



Infrared overtone spectroscopy of adsorbed hydrogen in MOF-5



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ABSTRACT

Overtone spectroscopy is used to observe the rovibrational spectra of the hydrogen isotopologues H₂, HD, and D₂ adsorbed in the metal–organic framework known as MOF-5. It is shown that the overtone spectrum facilitates the identification of hydrogen modes which are obscured in the fundamental region by the presence of MOF-5 features. Further, the overtone spectrum of H₂ at the primary adsorption site is greatly enhanced relative to other sites, and thus ambiguities about feature assignment can be avoided. The frequency (wavenumber) of the overtone modes are in good agreement with a Buckingham perturbative model while the relative intensity of the Q₂(0) pure vibrational mode is found to be anomalously large, most likely arising through mode coupling to the MOF-5 framework.

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1. Introduction

In recent years there has been much research studying adsorbed gases within porous materials. The motivation for this work has focused on gas storage and molecular separations. A technique that has proved successful for characterizing the interactions between adsorbates and adsorbents is infrared (IR) spectroscopy. There are three main methods being used: transmission through KBr-diluted compacts [1], transmission through pure pressed pellets [2], and diffuse reflectance spectroscopy using powdered material [3]. In each case spectra of the adsorbed species are determined by reference to that of the evacuated adsorbent. This analysis is often complicated by the strong IR features of the adsorbent material in the wavenumber range of interest. This is particularly true for porous materials having organic moieties, which exhibit quite complicated IR signatures even at higher wavenumbers.

Metal–organic frameworks (MOFs) are a class of materials consisting of metal coordination clusters joined together by organic linkers to form microporous structures [4–7]. The crystalline nature of these materials makes them readily amenable to both neutron and X-ray diffraction analyses. In many cases a set of clearly defined adsorption sites have been established [8–12]. Their primary appeal is that a myriad of different clusters and organic links can, in principle, be connected to form an ideal material with the

desired properties for a specific application. Much of the research into MOFs has focused on hydrogen storage and small molecule separations [4]. Given the many possible MOFs that can be formed, it is essential that accurate models be developed for the adsorbate interactions so that the properties of hypothetical structures can be reliably predicted and optimized.

MOF-5 is a prototypical framework that has been reported to have one of the largest hydrogen storage capacities by weight [13]. Neutron diffraction has provided the most descriptive experimental evidence of the preferred H₂ adsorption sites in this material [9,10]. Below 50 K the H₂ appears localized in the corners of the 1.5 nm pores, on alternate faces of the inorganic Zn₄O(O₂C–)₆ clusters. At lower temperatures and higher loadings, secondary sites are occupied, first around the inorganic clusters and then on the phenylene links. This behavior is analogous to that previously modeled for nitrogen and argon by X-ray diffraction analyses [8].

In an earlier paper we measured the rovibrational IR spectrum for H₂ in MOF-5 [3]. This established both the pure vibrational (Q), rotational sideband (S), and translational sideband transitions (Q_{trans}) for the fundamental part of the spectrum. These data were used by Kong et al. [14] to theoretically model the interaction potential between the H₂ and the MOF, and more recently by Matanovic et al. [15] using a more complete quantum mechanical five-dimensional approach. The significance of the quantum behavior is apparent in adsorption measurements showing MOFs to be highly effective in separating D₂ from H₂ via the difference in their translational zero-point energies [16]. Oh et al. [17] have proposed a prototype scheme in which MOF-based separation

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would supplant the traditional Girdler sulfide method for D₂ production [18]. It is therefore advantageous to obtain IR spectra on adsorbed D₂ to better understand the differences in the behavior of the isotopologues. However, as noted by Nijem et al. [19] this is extremely challenging due to the presence of MOF features in the spectral region of interest. In this paper we show that the use of IR overtone spectroscopy removes this problem, enables an additional means for distinguishing the features associated with different adsorption sites, and provides detailed information about the quantum dynamics of the different hydrogen isotopologues.

