Infrared emission spectra and equilibrium bond lengths of gaseous ZnH₂ and ZnD₂†

Alireza Shayesteh, a Iouli E. Gordon, b Dominique R. T. Appadoo c and Peter F. Bernath a,b

a Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, ON, Canada N2L 3G1. E-mail: bernath@uwatelse.ca; Fax: +1-519-746-0435;
Tel: +1-519-888-4814
b Department of Physics, University of Waterloo, 200 University Avenue West, Waterloo, ON, Canada N2L 3G1

c Canadian Light Source Inc., University of Saskatchewan, 101 Perimeter Road, Saskatoon, SK, Canada S7N 0X4

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A detailed analysis of the high resolution infrared emission spectra of gaseous ZnH₂ and ZnD₂ in the 800–2200 cm⁻¹ spectral range is presented. The ν₁ antisymmetric stretching fundamental bands of 64ZnH₂, 67ZnH₂, 68ZnH₂, 64ZnD₂, 67ZnD₂ and 68ZnD₂, as well as several hot bands involving ν₁, ν₂ and ν₃ were rotationally analyzed, and spectroscopic constants were obtained. Rotational l-type doubling and l-type resonance, local perturbations, and Fermi resonances were observed in the vibration–rotation bands of both ZnH₂ and ZnD₂, and equilibrium vibrational frequencies (ν₀, ν₂ and ν₃) were estimated. Using the rotational constants of the 000, 100, 010 and 001 vibrational levels, the equilibrium rotational constants (Bₒ) of 64ZnH₂ and 64ZnD₂ were determined to be 3.600 269(3) cm⁻¹ and 1.801 985(25) cm⁻¹, respectively, and the associated equilibrium bond lengths (rₒ) are 1.524 13(1) Å and 1.523 94(1) Å, respectively. The difference between the rₒ values of 64ZnH₂ and 64ZnD₂ is about 0.01%, and is mainly due to the breakdown of the Born–Oppenheimer approximation.

1. Introduction

Solid ZnH₂ has been known since 1951, and several methods have been reported for its synthesis.⁹⁻¹⁸ Chemical properties of solid ZnH₂, as well as its infrared absorption spectrum and the X-ray diffraction pattern were studied in the 1970s.⁶⁻⁸ Recently, Wang and Andrews⁹ recorded the infrared spectra of solid ZnH₂ and ZnD₂, and observed broad absorption bands characteristic of hydrogen-bridge bonding. Solid ZnH₂ decomposes to the constituent elements at 90 °C, and it is not possible to produce gaseous ZnH₂ by heating the solid. The lack of stability of solid ZnH₂ has been further confirmed by theoretical calculations.¹⁰ Linney and Russell found that ZnH₂ can be generated by the infrared laser pyrolysis of diethyl-zinc.¹¹ The reduction of aqueous Zn(ii) in acidic solutions with NaBH₄ results in formation of a volatile zinc-containing compound. This molecule has not been identified yet, but it might be zinc dihydride.¹²,¹³ Properties of the main-group metal hydrides, including hydrides of group 11 and 12 elements, have been reviewed by Aldridge and Downs.¹⁴

There have been a few ab initio theoretical studies on electronic structure and geometry of gaseous ZnH₂.¹⁵⁻²¹ A linear H–Zn–H structure and a closed-shell XΣ₉⁺ ground electronic state have been predicted by all theoretical calculations. The Zn–H bond distances estimated by various theoretical models¹⁵⁻²¹ were in the range of 1.492 to 1.662 Å. Vibrational frequencies of ZnH₂, ZnHD and ZnD₂ were calculated by Greene et al. at the MP2 and CCSD(T) levels of theory with relatively large basis sets.²¹ It was also calculated that the gas phase reaction: Zn(g) + H₂(g) → ZnH₂(g) is endoergic by only a few kcal mol⁻¹ for ground state (S) zinc atoms.²¹ The metastable P state of Zn, which is the first excited state, lies about 93 kcal mol⁻¹ above the ground state,²² so the production of gaseous ZnH₂ from the gas phase reaction of Zn(P) with H₂ is highly exoergic.

