.8 | weak |
| S(1)($j_i=1 \rightarrow j_f=3$) | ±1 | ±2 | 13.1 | -9 | 4 | 6 | -0.8 | weak |
| | | ±1 | 6 | 6 | 9 | 21.6 | weak |
| | | 0 | 11 | 2 | 3 | absent |
| | ±3 | ±3 | -78 | 0 | 0 | absent |
| | ±2 | 0 | 18.6 | -53 | 49 | 3 | -61 | weak |
| | ±1 | 0 | -33 | 6 | 8 | ~0 | absent |
| | 0 | ~0 | ~0 | ~0 | 21.6 | weak |
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