2. Spectroscopic principles

The rovibrational levels of a diatomic molecule are given by [20]:

$$E(v, J) = G(v) + F_v(J), \quad (1)$$

where

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \dots, \quad (2)$$

and

$$F_v(J) = B_v J(J + 1) - D_J J^2(J + 1)^2 + \dots \quad (3)$$

Here v and J are the respective vibrational and rotational quantum numbers, B is the rotational constant,

$$B(v) = B_e - \alpha_e(v + 1/2) + \dots, \quad (4)$$

and D is a centrifugal distortion term which represents a small correction. The constant ω_e is the harmonic vibrational wavenumber at equilibrium and α_e is a measure of the vibrational–rotational coupling. The various constants are known to many significant figures for gas phase H₂, HD and D₂ [20,21]. As the rotational constant depends upon v , the pure vibrational Q modes ($\Delta J = 0$) occur at:

$$Q_v(J) = Q_v(0) + (B_v - B_0)J(J + 1) + \dots \quad (5)$$

In this notation the subscript v refers to the vibrational quantum number of the final state, and since all molecules are initially in the $v = 0$ state, it also shows the change in the vibrational quantum number associated with a particular transition.

For the homonuclear molecules H₂ and D₂ the nuclear spin state of the molecule restricts the rotational J -levels to be either only even or only odd, as determined by quantum statistics. Since relaxation of the nuclear spin state is often extremely slow, there is a well known ortho–para splitting where even at very low temperatures a significant fraction of molecules are trapped in the excited $J = 1$ rotational state. Thus, both $Q_v(0)$ and $Q_v(1)$ transitions appear in spectra differing in wavenumber by $\sim 2v\alpha_e$. In the case of HD the nuclei are distinguishable, and only the $Q_v(0)$ transition is observed at low temperature [22].

Within the dipole approximation infrared transitions can only occur if they lead to a change in the dipole moment of the system defined as the hydrogen molecule and MOF-5 framework [23]. Neither H₂ nor D₂ have an intrinsic dipole moment and thus are infrared inactive.

The observed H₂ spectrum arises through the presence of interaction-induced dipole moments between H₂ and the neighboring framework atoms [24]. There are two dominant interaction mechanisms by which this occurs. In the first, the framework atoms interact with the H₂ polarizability to induce a dipole moment on the hydrogen molecule. Because the H₂ polarizability is largely isotropic, to a good approximation this mechanism only activates Q transitions and not those involving a change in the rotational state, i.e. $S(0)$ or $S(1)$ [25]. This *hydrogen polarization* mechanism is analogous to Raman spectroscopy where an incoming photon polarizes the molecule. In our system the electric field from the MOF acts as

a “photon of infinite wavelength” [26]. The second method of IR activation involves the H₂ permanent quadrupole moment inducing an interaction dipole moment on the framework atoms. Unlike the *hydrogen polarization* mechanism, this *quadrupole induction* mechanism activates the rovibrational $S(0)$ and $S(1)$ transitions in addition to $Q(1)$, because the H₂ quadrupole moment is highly anisotropic. However, $Q(0)$ transitions are not activated by the quadrupole induction mechanism because the $J = 0$ state is spherically symmetric and possesses no quadrupole moment [27]. The symmetry of the two mechanisms leads to dominant selection rules of $\Delta J = 0$ for the hydrogen polarization mechanism and $\Delta J = 0, \pm 2$ for the quadrupole induction mechanism. These same principles apply to H₂, D₂, and HD. While HD possesses a weak dipole moment, we do not observe any transitions associated with it, i.e. those with $\Delta J = \pm 1$.

Overtone features, those in which the vibrational quantum number, v , changes by two or more, arise from the anharmonicity in the hydrogen vibrational levels or a non-zero value for the second derivative of either the polarizability or quadrupole moment with respect to the internuclear separation. Normally the first overtone transitions, e.g. $Q_2(J)$, are quite weak, being reduced in intensity by roughly two orders of magnitude from the corresponding fundamental transition, $Q_1(J)$ [28]. They were first observed for adsorbed molecules by Förster and Frede, who estimated the overtone intensity of D₂ in NaCaA zeolites to be reduced by a factor of 35 relative to the fundamental [29].

3. Experimental procedure

The synthesis and characterization of the MOF-5 samples used in this paper have been presented in our previous report [3]. Infrared measurements were taken using both quartz halogen and global sources, in conjunction with a KBr beamsplitter, and mercury cadmium telluride and indium gallium arsenide detectors. In all cases measurements were performed using the diffuse reflectance technique outlined in our earlier work [3]. This technique significantly enhances the IR signal of adsorbed hydrogen in comparison to traditional transmission measurements. A custom-built cryogenic chamber allows the sample powders to be mounted, degassed, cooled, and dosed with hydrogen without exposing them to air [30].

