Calculation of neutron spectra for hydrogen in zeolites: rotational motions and translational motions in the Born–Oppenheimer limit

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Abstract

Inelastically scattered neutrons can probe the location and dynamical behavior of molecular hydrogen absorbed within zeolites. Hydrogen may, at certain temperatures, display mixed quantum/classical dynamics associated with its rotational and center-of-mass (CM) motions. When hydrogen diffusion occurs within a zeolite containing a unique adsorptive site, the spectrum is a simple convolution of (quantum) rotational and (classical) CM contributions. We present a jump diffusion model with a faujasite-type host which illustrates this behavior. A more general case would be a host which induces a spatially-dependent distribution of rotational frequencies. In order to address this more general situation, we present a formalism in which the standard time correlation function for neutron intensity:

$$C(q, t) = \langle e^{i\hat{H}_q t} e^{-i\hat{H}_A} \rangle$$

is approximated in the “Born–Oppenheimer” limit. A preliminary test of this formalism is performed for jump diffusion within a one-dimensional model system. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Inelastic neutron scattering has proven to be a versatile probe of the motion of molecular hydrogen in host solids. Neutron scattering techniques can probe both center-of-mass (CM) and rotational motions of H₂ [1]. In this paper, we will be interested in the behavior of H₂ within zeolites. From the incoherent scattering function, one can deduce favored adsorption sites, normal modes, models for and rates of self-diffusion, and relate these quantities to host properties like cage structure and cationic content [2–5].

Computer simulation has become a useful adjunct to spectroscopic experiments on adsorbed H₂ and other molecules [6–10]. In order to simulate the dynamics of H₂ in zeolites, one confronts the challenge of simulating a molecule with quantum rotational and vibrational degrees of freedom, but with CM motions that might be adequately described either semi-classically, or even classically. Then, there is the additional

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challenge of constructing a neutron scattering function, \( S(q, \omega) \), which is consistent with the simulation. While it is clear how to construct either a fully-classical or fully-quantum mechanical van-Hove time correlation function (TCF), \( C(q, t) \), it is less obvious how to do so for scattering from \( \text{H}_2 \) in a mixed quantum-classical limit. In this paper, we will derive a simple, convenient expression for the van-Hove correlation function of molecular hydrogen within the Born–Oppenheimer (BO) approximation. The primary advantage of the new expression is that it can be evaluated for a given classical trajectory, yet it goes beyond the commonly-used convolution approximation. Convolution turns out to be valid, for example, for the model of \( \text{H}_2 \) in faujasite discussed in Section 3. The new expression based on a symmetric Trotter expansion also seems capable of interpolating between the two limits of inhomogeneous broadening and motional narrowing.

In numerous studies, the transport of guests in zeolites has been found to proceed by hopping of guests between adsorption sites. Spectroscopic studies [2,3,11–15] assisted by molecular dynamics [9,16–20] and other [20–22] simulations have supported this picture and provided information about residency times, jump lengths, and the distribution of jump directions. It makes sense to postulate that at low temperatures, discrete jumps occur between a small number of distinct potential wells. At higher temperatures, there may be more frequent and shorter jumps with a continuous distribution of lengths, along the internal surface of the zeolite. We will test our new expression on a model where jump lengths are drawn from a continuous distribution, with rotational frequencies correlated with location in the lattice.

Methods that could be applied to go beyond the BO approximation, yet retain a classical description of the CM motions have been discussed elsewhere [23–31]. Further, there exist wholly classical methods that calculate neutron TCFs, which also rely on (classical) BO separations of molecular modes of motion [32]. Finally, there is a sizeable literature on neutron spectroscopy of quantized motions of small moieties and molecules other than hydrogen, particularly \( \text{CH}_3 \) groups and \( \text{CH}_4 \) [33–37].

2. An approximate neutron spectrum

We wish to describe the contribution of rotational and CM modes to the neutron spectrum of hydrogen in a zeolite; a mixed quantum/classical (or, at the low temperatures typical of neutron experiment, semiclassical) problem. Before we begin, we should note that (i) the argument could be generalized to the case of a neutron spectrum from any two coupled modes which correspond to such different time scales. Such issues have been treated in depth in the contexts of vibrational relaxation and the relaxation of electrons in solution [38–43]. (ii) It may be relevant, for a given application, to choose between various approximations to quantum TCFs in order to evaluate the neutron scattering function for a purely classical system [44–46]. (iii) While at room temperature and below the rotation of hydrogen must be treated with quantum mechanics, CM modes sometimes [47], but not always demand a quantum description. For example, adsorption sites in our model Na–X (Section 3) correspond to CM motions with frequencies at or above 150 cm\(^{-1}\). At the low temperatures typical of neutron experiment, the molecule is best described within our model as an oscillator in its ground state, which can occupy one of two low-lying rotational states. The BO approximation is applied to this system based on the slight degree to which the rotational state varies over the distance subtended by the ground state vibrational wave function. In a different \( \text{H}_2 \)/zeolite system, the approximation is justified based on fast rotational and slow vibrational CM timescales [48].

There are a number of derivations in the literature which give the pure rotational spectrum for a rigid-rotor model of \( \text{H}_2 \) [49–54]. We will use a notation which is similar to that of Ref. [54]. Consider the “master equation” for the neutron scattering function [55,56] \( S(q, \omega) \):

\[
S(q, \omega) = \sum_{x, \beta} \rho_x |\langle x | \hat{\beta}_q | \beta \rangle|^2 \delta(\omega_{x\beta} - \omega),
\]  

(1)
where
\[
\hat{b}_q = \sum_{j=1}^{n} B_j e^{i q r_j}, \quad B_j = b_{\text{coh}} + b_{\text{inc}} s_N \cdot s_j \approx b_{\text{inc}} s_N \cdot s_j.
\] (2)

In Eq. (2), \( r_j \) indexes the position of the \( j \)th hydrogen nucleus (proton), and spins \( s_N \) and \( s_j \) represent the incident neutron and the proton. (These are operators, but we will suppress operator notation where it is self-evident.) The incoherent scattering amplitude, \( b_{\text{inc}} \) is presumed to dominate the scattering function for hydrogen [56]. The states \( |\alpha\rangle \) and \( |\beta\rangle \) in Eq. (1) can be interpreted as initial and final states of the system of \( n/2 \) hydrogen molecules plus neutron; which include quantum numbers corresponding to the following degrees of freedom for each molecule: CM position \( R_j \), orientation of bond axis \( \Omega_j \), and spin of the two nuclei on each molecule \( s_{j1}, s_{j2} \). \( \rho_a \) is the density of initial states.