4. Results and discussion

4.1. Q -transition frequencies (wavenumbers)

Understanding the complex quantum dynamics of a trapped molecule can be greatly assisted by observing the behavior of more than one isotopologue. To date, only a few studies of adsorbed hydrogen in MOFs have included spectra for D₂. This is because the D₂ vibrational mode, occurring at a frequency of $\sim 1/\sqrt{2}$ that of H₂, is located in a region where framework materials exhibit many strong absorbance features. Fig. 1 shows the raw spectra obtained with MOF-5 before and after adding D₂. The top panel displays the spectral region of the D₂ fundamental mode and the lower panel the overtone region. In the case of the fundamental it is challenging to distinguish the new D₂ features at 2974 and 2971 cm⁻¹ from the existing MOF background. In contrast, the overtone region is largely devoid of framework absorption features, and the assignment of the expected D₂ ortho–para pair of transitions is obvious.

In his seminal paper [35], Buckingham showed that for a diatomic molecule with rotational constant B_v and harmonic wavenumber ω_e the fractional shift in the vibrational transitions is given to second order perturbation by

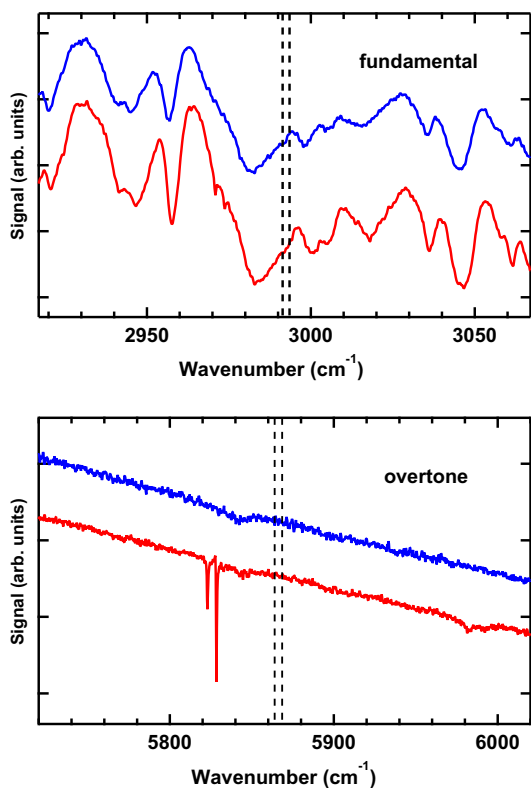


Fig. 1. Raw infrared spectra measured at 30 K for evacuated MOF-5 (blue) and MOF-5 with a concentration of 0.5 D₂ per Zn (red). The region encompassing the D₂ fundamental vibrational values is shown in the top frame, where the dashed lines mark the gas phase values for Q₁(0) and Q₁(1). The overtone region of these same spectra are shown in the bottom frame, where the dashed lines mark the gas phase values for Q₂(0) and Q₂(1). Spectra are offset vertically for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\frac{\Delta\omega_{0\rightarrow v}}{\omega_e} = v \frac{1}{hc} \frac{B_e}{\omega_e^2} \left(\frac{d^2U}{d\xi^2} - 3a \frac{dU}{d\xi} \right), \quad (6)$$

where U is the potential energy due to interaction of the hydrogen with the MOF, ξ is the dimensionless H₂ internuclear separation defined as $\xi = (r - r_e)/r_e$, and a is the anharmonicity of the internal H₂ potential energy function. Because the ratio of B_e/ω_e^2 is unaffected by isotopic substitution, the fractional vibrational wavenumber shift (relative to the gas phase) of different hydrogen isotopologues should be equal: $\Delta f/f_{gas} \approx \Delta\omega/\omega_e = \text{constant}$. Eq. (6) also predicts that the vibrational shift of the overtone mode should be twice that of the fundamental. Thus the percentage redshift of all three isotopologues, both for the fundamental and overtone regions, should be the same. Discrepancies from this behavior can be used to assess the level of vibrational-translational coupling and the degree to which MOF interactions produce additional anharmonicity in the adsorbed molecule. Fig. 2 shows the IR absorption spectra plotted in terms of the percentage wavenumber shift for concentrations of 0.2 and 0.7 hydrogen molecules per Zn. The actual transition values, along with those of the S transitions, are listed in Table 1. At the lower concentration it is expected based on neutron diffraction that the majority of the adsorbed molecules are in the so-called “cup site”, in the corners of the pores, while at the higher concentration significant occupancy of both the “cup” and “oxygen” sites should occur [9,10].

Focusing on the low concentration spectra in Fig. 2, there is good agreement with the Buckingham model when comparing peak locations in the fundamental and overtone regions. Both

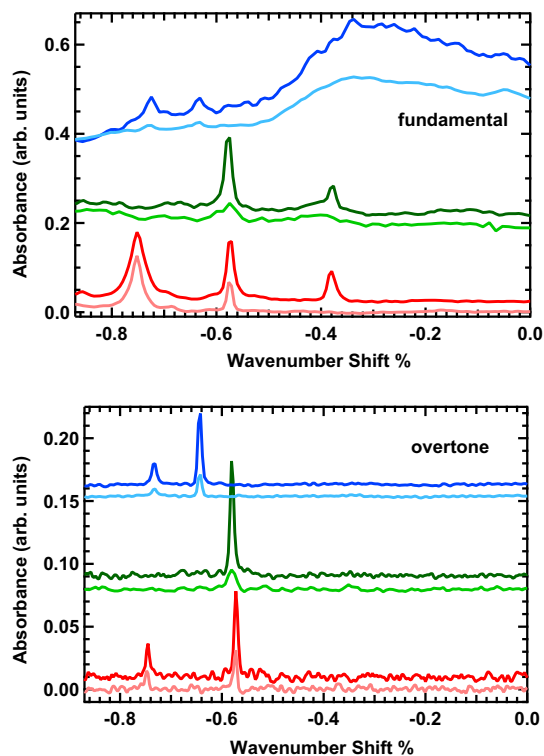


Fig. 2. Infrared absorption spectra for adsorbed H₂ (red), HD (green) and D₂ (blue) in MOF-5 at 35 K. All spectra are referenced to the background spectrum of evacuated MOF-5 and plotted in terms of percentage wavenumber shift relative to the respective gas phase Q_v(0) value for direct comparison of the isotopologues. The top frame shows the fundamental region, the bottom frame is the overtone region, where pale traces correspond to 0.2 molecules per Zn and dark traces correspond to 0.7 molecules per Zn. Spectra are offset vertically for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

display H₂ and D₂ ortho-para pairs whose assignment is confirmed by difference spectra taken over time (Fig. S1). As expected, there is only one HD vibrational feature, since the nuclei are distinguishable and virtually all molecules occupy the ground rotational state at the experimental temperature. There is a slight increase in the Q_v(0) shift from H₂ to HD to D₂ which is readily apparent when comparing the overtone features. This represents a deviation from the Buckingham model, which predicts the fractional shift to be the same for all isotopologues up to small higher-order correction terms on the order of $(B_e/\omega_e)^2 \approx 10^{-4}$ [21,36]. The deviation is explained through vibrational-translational coupling: as the mass of the molecule increases, the translational wavefunction becomes more localized and the more massive isotopologues sit deeper in the potential well and experience a greater binding energy [16]. Increased binding energy has been shown to correlate with increased redshift [37,38].

At a higher adsorbate concentration, new features appear in the fundamental region due to more crystallographic sites being occupied. The corresponding features are not observed in the overtone region. In Fig. 2 we see that the fundamental region contains at least two features for D₂, two features for HD, and three features for H₂. In our original study [3] of H₂ in MOF-5 a detailed concentration and time dependent analysis indicated that the feature at 4128 cm⁻¹ (shift of -0.75% in Fig. 2) should be assigned to the Q₁(1) transition of H₂ at the primary site (cup site), while the feature at 4143 cm⁻¹ (shift of -0.38% in Fig. 2) arose from a Q₁(0) transition of H₂ at a secondary site. However, the assignment of the middle feature at 4136 cm⁻¹ (shift of -0.57% in Fig. 2) was less clear and appeared to be composed of an overlapping Q₁(0)

Table 1

Wavenumbers of the observed $Q_v(0)$, $Q_v(1)$, $S_v(0)$, and $S_v(1)$ transitions of H_2 , HD and D_2 at the primary binding site in MOF-5. The $S_1(1)$ transition of D_2 was not observed, likely due to it being obscured by MOF-5 features in that spectral region. Transition values are in cm^{-1} .