Next, we change to CM, \( R_j \), and relative, \( \Omega_j, d \), coordinates in Eq. (2). (\( d \) is the intramolecular bond length.) We define
\[
M^{a\beta} = \sum_{j=1}^{n/2} \sum_{\nu=1}^2 e^{i q R_j} (\alpha | V_j | \beta),
\] (3)

where
\[
V_{j1} = b_{\text{inc}} s_N \cdot s_j \cos(q \cdot \Omega_j d/2), \quad V_{j2} = i b_{\text{inc}} s_N \cdot \Sigma_j \sin(q \cdot \Omega_j d/2).
\] (4)

(From here on, we will omit the factor of \( b_{\text{inc}} \) from written formulae, since only incoherent scattering will be assumed relevant.) In the above equation, \( S_j = s_{j1} + s_{j2} \) while \( \Sigma_j = s_{j1} - s_{j2} \). With the definitions of Eqs. (3) and (4), Eq. (1) becomes
\[
S(q, \omega) = \sum_{a, \beta} \rho_a |M^{a\beta}|^2 \delta(\omega_{a\beta} - \omega).
\] (5)

Now, we invoke the familiar approximation; that each eigenstate of the rotor can be approximated as a product of BO states:
\[ \langle R, \Omega | \phi_{k,l} \rangle \equiv \Psi_{k,l}(R, \Omega) \approx \phi^k_R(\Omega) \chi^l(R). \] (6)

(Derivations of the BO approximation appear in standard texts in physical chemistry.) We model the Hamiltonian for hydrogen within a zeolite as [48]
\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V_0(R) - \frac{\hbar^2}{2I} \hat{L}^2 + V_{\Omega}(\Omega) \equiv \hat{H}_0(R) + \hat{H}_{\Omega}(\Omega). \] (7)

The first and last two terms constitute \( \hat{H}_0 \) and \( \hat{H}_{\Omega} \), respectively. \( \hat{L} \) is the angular momentum operator for a rigid, linear rotor and \( I \), the moment of inertia. \( \nabla \) denotes differentiation with respect to the CM coordinate \( R \). We assume (as calculations in Ref. [48] show for \( \text{H}_2 \) within Na–A) that the adiabatic rotational eigenstates \( \phi^k_R \equiv |k; R \rangle \) depend weakly on \( R \) over short distances in the zeolite. Under these circumstances, the CM and rotational states evolve according to
\[ \hat{H}_{\Omega} \phi^k_R = \epsilon^k_R \phi^k_R, \] (8)

\[ i\hbar \frac{\partial \chi^l}{\partial t} = \hat{H}_{\text{BO}} \chi^l \quad \text{with} \quad \hat{H}_{\text{BO}} = -\frac{\hbar^2}{2m} \nabla^2 + V_0(R) + \epsilon^k_R. \] (9)

Eigenvalues of Eq. (9), \( \hbar \omega_k \), are the BO approximations to the energies of the system.
This approximation is particularly vulnerable to breakdown in the case of near-degeneracy of rotational levels. This case is explored in detail in the work of Refs. [57–59]. In the analogous electronic problem this results in nonadiabatic transitions between electronic states. Such degeneracy is not anticipated for H$_2$ in zeolites at low temperatures, where strong adsorption breaks the degeneracy of low-lying excited states.

We now expand the state notation, writing explicitly that $|\Omega\rangle = |i\rangle|i, i; R\rangle$, $|\beta\rangle = |f\rangle|f, f; R\rangle$, where $|i\rangle$ denotes an initial CM BO state, and $|i, i; R\rangle$ denotes the corresponding initial rotational state coupled to the nuclear spin state (as symmetry demands); and similarly for the final states. The different ket shapes provide a needed distinction between CM and rotational states. While later it will be important to add a nuclear spin state (as symmetry demands); and similarly for the final states. The different ket shapes in the notation $|\Omega\rangle = |i\rangle|i, i; R\rangle$ are $|i\rangle$ and $|i, i; R\rangle$. For example, in our notation: $\psi_{k/\ell}(R, \Omega) = \langle R|k, l\rangle\langle\Omega|i_k, i_l; R\rangle$.

Eq. (5) now becomes

$$S(q, \omega) = \sum_{i_k, f, f_k} \rho_{i_k} \sum_{j, f} n/2 \sum_{j, f} (|i\rangle|e^{i q R}|f\rangle|e^{-i q R}|i\rangle) \langle i, i, f; R\rangle \langle f, f, f; R\rangle \delta(\omega_{i f} - \omega).$$

Note that the $\omega_{i f}$ in Eq. (10) are now considered to be the difference in BO energies between the initial and final BO states. Under the simplifying assumption that the CM degrees of freedom are uncorrelated for different H$_2$ molecules, the sum over $j, f$ in Eq. (10) will vanish unless $j = f$. However, the dynamics of CM and rotations of an individual molecule remain coupled.

It is a common approximation in the condensed matter literature [11,60–62] to assume that the TCFs describing these two motions are independent, so that one can write the incoherent scattering function as a convolution of scattering functions from the two independent motions:

$$S(q, \omega) = S_R(q, \omega) * S_\phi(q, \omega),$$

with

$$S_R(q, \omega) = \sum_{i, f} n/2 \sum_{j, f} (|i\rangle|e^{i q R}|f\rangle|e^{-i q R}|i\rangle) \delta(\omega_{i f} - \omega),$$

where $i_k = f_k$, which is to say that the CM spectrum does not include rotational lines. These arise in the second term of Eq. (11), the so-called “stick” spectrum (appropriate for a “static” CM limit), which comes from rotational transitions, unBroadened by the CM motions:

$$S_\phi = \int dR \rho_{R} \sum_{i, f, f_k} \rho_{i_k} \sum_{j, f} n/2 \sum_{j, f} (|i, i, f; R\rangle|f, f, f; R\rangle \langle f, f, f; R\rangle|e^{-i q R}|i, i, f; R\rangle \delta(\omega_{i f} - \omega).$$

A few more steps allow Eq. (13) to be readily evaluated. These are contained in Appendix A. The final expression, Eq. (A.4), is a limit of small $q$, in which averaging has been done over initial and final spin states, and over orientations in space. This expression forms the basis for the calculated spectrum of H$_2$ in Na–A in Ref. [10], and for the calculation on Na–X in Section 3.

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1 For a study of methane in zeolite A, hydrogen in mordenite and liquid deuterium see Refs. [60–62].
3. Application: hydrogen in faujasite

Faujasite has an open pore structure, with a cubic unit cell of length 25 Å. The “supercage” which is surrounded by smaller “sodalite” cages (Fig. 1) can be accessed through a 12-membered oxygen ring with a free diameter of about 7.4 Å. The unit cell contains 192 Si and Al atoms; zeolites with varying Si/Al ratios from 1 to greater than 75 have been synthesized. Synthetic faujasites, in cation-substituted, activated form, are commonly-used industrial catalysts for various hydrocarbon transformations [63]. Zeolite Y is still the most widely used catalyst for cracking organics in crude oil [64]. While the faujasite aperture diameter is rather large (approximately 8 Å) to make them effective at separating small molecules [65], separation of various aromatics from air and O₂ production have been achieved in zeolite X [64]. Not only have cation-exchanged zeolites X (Si/Al < 1.5) and Y (Si/Al > 1.5) a demonstrated utility in a number of important separation and catalytic processes [66,67]; but they have recently been used to form materials with novel optical properties [68].

A number of IR and neutron scattering studies have looked at H₂ within zeolites X and Y. The number and preferred location of cations varies with Si/Al content, so results can be quite diverse for faujasite species. For example, from X-ray and neutron diffraction data [69] one expects that cationic sites of type S₁, S₁I and S₁II will be occupied in zeolite Na–X; the last two exist within the supercage where H₂ will be preferentially adsorbed. While in Na–Y (Si/Al = 3) there are no occupied S₁II sites and H₂ adsorption at 77 K in the supercage is associated with adsorption at S₁I sites [70], adsorption takes place at both S₁I and S₁II in Na–X, according to an IR study [71].

Neutron scattering studies have presented a somewhat different picture. While H₂ is thought to be able to enter sodalite cages in zeolite Li–X, it is unable to enter these in Na–X under the conditions of the neutron scattering study of Ref. [5], and is thought to be unable to enter the sodalite cages in either the Li–X or Na–X in the FT-IR study of Refs. [72,73]. In Na–X, a neutron spectral peak at 18 cm⁻¹ is attributed to hindered rotation at an adsorption site in the supercage, S₁II. There is another peak at 47 cm⁻¹ which is, based on experiments with HD and the isotope effect [74], assigned to a CM translational mode. In Li–X, two peaks

Fig. 1. Fragment of the faujasite crystal lattice. Sites S₁ (within hexagonal prisms), S₁I (near hexagonal faces) and S₁II (near square faces) are occupied by Na cations in our model.
at 15 and 38 cm\(^{-1}\) are attributed to rotational transitions (the first possibly in the sodalite cage, so perhaps associated with the S\(_1\) site). These studies were performed on 13X, with Si/Al = 1.3.

As a first simulation of faujasite with our technique, we have chosen the most symmetric possible choice of atomic locations, taking Si/Al = 1.0, so that Si and Al atoms (T atoms) alternate in a lattice with space group symmetry Fd\(\overline{3}\). We have placed 96 Na cations with 48 at position S\(_{III}\), 32 at S\(_{II}\) and 16 at S\(_{I}\), as was used for example for a study on the interaction of benzene with faujasite in Ref. [75]. Our methods have been described in detail elsewhere [48], and we just sketch them here. Our simulation does not distinguish between Si and Al, and host atom–guest interactions take place only between zeolitic ions and the H\(_2\) guest. The unit cell length was taken as 25.52 \(\text{Å}\). The potential energy for the H\(_2\) guest is a sum of terms:

\[
U = U_{\text{disp}} + U_{\text{rep}} + U_{\text{pol}} + U_{\text{multipole}}.
\]  

A number of studies have evaluated the effective charges that should be assigned to host atoms. In our model, where all atoms of a species are treated identically, there is only one free parameter, the charge on Na. Ab initio simulations and fits to experiment data agree that in faujasite (and in contrast to zeolite A) there is little charge transfer between Na and the rest of the zeolite structure [76,77]. Thus, a charge of 1.0\(e\) was chosen for Na, as in a number of previous simulations of guests in faujasite [78–82], implying that the charge on O is \(-1/4e\) for zeolite Na–X.

We solve the Schrodinger equation (8) for the rotational state of hydrogen:

\[
\left(-\frac{\hbar^2}{2I} \hat{L}^2 + V_R(\Omega)\right)\phi^k_R = \epsilon^k_{\text{eff}} \phi^k_R
\]  

at a given CM position \(R\), where \(V_R\) consists of the last three terms of Eq. (14). The solution is achieved with a block Lanczos algorithm [83,84]. The algorithm yields energy levels \(\epsilon^k_R\) and also eigenfunctions, \(\phi^k_R(\Omega)\), where \(\Omega\) is chosen on a discrete (32 \(\times\) 32) angular grid for \(k = 1, \ldots, N_{\text{states}}\). In the current study, we report on \(N_{\text{states}} = 9\) rotational eigenstates. The internuclear distance \(d_0\), in terms of which \(I = m/2d_0^2\), is taken as 0.77 \(\text{Å}\). We then use a simulated annealing technique to identify locations \(R\) at which \(V_0(R) + \epsilon^0_R \equiv U_{\text{eff}}(R)\) is minimized; which we interpret as regions of adsorption at low temperature. We place the model H\(_2\) molecule within the supercage at room temperature and systematically lower the temperature to a final value; repeating the procedure with various starting locations. At each temperature, H\(_2\) is allowed to perform a random walk, with a standard Monte Carlo (MC) acceptance/rejection procedure [48] guiding its steps. At the final temperature of 50 K, we are able to identify regions of strong local adsorption in model Na–X, and to use a cartesian grid to search further for the most favorable adsorption locations. We then evaluate the matrix elements of Eq. (A.4) at these locations.

For our model, only one unique crystallographic adsorption site was found; to that site corresponds a single set of rotational transition energies. For this system, the convolution approximation of Eqs. (11)–(13) will capture the features of the neutron spectrum. The site is of 96\(i\) symmetry, located at \(x = y = 0.32, z = 0.19\) within the primitive unit cell. Applying the symmetry operations produces a set of physical adsorption sites which can be related to the cationic positions. Fig. 2a is a view of the Na–X framework looking down a 2-fold axis at a Na\(_{III}\) cation. (O atoms are not shown.) Interestingly, even in this open zeolite structure, the binding is not to a single cation. The small squares mark the locations of two equivalent adsorption sites in the neighborhood of the closest cation, Na\(_{III}\). At each of these minima, the Na\(_{III}\) is at a distance of approximately 2.4 \(\text{Å}\). Each of these sites is not too far, 3.6 \(\text{Å}\) distant, from the nearest Na\(_{II}\) cation. Fig. 2b is a view looking down a 3-fold axis, showing how three adsorption sites are coordinated with this cation. The closest Na\(_{I}\) cation is 5.4 \(\text{Å}\) distant; the next-closest Na\(_{II}\) cations (a pair) are also 5.4 \(\text{Å}\) distant, and the next-closest Na\(_{III}\) cations (a pair) are 6.8 \(\text{Å}\) distant. All other cations are at a distance greater than 7 \(\text{Å}\). The multiplicity of equivalent adsorption sites near the cations (e.g., one can think of there being two sites quite near Na\(_{III}\), or alternatively, three sites fairly near Na\(_{III}\)) may be related to...
the speculation that, based on co-adsorption measurements with $\text{N}_2$ [74], $\text{H}_2$ is delocalized in its adsorption about the cationic site (because the rotational band is unaffected when cationic coverage is increased).

While we have not performed a full mapping of the effective potential energy surface, $U_{\text{eff}}(\mathbf{r})$, we have estimated the Hessian matrix elements: $\partial U_{\text{eff}}/\partial x_i \partial x_j$ using a finite-difference expression centered on one of the minima. Diagonalization allows us to estimate the normal mode frequencies for harmonic motion in these wells. These frequencies turn out to be roughly 350, 250, and 150 cm$^{-1}$. These might be compared

Fig. 2. Two adsorption sites (\(\square\)) shown in the neighborhood of (a) an $\text{S}_{\text{III}}$ site and (b) $\text{S}_{\text{II}}$ site. White spheres are Na cations; balls-and-sticks represent aluminosilicate framework.
with a 200 cm\(^{-1}\) mode calculated for H\(_2\) in Na–A [85], or a 190 cm\(^{-1}\) perpendicular mode (near a Ca ion) calculated for H\(_2\) in CaNa–A [86]; while in experiment Eckert and coworkers [87] find a CM mode at 141 cm\(^{-1}\) CaNa–A. Our normal mode frequencies suggest that, at temperatures typical of IR and neutron scattering experiments, the CM does not undergo classical motion. Rather, it is appropriate to view the CM in a well-localized (a fraction of an A in extent) vibrational ground state. More information about the potential surface in the vicinity of the wells would give us information about the rate of transport between adjacent wells. It would also illuminate the question of why diffusion in Na–X appears to be jump-like at room temperature (see below). Over the extent of the ground state, harmonic, wave function, we find that the BO state \(\ket{k; R}\) varies very little. For example \(\ket{\langle k; R | k'; R' \rangle} \ll 1\) for \(k \neq k'\) and \(R, R'\) within 1/2 A of the well center. So Eqs. (8) and (9) would seem to be appropriate over the extent of a single well, with \(e_k^R\) fairly independent of \(R\) within that well.