Isotopologue	$Q_1(0)$	$Q_1(1)$	$S_1(0)$	$S_1(1)$	$Q_2(0)$	$Q_2(1)$	$S_2(0)$	$S_2(1)$
$H_2(\text{gas})$	4161.1 ^a	4155.2 ^a	4497.8 ^c	4712.9 ^c	8087 ^b	8075.3 ^c	8406.3 ^c	8604.2 ^c
$H_2(\text{MOF-5})$	4135.8	4128.0	4448.5, 4491	4676, 4712, 4734.5	8036.7	8021.5	8332	8541
HD(gas)	3632.1 ^a	3628.2 ^a	3888 ^f	4052 ^f	7087 ^f	7079.2 ^d	7331.1 ^d	7484.3 ^d
HD(MOF-5)	3609.6		3849		7042		7268, 7280	
$D_2(\text{gas})$	2993.5 ^a	2991.4 ^a	3166.4 ^e	3278.5 ^e	5868.5 ^b	5863.9 ^e	6034.7 ^e	6140.6 ^e
$D_2(\text{MOF-5})$	2974	2971	3127, 3135		5828	5823	5980, 5989	6094

^a Ref. [20], ^b Ref. [31], ^c Ref. [32], ^d Ref. [33], ^e Ref. [34], ^f Calculated from Ref. [20].

feature from H_2 at the primary site and $Q_1(1)$ from H_2 at the secondary site. Since the spectra could not be measured at low enough temperature to ensure that only the primary site was occupied, it was not possible to resolve the two features. It was later proposed that the induced intensity of the $Q_1(0)$ mode at the primary site was close to zero which was a possible explanation for why it was not clearly observed in the original spectra [14].

In the overtone region, however, there is a well-defined and relatively intense feature at 8036 cm^{-1} (shift of -0.57% in Fig. 2) whose $Q(0)$ nature is confirmed by difference spectra taken over time (see Fig. S1). There is no evidence of overtone features corresponding to the secondary site until a much higher concentration of 3 H_2 per Zn is reached (see Fig. S2), when a small feature appears at 8053 cm^{-1} (shift of -0.39%), corresponding to the large fundamental feature at 4144 cm^{-1} (shift of -0.38%). This weak feature is the only indication of a secondary site transition in the overtone region and its intensity is greatly reduced, by almost two orders of magnitude from the corresponding secondary site feature in the fundamental region. The large difference in the intensities of the overtone modes for different sites should prove useful for transition assignments in other studies of H_2 in porous materials.

We hypothesize that the large relative enhancement of the primary site overtone modes occurs through some form of mode coupling with the MOF framework. This is supported by the presence of an IR absorption feature that scales with primary site H_2 concentration at 1622 cm^{-1} above the respective $Q_1(0)$ primary site value for all three isotopologues (see Fig. S3). This combination feature is almost certainly due to coupling to the carboxylate stretch of the framework at the primary site, which is known to occur in this wavenumber range and is very intense for MOF-5 [38]. We eliminated the possibility that the coupling is to a framework C–H stretch by repeating measurements with deuterated and non-deuterated MOF-5. No change in the feature's wavenumber value was observed. It is notable that we did not observe any corresponding combination feature for molecules adsorbed at the secondary sites.

4.2. Intensity

The theoretical line intensity of a transition at wavenumber f_0 from the ground vibrational state is given by

$$I_{0JM \rightarrow v'J'M'} \propto f_0 P_{JM} |\langle 0JM | \vec{\mu} | v'J'M' \rangle|^2, \quad (7)$$

where P_{JM} is the relative population in the J, M level and $\vec{\mu}$ is the induced dipole moment operator that is given, to a first order approximation, by:

$$\vec{\mu}_{\text{sys}} = \vec{\mu}_{\text{polar}} + \vec{\mu}_{\text{quad}}, \quad (8)$$

where

$$\vec{\mu}_{\text{polar}} = \vec{E}_{\text{mof}} \cdot \alpha_{H_2}, \quad (9)$$

and

$$\vec{\mu}_{\text{quad}} = \sum_i \vec{E}_{QH_2} \cdot \alpha_{i,\text{mof}}. \quad (10)$$