Hopping between these wells would be detectable by neutron experiment with momentum transfers on the order of A\(^{-1}\). One might posit that H\(_2\) molecules are able to jump between equivalent sites as described above. The shortest jump will be about 3.9 A in length, between two locations equidistant from the same Na\(_{\text{III}}\) cation as in Fig. 2a. The next shortest jump will be about 4.9 A in length, between two of the three locations equidistant from the same Na\(_{\text{II}}\) cation as in Fig. 2b. However, neither of these processes will lead to bulk transport; H\(_2\) will not leave its original supercage. The next-closest jump is of length 5.5 A, and will involve the H\(_2\) crossing the 12-windows that bound supercages. These window-crossings can be visualized from Fig. 3. (Note that the square faces of the sodalite cages correspond to the S\(_{\text{II}}\) sites. A square face shares two sides with two hexagons, each of which correspond to an S\(_{\text{II}}\) site, but in separate cages.)

Other elementary jump processes might occur, though as a rule one would expect that distant jumps are suppressed by the kinetics of this activated diffusion process. Neutron experiments involving wave vectors of magnitude an A\(^{-1}\) or less will probe motions on length scales of several A or more; such experiments were performed by Jobic and coworkers [4,11]. PFG NMR and QENS techniques agreed on the diffusivity of H\(_2\) in Na–X, and the concentration dependence suggests that the molecules do not diffuse in a gas-like manner, but rather interact with the cations. The \(q\)-dependence of the widths of the QENS peaks suggest a
jump diffusion process. At $T = 100$ K, the jump lengths are predicted to best fit a single-jump-length model if the length is 5.9 A, and the typical time between jumps is 9 ps [11]. Without a detailed calculation of the potential energy along the diffusion path, and an understanding of the barriers at the transition states between equivalent wells, we cannot predict which basic jumps will contribute to bulk diffusion, and what rate should be associated with those jumps. However, the experimental value of 5.9 A is rather close to our calculated distance of 5.5 A, for the shortest jumps that will contribute to bulk transport.

In order to construct the neutron spectrum, we require the rotational states. The map of the rotational potential $V_R\left(\Omega\right)$ in Fig. 4 shows that at the adsorption site, there is a typical in- and out-of-plane hindering form [10], with a small in-plane barrier of approximately 1B, where $B$ is the rotational constant of H$_2$ ($B = 57$ cm$^{-1}$ for our model.) At low temperature, one is only concerned with the ground-to-first-excited, or tunnel-splitting state. We find that this occurs at $\omega_R^{01} = 46$ cm$^{-1}$ where R is the minimum of the adsorption well. (The zero point motion is calculated to produce a range of $\omega_R^{01}$ values of several cm$^{-1}$. The shape of the peak is thus determined by a combination of zero point motion and hopping dynamics.)

Our calculated tunnel-splitting frequency is much higher than the $\omega_R^{01} = 18$ cm$^{-1}$ attributed to this transition in neutron experiment. It would be important to study the effect of changing the cationic distribution in the model, and in particular, distributing cations in a way which is realistically typical of zeolite 13X. A model like ours, which distributes cations in order to fully occupy sites S$_1$, S$_II$ and S$_III$ seems incapable of producing the strong hindering environment within the supercage that the neutron experiment would indicate exists. For example, a recent study by our group [25] found that in Na–A two close cations, Na$_{II}$ and Na$_{III}$, created a region of adsorption in which the in-plane barrier exceeded 8B. This resulted in a tunnel-splitting frequency $\omega_R^{01} = 14$ cm$^{-1}$.

In Fig. 5, we show the neutron scattering function, $S(q, \omega)$, using the value of $\omega_R^{01}$ given above, and resulting from a simulation in which the adsorption sites in Na–X form the lattice on which CM hopping takes place. It uses $q = 0.5$ A$^{-1}$, a value which probes motions on the length scale of several A. We allow hopping between nearby sites, both 3.9 and 4.9 A distant, to occur with probability determined by Poisson statistics with a mean time of $\tau_1$. Jumps of length 3.9 A merely allow the guest to move back and forth in the neighborhood of a single Na$_{III}$ ion, but the two types of hop together allow the guest to diffuse within a single supercage, among 12 adsorption sites. Further, with a mean residence time of $\tau_2$, the molecule may jump from its current site to a neighboring site which is 5.5 A distant, and which resides in a new supercage.
Fig. 5, shows data with $\tau_1 = 5$ ps, $\tau_2 = 10$ ps (to correspond roughly with the experimental value). Though these parameters are ad hoc, the model has some features that may be relevant to experiment. First, even in the case that there is only one, crystallographically unique, adsorption site, jumps that contribute to bulk transport are of more than one length. In general, the timescale for jumps of different lengths is different. If $\tau_1 \ll \tau_2$ then there will be a short timescale on which the motion of H$_2$ is bounded, and limited to a single supercage. (We should emphasize that this caging does not occur, as in some other zeolitic systems, because there is an energetic or steric barrier in the doorways limiting cage-to-cage transport. Rather, it comes from the placement of adsorption sites with respect to cage boundaries, and the assumption that kinetics disfavors longer jumps in favor of shorter ones.) On the longer timescale, the rate of diffusion will be slower than at short times, but will lead to bulk transport of H$_2$. The morphology of this spectrum was noted to vary with $\tau_1/\tau_2$. For the values chosen in Fig. 5, an effective diffusion constant is determined from $\langle x^2(t) \rangle = 2Dt$ to be $D \approx 1$ Å$^2$ ps$^{-1}$. A fit to a Lorentzian form yields a HWHM of 1.2 cm$^{-1}$, less than the value expected from Fickian diffusion (and no greater than the width from zero point motion, though this might change upon variation of rate parameters in the jump model).

4. Neutron spectrum for coupled motions

For hosts with various unique adsorption sites, Eq. (11) might not describe the neutron spectrum of adsorbed H$_2$; to show this, we turn to the case of coupled rotational and CM dynamics. Looking at the form of Eq. (1), we make the standard observation that this is the Fourier transform of a TCF [56]:

$$S(q, \omega) = \int C(q, t)e^{-i\omega t}dt, \quad C(q, t) \equiv \sum_x \rho_x(z) e^{iHt}b_q^\dagger e^{-iHt}b_q^\dagger(z).$$  \hspace{1cm} (16)

(Henceforth, we set $\hbar = 1$.) C is itself the spatial Fourier transform of the van Hove self-correlation function [88].

\footnote{For example, if intercage jumps are suppressed entirely, the peak was noted to be narrow, but centered on a broad, shallow background feature that arises from diffusion within the cage.}
After a number of manipulations which are given in Appendix B, we arrive at
\[
C(q, t) = \frac{n}{2} \left[ \sum_{\text{ortho}_{i_{R}j_{k}}} \rho_{ij_{k}} \sum_{f_{k}} \exp \left( i \hat{H}^{\text{orb}}_{\text{BO}, f_{k}} t \right) \exp \left( i q \cdot \hat{R} \right) V^{f_{k}/i_{R}}_{1, \text{R}} \exp \left( - i \hat{H}^{\text{orb}}_{\text{BO}, f_{k}} t \right) \exp \left( - i q \cdot \hat{R} \right) V^{i_{R}/f_{k}}_{2, \text{R}} \exp \left( i L \cdot \hat{R} \right) \right] .
\]

In order to make this form useful in a calculation, we might introduce a Trotter approximation:
\[
e^{i H_{0} t} \approx e^{-i H_{0} t/2} e^{-i \hat{W} t/2} , \quad \text{where} \quad \hat{H}_{0} = \hat{H}^{\text{orb}}_{\text{BO}} - \hat{W} ,
\]
and where the correction in Eq. (18) is on the order of \( t^{2} [\hat{H}_{0}, \hat{W}] \). One might obtain better results still with a symmetric Trotter approximation:
\[
e^{i H_{0} t} \approx \exp \left( -i H_{0} t/2 \right) e^{-i \hat{W} t/2} ,
\]
where the correction in Eq. (19) is on the order of \( t [\hat{H}_{0}, \hat{W}] \). (Short-time approximations beyond these two involve higher-order TCFs; as in the hierarchy of electronic state correlation functions in Ref. [38], where these are identified with multi-photon processes.) At low temperature, occupied BO rotational states \( |k; R \rangle \) will be predominantly the pair of tunnel-splitting states, \(|0; R \rangle \) and \(|1; R \rangle \). Typical values for the tunnel-splitting energy for H\(_{2}\) adsorbed in zeolites are shown by neutron scattering measurements to fall in the range \( \omega_{1} - \omega_{0} \approx 15-35 \text{ cm}^{-1} \) (depending on the host solid structure, ionic content, and so on) [74,87,89,90]. The two states have orbitals with similar morphologies [10]. Making the choice
\[
\hat{W} = \frac{\epsilon_{k}}{R} - \frac{\epsilon_{0}}{R}
\]
implies a dynamics where the CM propagates on the \( k = 0 \) rotational state surface. When the in-plane hindering potential is strong, as is the case for H\(_{2}\) adsorbed in a variety of zeolites, and the excited and ground state orbitals have such similar angular probability densities, we expect the CM dynamics to be quite similar to the dynamics one would observe on the excited state potential surface,\(^3\) and indeed on a surface on which nonadiabatic transitions between rotational states are allowed.

For compactness, we write Eq. (17) in a slightly more condensed form:
\[
C(q, t) = \sum_{n=1}^{3} C_{n}(q, t)
\]
with
\[
C_{n}(q, t) = \rho_{n} \exp \left( i q \cdot \hat{R} \right) M_{n, \text{R}} \exp \left( - i \hat{H}^{\text{orb}}_{\text{BO}, f_{k}} t \right) \exp \left( - i q \cdot \hat{R} \right) M_{n, \text{R}} .
\]

\(^3\) Propagation on either the ortho- or para-H\(_{2}\) surfaces alone in zeolite Na–A at 100 K lead to similar CM MC trajectories, and statistically indistinguishable separation factors and neutron spectra. (A.L.R. Bug, unpublished result).
where
\[ c_1 = n/4, \quad c_2 = n/8, \quad c_3 = 3n/8, \quad M^{f/k\downarrow}_{1,R} = V^{f/k\downarrow}_{1,R}, \quad M^{f/k\downarrow}_{2,R} = M^{f/k\downarrow}_{3,R} = V^{f/k\downarrow}_{2,R}, \] (23)
and the restrictions on the sums in Eq. (22) correspond to the restrictions to ortho or para states in Eq. (17). Note that the density of initial states is actually an operator which involves \( \hat{\mathbf{R}}; \rho_{ik,l} | i_k \rangle | l_l \rangle \equiv (i_k l_l) | e^{-\beta H_0} | i_k l_l \rangle \), where \( \beta \) is the inverse temperature. We will incorporate this notation in what follows.

If we apply the (symmetrized) Trotter approximation, Eq. (19) together with Eq. (20), we obtain
\[ C_n(q, t) = c_n \sum_{l_k} \sum_{i_k} i_k | \hat{\rho}_0 \exp \left( i \hat{H}_0 t \right) \exp \left( \left( \epsilon_{i_k, R} - \epsilon_{l_k, R} \right) t / 2 \right) \exp \left( i \mathbf{q} \cdot \hat{\mathbf{R}} \right) M^{f/k\downarrow}_{n, R(t)} | l_k l_l \rangle \times \exp \left( - i \hat{H}_0 t \right) \exp \left( \left( \epsilon_{l_k, R} - \epsilon_{l_l, R} \right) t / 2 \right) \exp \left( - i \mathbf{q} \cdot \hat{\mathbf{R}} \right) M^{f/k\downarrow}_{n, R(0)} | i_k l_l \rangle. \] (24)

In Eq. (24), we might make a Trotter approximation to the thermal weight:
\[ \hat{\rho}_0 \approx e^{-\beta \hat{H}_0} e^{-\beta \hat{H}_0} \] (25)
or alternatively
\[ \hat{\rho}_0 \approx e^{-\beta \hat{H}_0 / 2} e^{-\beta \hat{H}_0 / 2}. \] (26)

In the model calculations in Section 5, spectral lines arise from a single tunnel-splitting transition at each location, \( \mathbf{R} \), so this distinction will not enter into the calculation.

How does Eq. (24) help us calculate the neutron spectrum? In this form, the Hamiltonian seen by the CM motion is free from rotational indices. If we make the ansatz that any function, \( F(\mathbf{R}) \), of the CM operator propagates in time according to
\[ F(\hat{\mathbf{R}}(t)) = e^{i \hat{H}_0 t} F(\hat{\mathbf{R}}) e^{-i \hat{H}_0 t}, \] (27)
then our expression for the neutron TCF \( C_n \) is
\[ C_n(q, t) = c_n \sum_{l_k} \sum_{i_k} i_k | \hat{\rho}_0 \exp \left( i \left( \epsilon_{l_k, R(t)} - \epsilon_{l_l, R(t)} \right) t / 2 \right) \exp \left( i \mathbf{q} \cdot \hat{\mathbf{R}}(t) \right) M^{f/k\downarrow}_{n, R(t)} \exp \left( - i \mathbf{q} \cdot \hat{\mathbf{R}}(0) \right) M^{f/k\downarrow}_{n, R(t)} | i_k l_l \rangle \] (28)
or
\[ C_n(q, t) = c_n \sum_{l_k} \sum_{i_k} i_k | \hat{\rho}_0 \exp \left( i \left( \epsilon_{l_k, R(0)} - \epsilon_{l_l, R(0)} \right) t / 2 \right) \exp \left( i \mathbf{q} \cdot \hat{\mathbf{R}}(0) \right) M^{f/k\downarrow}_{n, R(t)} \times \exp \left( i \left( \epsilon_{l_k, R(0)} - \epsilon_{l_l, R(0)} \right) t / 2 \right) \exp \left( - i \mathbf{q} \cdot \hat{\mathbf{R}}(0) \right) M^{f/k\downarrow}_{n, R(0)} | i_k l_l \rangle \] (29)
depending on whether the naive Trotter (Eq. (18)) or symmetric Trotter (Eq. (19)) approximation is used. Let us say that, for example, we wish to specialize to the classical limit of CM motion. That is, we insert a complete set of \( \mathbf{R} \) states in Eq. (29) and then argue that \( \mathbf{R}(t) \) is a classical variable, precisely determined by the initial conditions \( \mathbf{R}(0) \), \( \mathbf{R}(0) \) under the action of a classical Hamiltonian \( H_0 \). A simulation which in-