Here \vec{E}_{mof} is the electric field due to the MOF at the site of the adsorbed molecule, α_{H_2} is the H_2 polarizability tensor, and \vec{E}_{QH_2} is the electric field due to the permanent H_2 quadrupole moment. At every point on the surface, \vec{E}_{QH_2} depends upon the location of the MOF atoms relative to the H_2 , so in order to determine $\vec{\mu}_{\text{quad}}$ a vector sum must be performed over the MOF polarizability, $\alpha_{i,\text{mof}}$. The intensity of a transition is therefore

$$I_{0JM \rightarrow v'J'M'} \propto |\langle 0JM | \vec{\mu}_{\text{sys}} | v'J'M' \rangle|^2 = |C \langle 0JM | \alpha_{H_2} | v'J'M' \rangle + D \langle 0JM | Q | v'J'M' \rangle|^2, \quad (11)$$

where Q is the hydrogen quadrupole tensor and C and D are unknown constants of proportionality.

The line intensity I_{f_0} is determined experimentally by the area of the absorbance feature as

$$I_{f_0} \propto \int_{\text{line}} A(f) df, \quad (12)$$

where f is the wavenumber, A the absorbance, and the constant of proportionality depends on the H_2 concentration and optical path length within the sample. In our case we cannot measure the constant of proportionality but we can use Eq. (12) to determine the relative intensity of the different transitions.

It is apparent from Fig. 2 that the relative intensity of $Q(0)$ versus $Q(1)$ (features at wavenumber shifts of -0.57% and -0.75%) is reversed in the overtone with the $Q_2(0)$ now dominating in intensity. In Fig. 2 the displayed H_2 fundamental and overtone regions were acquired simultaneously (being the Fourier transform of the same interferogram), and so correspond to the same ortho to para ratio. In fact, the magnitude of the $Q_2(0)$ enhancement is larger than is evident, because the $Q_1(0)$ in the fundamental region overlaps with a secondary site feature which increases its apparent intensity. Ab initio calculations for both polarizability and quadrupole matrix elements of free hydrogen molecules predict that the relative intensity of the $Q(0)$ to $Q(1)$ decreases in the overtone, the opposite of our observation [39,40].

Analysis of the $Q_v(1)$ intensity is complicated by cross terms between the polarization and quadrupole induction mechanisms (Eq. (11)). A simpler approach is to compare the intensity ratio of the $Q_v(0)$ transitions (which involve isotropic states and thus arise solely from the polarization mechanism) to that of the S transitions, which we can assume arise almost entirely from the quadrupole induction mechanism. This assumption is justified by Raman spectroscopy which arises solely through the hydrogen polarizability and shows a negligible S to Q transition intensity ratio [41,42,20]. Since the S and Q features of H_2 in MOF-5 have comparable intensity in the fundamental region [3] it can be concluded that the majority of the S transition intensities arise from the quadrupole induction mechanism. As shown in Fig. 3, while the $S_v(0)$ and $S_v(1)$ features dominate in the fundamental region they are quite weak compared to the $Q_2(0)$ feature in the overtone region. This indicates that there is a greater reduction in the quadrupole induction term than the polarization term (Eq. (11)) on going from fundamental to overtone. In fact, as shown in Table 2, the decrease