\[ ^4 \text{The symmetric approximation (26) will produce a smaller error. Both approximations allow propagation on a single, } \hat{H}_0 \text{ surface. Using Eq. (25), the two operators that participate in the correlation sum differ by a factor of } e^{-\beta \hat{H}_0} \text{ while with Eq. (26), the thermal weights enter equivalently into the two operators.} \]
includes a method to evaluate the rotational energies $\epsilon_{R(0)}^0$ and $\epsilon_{R(t)}^1$ can produce the trajectory $R(t)$. Then one would apply the following classical limiting form of Eqs. (28) and (29).

$$C_n(q, t) = c_n \int \int dR(0) d\dot{R}(0) \rho_{R(0), \dot{R}(0)} \sum_{i_k} \rho_{i_k} \sum_{f_k} \exp(i\Phi(t)) \exp(iq \cdot R(t)) \times \exp(-iq \cdot R(0)) M_{nR(t)}^{i_k f_k} M_{nR(0)}^{f_k i_k}, \tag{30}$$

where

$$\Phi(t) = \exp\left(i (\omega_{R(0)}^{i_k f_k}) t\right), \quad \rho_{i_k} = \exp\left(-\beta \omega_{R(0)}^{i_k i_k}\right) \tag{31}$$

from Eq. (28) and

$$\Phi(t) = \exp\left(i (\omega_{R(t)}^{i_k f_k} + \omega_{R(0)}^{i_k f_k}) t/2\right), \quad \rho_{i_k} = \exp\left(-\beta (\omega_{R(0)}^{i_k i_k} + \omega_{R(t)}^{i_k i_k})/2\right) \tag{32}$$

from Eq. (29). In Eq. (30), the frequency $\omega_{R}^{i_k i_k} = \epsilon_{R(0)}^{i_k} - \epsilon_{R(t)}^{i_k}$ is the energy difference between two rotational states at a fixed value of $R$. Substituting Eq. (30) into Eq. (21), and taking the Fourier transform, one arrives at an approximation to the scattering function, $S(q, \omega_0)$. Our argument has depended both on the validity of both the BO and Trotter limits, and for example, will break down if correlations exist at times so long that the Trotter approximation fails. (Of course, if the CM motions are truly described by the extreme classical limit, then the Trotter approximation will not fail in this way.)

The formula Eq. (30) is interesting and convenient to simulate for a couple of reasons. It involves a classical trajectory, evolving on a single rotational energy surface. It incorporates details of the local, CM environment into the rotational spectrum in a way which goes beyond the convolution approximation. And it has as limits the case of inhomogeneous broadening and motional narrowing. In the former, the CM environment decorrelates so slowly that all broadening arises from static disorder; this is the stick spectrum limit of Eq. (13). The motional narrowing limit is one in which fast CM dynamics will result in lines that are narrowed and merged into an averaged frequency [91].

Of course, taking the classical limit in the standard way suffers from well understood deficiencies that have been studied in the past [45,46]; the scattering function does not properly fulfill detailed balance, and recoil effects are neglected. Quantum correction factors to the analogous classical correlation functions have been evaluated for several exactly solvable models [44]. Neglect of recoil is probably quite a reasonable approximation for low wave number scattering from H$_2$ interacting with the zeolite lattice [92]. Based on the extensive theoretical literature on semiclassical approximations to quantum TCFs, we should note that (i) the generation of the correct semiclassical limit of $C(q, t)$ in Eq. (30) is subtle and, based on the work of Refs. [45,46], would require more than a classical MD simulation of the CM of H$_2$. (ii) While fully quantum TCFs are uniquely defined by the Hamiltonian, a specific choice of the hamiltonian on which $R(t)$ propagates will yield a specific, and nonunique classical TCF when the limit is taken in the manner of Eq. (30) [43]. However, in the case of small differences in the CM potential energy surfaces corresponding to different adiabatic rotational states, we expect the classical limit to become insensitive to this choice. (iii) Much work has been done on obtaining semiclassical TCFs [23–31,43,45,46,93–95]. These methods typically require one to enumerate all paths which minimize the associated classical action. Nevertheless, for any given prescription for evaluating a QT CF like Eq. (A.4), there is a classical limit, like Eq. (30). This can be obtained in the $\hbar \to 0$ limit by, for example, expanding the action difference between "forward" and "backward" stationary paths and using well-known properties of the Wigner distribution function [94].

Bearing in mind that algorithms which attempt to simulate mixed quantum-classical dynamics must be chosen with care [95], one may use Eq. (30) together with an appropriate simulation scheme to effectively study neutron scattering, within our approximations and with well understood error. The work of Coker,
and others [96–100] demonstrate methods that one might use to calculate Eq. (30), and to generate a classical CM trajectory of H₂, in the “zero back reaction” limit (in our case, corresponding to the assumption that the CM propagates on a rotational surface independent of rotational state). These studies have calculated rotational Raman spectra in both the adiabatic and nonadiabatic limits. Our BO TCF is similar in spirit to the adiabatic TCF in these papers, but there are significant differences (beyond the basic fact that the operators to be time correlated, $A$ and $B$, are polarizability anisotropy operators in the application to Raman spectroscopy). The adiabatic approximation in Refs. [96–100] is based on matrix elements of operators that change slowly with CM coordinates. This is clearly not the case in the neutron scattering application, where $e^{i\mathbf{q} \cdot \mathbf{R}}$ is one term in these operators. Thus for example, the classical adiabatic limit in the Raman application involves $A(\mathbf{R}(0))B(\mathbf{R}(0))$ whereas ours involves $A(\mathbf{R}(t))B(\mathbf{R}(0))$. The phase factor, $\Phi(t)$ of our Eqs. (31) and (32) also has a different analog in the Raman work, and involves an integral over the time of the trajectory. Instead, our symmetric Trotter approximation Eq. (32) features a simple average using the endpoints of that integral. Finally, in order to enhance the symmetry of the two operators to be correlated, the thermal weighting is distributed evenly in Eq. (32) between weights from initial and final rotational states, whereas in most TCF treatments it depends on initial state only. The static limit in Refs. [96,97,100] compares quite directly with $S_\Phi(q, \omega)$ of Eq. (13), being a “histogram of instantaneous energy gaps” [96,97].