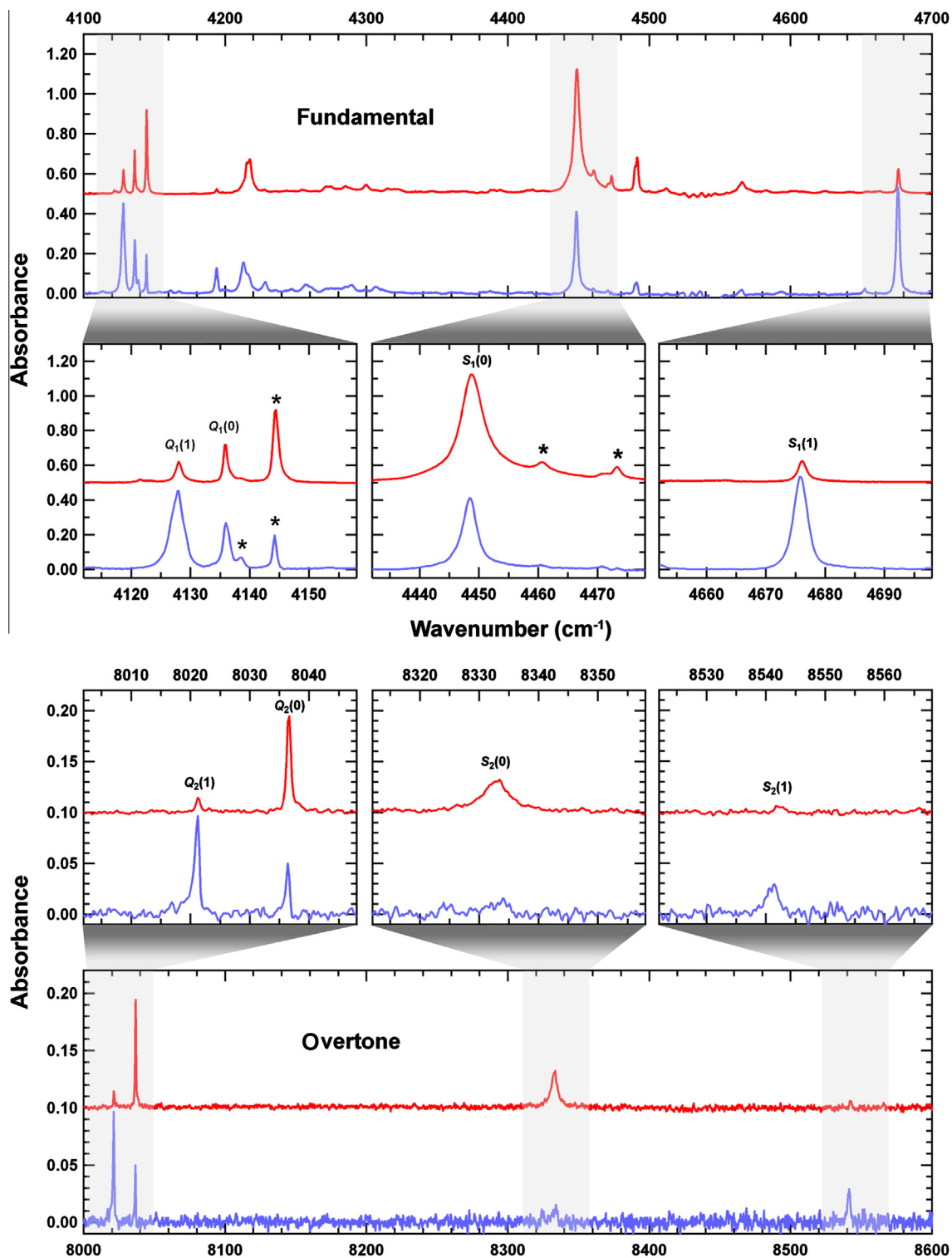


Fig. 3. Infrared absorbance spectra for adsorbed H_2 in MOF-5 at 40 K with a concentration of 0.9 H_2 per Zn. Blue traces are the initial spectra collected shortly (4 min) after loading, while red traces are the spectra acquired after ortho–para conversion is nearly complete (10 h). The fundamental vibrational wavenumber regions are shown in the top frames and the overtone regions of the same spectra are shown in the bottom frames. The inset frames emphasize the differences in relative intensity among the fundamental and overtone features, with the same wavenumber span used in all cases. Asterisks indicate features arising from H_2 adsorbed at secondary sites in the material. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in S transition intensities agrees well with theoretical expectations for free hydrogen while the $Q_2(0)$ in the overtone is much larger than expected. The $Q_2(1)$ to $Q_1(1)$ intensity ratio lies between the two extremes, which is consistent with it resulting from a combination of the two mechanisms.