The nonadiabatic approach in Refs. [96–99] makes a dramatic improvement in agreement between Raman spectroscopic experiment and theory for H₂ both in water and in ice, as the static and adiabatic approximations give “artificial structures” in the spectrum stemming from nonexistent transitions between adiabatic states. Hunter et al. [100] note that having few apparent crossings (on the MD time scale) of adiabatic states is a measure that the adiabatic calculation is sufficient. Certainly, strongly rotationally-hindered H₂ in a zeolite is a candidate for an adiabatic treatment, since at 77 K and below it is essentially a two-level system where level crossings are forbidden by spin symmetry. At much higher temperatures, when a second and higher excited states may be populated, it may well be that nonadiabatic effects will be important in determining the neutron spectrum.

5. Application: diffusing rotor

Though the final formula Eq. (30) of Section 4 was posed for a smooth classical trajectory, it may be applied to calculate the neutron spectrum of a model rotor whose CM is engaged in a stochastic hopping process. In a zeolite, the tunnel-splitting frequency, $\omega_R(t)|^0^1$, is a periodic function of location, $\mathbf{R}(t)$. Fig. 6a is a sketch of a simple one-dimensional “host lattice” with this feature. The hydrogen molecule is modelled as a two-level system, which undergoes transitions between states $|0\rangle$ and $|1\rangle$ with transition frequency $\omega_{|0|}^I$ or alternatively between states $|0\rangle^I$ and $|1\rangle^I$ with transition frequency $\omega_{|1|}^I$; depending on the location of the CM within the lattice. Because the same features of the guest-host potential that affect the transition frequency may affect the likelihood of adsorption within a region, we allow the molecule to diffuse at different rates in the different regions. This is accomplished by varying the jump length in the two regions. (In a more realistic model of guest motion in a zeolite, one might also vary the typical time between jumps.) Naively, one might expect that a lower tunnel-splitting frequency corresponds to a region of stronger adsorption, hence slower diffusion (shorter jumps) within it. Fig. 6b shows a typical RW trajectory with this character. Symbol color denotes the transition frequency: dark grey for $\omega_{|0|}^I$ and light grey for $\omega_{|1|}^I$.

Fig. 7a compares the neutron spectra for formulae of Sections 2 and 4, for $q = 0.5$ Å. The transition energies are $\omega_{|0|}^I = 7$ cm⁻¹ and $\omega_{|1|}^I = 21$ cm⁻¹. The maximum step lengths are $l_0 = 0.5$ Å, $l_0 = 2.0$ Å in regions I and II. Steps were taken every $\Delta t = 0.2$ ps. These length and time scales yield a diffusion constant of $D = l_0^2/6\Delta t \approx 1$ Å² ps⁻¹ which is not atypical of small zeolitic guests like hydrogen, deuterium and methane. The periodicity of this lattice is chosen to be 3 Å. (The small lattice constant was chosen for
computational speed.) Filled circles in Fig. 7a are the asymmetric Trotter approximation (30) and (31); crosses are the convolution approximation (11). The trajectories used for the two approximate calculations were identical. In particular, this means that the likelihood of measuring the rotor in the state $x_{01}$ vs. the state $x_{02}$ did not differ between calculations.

Clearly, the convolution and Trotter formulae are in good agreement. Under what circumstances might we expect there to be disagreement? A relevant parameter is the ratio of the time to cross a region of given rotational frequency, $\tau_{\text{cross}}$, and the time over which the CM motions are correlated, $\tau_{\text{corr}}$. A trajectory composed of random jumps will have a neutron scattering function with a Lorentzian shape [101,102]:

$$S(q, \omega) \propto \frac{\Sigma}{\omega^2 + \Sigma^2}. \quad (33)$$

In the limit of small $q$, the width $\Sigma$ of the Lorentzian is $\Sigma = Dq^2$. $D$ is the diffusion constant, $D = d_0^2/2d\tau_0$; $\tau_0$, the typical time in between jumps, and $d$, the dimensionality. For larger $q$, the system can be probed at smaller distances, and information about the jump statistics will emerge from an analysis of the width $\Sigma$. For example, Cohen de Lara et al. [12] were able to rule out jumps which take place on a simple cubic lattice, in favor of an isotropic liquid-like jump model, in order to describe transport of $H_2$ in zeolite Na-A.

5 For larger $q$, the system can be probed at smaller distances, and information about the jump statistics will emerge from an analysis of the width $\Sigma$. For example, Cohen de Lara et al. [12] were able to rule out jumps which take place on a simple cubic lattice, in favor of an isotropic liquid-like jump model, in order to describe transport of $H_2$ in zeolite Na-A.
with the way that diffusion rate is coupled to tunnel-splitting frequency in the two different regions of Fig. 6a. The convolution approximation errors by “averaging” over the different dynamics in the different regions.

There are only slightly discernible differences between the Trotter (circles) and symmetric Trotter (diamonds) formulae in Fig. 7b. Large differences between the symmetric and asymmetric Trotter results may indicate a breakdown of the approximations employed in the derivation. However, there is another possibility, as was mentioned above in Section 4. The new expression derived using the symmetric Trotter approximation contains the motional narrowing limit [91]. That is, if the CM motion modulates the rotational frequencies quickly, lines eventually narrow and peaks begin to “grow in” at the average frequencies (apparent from the explicit form of $\Phi(t)$ in Eq. (32)). Motional narrowing will occur when the time scale, $\tau_e$, for environment-induced changes in the transition frequency, is less than the time scale associated with the static width of the distribution, $\tau_{\Delta w}$. (When these time scales are extremely different, we have the “Redfield limit” [100,103].) Fig. 8 shows an example of this behavior. The CM dynamics is as in Figs. 3 and 4a but $\omega^{01}_c$ varies sinusoidally between 1 and 3 cm\(^{-1}\) with a spatial period of 6 Å. In the data of Fig. 8, if we consider $\tau_e$ as the typical time to move across a significant portion of the spatial pattern, then $\tau_e \approx \tau_{\Delta w} \approx 20$ ps. Enhancement at the average frequency is seen with the symmetric Trotter approximation (diamonds). The inhomogeneously-broadened spectrum is represented by the convolution approximation (crosses). In
this case (not one of extreme motional narrowing) convolution agrees well with the asymmetric Trotter approximation (not shown).

6. Conclusions

In this paper, we have introduced an approximate expression for the van-Hove correlation function of molecular hydrogen. The expression allows one to follow both the CM and rotational dynamics of H₂ adsorbed in a host solid. It provides a simple, convenient way to evaluate a neutron spectrum which may be based on classical CM trajectories. We have shown how the approximation may or may not produce different results from the commonly used convolution approximation, depending on the time scales on which rotational and CM motions are correlated. Clearly, the tests we have provided are preliminary. More testing against analytically solvable models is needed to realistically evaluate the strengths and limitations of the new formalism.

We have performed a BO calculation to evaluate the tunnel-splitting energy of H₂ within an idealized model of zeolite Na–X. We have found an adsorption site nearest to S_{III}, in agreement with the conclusion of an earlier neutron scattering study; the site is further (by about 1 Å) from a nearby S_{II} site. Intercage hopping between these sites corresponds to hopping distances which are fairly close to QENS transport measurements. Given that only one adsorptive site was found for our simple Na–X model, the convolution approximation sufficed to calculate the neutron spectrum. A hopping model was devised to produce a simulated neutron spectrum.

The tunnel-splitting frequency we found at the single adsorption site was not consistent with neutron experiment. Clearly, models with other distributions of cations should be explored. Cation occupation has been shown to occur at variants: S_I, S_{II}, and S_{III} of the sites considered in our model. (Of these, site S_{III} is also in the supercage.) A distribution with fewer S_{III} ions with S_{II} type positions, and more S_I ions, would most closely resemble experiment for this type of Na–X [79,104]. Moreover, there is more than one unique position for some of these additional sites [69,78,79]. For each distribution of cations considered, one could calculate the rate at which basic jumps occur between adsorption minima via transition state theory [20,105–110]; leading to an elementary hopping model which could be used with the BO theory. As an

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6 For quantum transition state theory applied to hopping on surfaces and in solids, see e.g. Ref. [105].
alternative to a hopping model, a mixed quantum-classical calculation of the full dynamics might be performed. In either case, if the conditions of the BO approximation are found to be good, the approximation may be combined with dynamical information in order to calculate a neutron spectrum involving both translational and rotational motion of a H₂ guest.

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Appendix A

Eq. (13) can be summed over initial and final spin states. As a result terms with \( m \) vanish, and we arrive at

\[
S_\phi(q, \omega) = \sum_{j=1}^{n/2} \int \text{d}R \, \rho_R \left( \frac{1}{2} \sum_i \rho_i \sum_f |\langle i; R| V_j |f; R \rangle|^2 \delta(\omega_f - \omega) \right. \\
+ \frac{1}{4} \sum_i \rho_i \sum_f |\langle i; R| V_2 |f; R \rangle|^2 \delta(\omega_f - \omega) \right. \\
+ \frac{3}{4} \sum_i \rho_i \sum_f |\langle i; R| V_2 |f; R \rangle|^2 \delta(\omega_f - \omega) \Bigg).
\]

(A.1)

(The spin index has been, understandably, removed in Eq. (A.1).) The likelihood, \( \rho_j \), to observe a particular rotational state \( i \) is \( \rho_i = g(i)e^{-\epsilon_i/kT}/ \sum_n g(n)e^{-\epsilon_n/kT} \), and the degeneracy \( g(i) = 3 \) or 1 for rotational states of odd or even parity respectively.

The potentials \( V_1 \) and \( V_2 \) can be expanded in spherical harmonics in the angle \( \gamma \) between the momentum transferred \( q \) and the bond vector \( \Omega \). Experiments often place us in the limit where \( qd \) is a small quantity, and in that case we can truncate the series so that

\[
V_1 \approx j_0(qd/2) - 4\pi j_2(qd/2) \sum_{m=-2}^{2} Y_{2,m}^{*}(\hat{q}) Y_{2,m}(\hat{\Omega}),
\]

(A.2)

\[
V_2 \approx 4\pi j_1(qd/2) \sum_{m=-1}^{1} Y_{1,m}^{*}(\hat{q}) Y_{1,m}(\hat{\Omega}).
\]

(A.3)

Finally, because experiment treats a polycrystalline material, we require the average \( |\langle i| V_j |f \rangle|^2 \) over all orientations \( \hat{q} \) in Eq. (A.1). The resulting expression for the rotational scattering function is, thus,
\[ S_\phi(q, \omega) = \sum_{j=1}^{n/2} \int dR \rho_R \left( \frac{1}{2} \sum_i \rho_i \sum_f f_0^2(qd/2) \delta(\omega) \right. \]
\[ + 4\pi j_0^2(qd/2) \sum_{m=-2}^2 |\langle i; R|Y_m^m(\Omega)|f; R \rangle|^2 \delta(\omega_{i_1} - \omega) \]
\[ + \frac{4\pi}{4} \sum_{i} \rho_i \sum_f j_1^2(qd/2) \sum_{m=-1}^1 |\langle i; R|Y_m^m(\Omega)|f; R \rangle|^2 \delta(\omega_{i_1} - \omega) \]
\[ + \frac{3\pi}{4} \sum_{i} \rho_i \sum_f j_1^2(qd/2) \sum_{m=-1}^1 |\langle i; R|Y_m^m(\Omega)|f; R \rangle|^2 \delta(\omega_{i_1} - \omega) \right). \quad (A.4) \]

Appendix B

Eq. (10) is equivalent to

\[ C(q, t) = \frac{n}{2} \int \int dR dR' \left[ \frac{1}{2} \sum_{i} \rho_i \sum_f V_{1R}^{iR} V_{1R}^{fR} + \frac{1}{4} \sum_{i} \rho_i \sum_f V_{2R}^{iR} V_{2R}^{fR} \right] \]
\[ \times \left( f \right) \exp(-i q \cdot R) \right) \langle R'| \langle i, f, R' | \exp(-i \hat{H}_{\text{BO}} t) \right) \right) \langle R'| \langle i, f, R' | \exp(-i q \cdot R) \right) \right) \langle R'| \langle i, f, R' | \exp(-i q \cdot R) \right). \quad (B.1) \]

As before, cross terms from different \( H_2 \) molecules vanish, and one can average Eq. (B.1) over spin states. We can also simplify our notation a bit by noting that we can drop the \( j \) index on all operators, since averaging over a thermal distribution of states means that all molecules will contribute equally to the sum above. Thence we can note the matrix element \( \langle i; R| \hat{V}_j^f | f, R \rangle \equiv \int d\Omega \langle i; R| \Omega \rangle \hat{V}_j^f | \Omega | f, R \rangle \) as \( V_{iR}^{jf} \). With this abbreviated notation, Eq. (B.1) becomes

\[ C(q, t) = \frac{n}{2} \int \int dR dR' \left[ \frac{1}{2} \sum_{i} \rho_i \sum_f V_{1R}^{iR} V_{1R}^{fR} + \frac{1}{4} \sum_{i} \rho_i \sum_f V_{2R}^{iR} V_{2R}^{fR} \right] \]
\[ \times \langle f \rangle \exp(-i q \cdot R) \right) \langle R'| \langle i, f, R' | \exp(-i \hat{H}_{\text{BO}} t) \right) \right) \langle R'| \langle i, f, R' | \exp(-i q \cdot R) \right) \right) \langle R'| \langle i, f, R' | \exp(-i q \cdot R) \right). \quad (B.2) \]

At this point, it is appropriate to note initial and final states with subindices \( l \) (CM) and \( k \) (rotational) so that Eq. (B.2) appears as

\[ C(q, t) = \frac{n}{2} \int \int dR dR' \left[ \frac{1}{2} \sum_{i, k} \rho_{i, k} \sum_{f_L} V_{ikL}^{iR} V_{fL}^{fR} \right. \]
\[ \left. + \frac{1}{4} \sum_{i, k} \rho_{i, k} \sum_{f_L} V_{ikL}^{iR} V_{fL}^{fR} \right] \langle i, k, f_L | \exp(i \hat{H}_{\text{BO}} t) \right) \exp(i q \cdot R) \right) \langle R'| \langle i, k, f_L | \exp(-i \hat{H}_{\text{BO}} t) \right) \right) \langle R'| \langle i, k, f_L | \exp(-i q \cdot R) \right) \right) \langle R'| \langle i, k, f_L | \exp(-i q \cdot R) \right). \quad (B.3) \]

Written in this way, we can use completeness of the BO states,
\[
\sum_i (k_i|\mathbf{R})(\mathbf{R}'|k_i) = \delta(\mathbf{R} - \mathbf{R}'),
\]

in order to arrive at Eq. (17).

References