There are several possible explanations for the relative enhancement of the $Q_2(0)$ mode in the overtone. Kong et al. [14] proposed that the $Q_1(0)$ mode is suppressed in the fundamental due to an accidental cancellation with higher order terms. According to these authors the induced dipole moment on the H_2 creates

Table 2

Intensity ratios, with the middle row showing the theoretical prediction for free H₂, and the bottom row the experimentally observed ratio as defined by the area under the respective absorbance curves, for H₂ in the primary site of MOF-5 at 35 K. Quad refers to the quadrupole induction mechanism.

	Q(0)	Q(1)	S(0)	S(1)
Mechanism	Polarization	Both	Quad	Quad
I_{0-2}/I_{0-1} (free H ₂ , theory)	1/60	–	1/20	1/20
I_{0-2}/I_{0-1} (H ₂ in MOF-5, expt.)	1/(2.5±0.5)	1/(14±3)	1/(17±1)	1/(22±4)

an electric field that in turn induces opposite dipole moments on the MOF. While their paper makes no reference to overtone modes, it is reasonable to further propose that this cancellation is incomplete for the overtone mode and hence the relative enhancement of Q₂(0). However, this would not explain the enhancement of the overtone primary site modes relative to all other sites. Knippers et al. [21] has shown the relative intensity of the Q₂(0) to Q₁(0) transitions to be:

$$\frac{I_{0-2}}{I_{0-1}} = \frac{B_e}{\omega_e} \left(a + \frac{d^2 \bar{\alpha}}{d\xi^2} \bigg/ \frac{d\bar{\alpha}}{d\xi} \right)^2, \quad (13)$$

where both the polarizability and the potential experienced by the hydrogen molecule are Taylor expanded in terms of ξ , the dimensionless internuclear separation. At the equilibrium separation, $\frac{d^2 \bar{\alpha}}{d\xi^2} / \frac{d\bar{\alpha}}{d\xi} = 0.537 \pm 0.002$ [36], and the anharmonicity term, $a = -1.607$ [21]. As shown in Table 2, this predicts the relative intensity I_{0-2}/I_{0-1} to be 1/60 for free hydrogen while experimentally in MOF-5 we observe a ratio of 1/(2.5±0.5). Because the intensity ratio of the S features agrees with predictions for the quadrupole matrix element of free H₂, and the fact that the wavenumber values of all the peaks agree with the Buckingham model, it is unlikely that there is any significant change in the anharmonicity of the H₂ upon adsorption. Similarly, it seems improbable that the ratio of the polarizability derivatives is altered by the large amount that is needed to account for the observed intensity ratio. Rather than arising from a large modification of the internal properties of the adsorbed H₂ it seems more likely that the anomalous Q₂(0) intensity arises from a mode coupling with the MOF. A mode coupling behavior that alters the Q(1) to Q(0) intensity ratio has long been observed in solid hydrogen [43]. Similarly, Sweany et al. invoked coupling to framework ions to explain the extremely intense luminescence overtone for H₂ in zeolites [44].

Finally, we note that in Fig. 3, in which all the middle panels have the same wavenumber span, the Q₁(0), Q₂(0), and Q₂(1) have roughly the same width (0.8 cm⁻¹) while the Q₁(1) is significantly broader, with a shape indicative of closely spaced sidebands. The relative intensity of these sidebands decreases with decreasing ortho concentration. Similar behavior has been identified in solid hydrogen with the presence of sidebands in the fundamental region attributed to quadrupole–quadrupole coupling between adjacent ortho molecules [45–47]. The absence of such sidebands in our overtone spectrum is again consistent with coupling to the MOF in which the polarization mechanism is enhanced relative to the quadrupole induction mechanism.

5. Summary

Examination of the overtone region of the vibrational spectrum has been shown to provide clearer information about adsorbed D₂ than the traditional analysis of the fundamental region alone. The fractional wavenumber shift of the Q₁(0) and Q₂(0) modes are the same for the H₂, HD, and D₂ isotopologues. This indicates that interactions with the MOF lead to minimal perturbation of the internal H₂ anharmonicity. The overtone intensity is greatly

enhanced for H₂ at the primary site relative to all other sites. In particular, the Q₂(0) shows an intensity that is at least an order of magnitude greater than predicted for free H₂. We hypothesize that this is due to mode coupling to the carboxylate stretch of the MOF-5 framework. This is supported by the presence of a feature at 1622 cm⁻¹ above the respective Q₁(0) value for all three isotopologues.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jms.2014.11.001>.

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