The gas phase reaction of excited zinc atoms with molecular hydrogen has been studied extensively, both by theoretical calculations and by laser pump–probe techniques.²³⁻²⁹ Although the ground state Zn(S) does not react with H₂ due to a high energy barrier, excited zinc atoms in P or P' states can insert into the H–H bond.²²,²⁹ The resultant intermediate is an excited bent [H–Zn–H]⁺ complex, which can dissociate to ZnH and H free radicals. All theoretical and experimental studies on this reaction²³⁻²⁹ considered ZnH and H as the only products, and no attention was given to the possible formation of the ground state linear H–Zn–H molecule. The activation of H–H bond with excited Mg, Zn, Cd and Hg atoms has been reviewed by Breckenridge.²⁹

Matrix isolation, followed by infrared absorption spectroscopy, has been used to study many metal hydrides.²⁰ The ZnH₂, ZnHD and ZnD₂ molecules were formed in solid argon and krypton matrices at ~12 K from the reaction of excited zinc atoms with hydrogen.²¹,²¹ Infrared absorption spectra of these species (trapped in solid matrices) were recorded, and vibrational frequencies for the antisymmetric stretching (ν₁) and bending (ν₂) modes were obtained. Wang and Andrews⁹ have recently repeated this experiment using solid hydrogen and neon matrices at 4.5 K, and recorded the infrared absorption spectra of several zinc hydride species at a relatively high resolution. ZnH₂ has also appeared as a byproduct in the matrix isolation experiments studying the reactions of Zn with SiH₄, HCl and H₂O.³₂,³³

We have recently reported the first observation of ZnH₂, CdH₂ and HgH₂ molecules in the gas phase.³⁵⁻³⁷ The molecules were generated by the reactions of metal vapor with molecular hydrogen in the presence of an electrical discharge.

† Electronic supplementary information (ESI) available: A complete list of the observed line positions and the outputs of least-squares fitting program (Tables S1–S13). See http://dx.doi.org/10.1039/b005359d
Gaseous ZnH2, CdH2 and HgH2 were unambiguously identified by their high resolution infrared emission spectra, and the ν1 fundamental bands were rotationally analyzed to determine the r0 metal–hydrogen bond distances.35–37 The only other metal dihydrides observed in the gas phase are FeH2, BeH2 and MgH2.38–40 A complete analysis of all the vibration–rotation bands observed in the infrared emission spectra of gaseous ZnH2 and ZnD2 is presented in this paper.

2. Experiment and results

Gaseous ZnH2 and ZnD2 were generated in a furnace-discharge emission source, which was described in detail in our earlier papers.35,36 Zinc rods were placed inside an alumina tube and heated to 470 °C. The tube contained two stainless-steel electrodes, and was evacuated using a rotary pump. Pure hydrogen or deuterium (0.5–2.5 Torr) flowed slowly through the tube, and a dc discharge was created between the electrodes. The emission from the tube was focused onto the entrance aperture of a Bruker IFS 120 HR Fourier transform spectrometer. Emission spectra were recorded using a KBr beamsplitter and a HgCdTe (MCT) detector, cooled by liquid nitrogen. The spectrum of ZnH2 was recorded in the 1200–2200 cm⁻¹ spectral range using a 2200 cm⁻¹ long-wave pass filter, and the instrumental resolution was set to 0.01 cm⁻¹. In order to improve the signal-to-noise ratio, 200 scans were co-added during three hours of recording. The spectrum of ZnD2 was recorded in the 800–1600 cm⁻¹ spectral range using a 1600 cm⁻¹ long-wave pass filter. The instrumental resolution was 0.01 cm⁻¹, and 400 scans were co-added. The signal-to-noise ratios for the strongest emission lines of ZnH2 and ZnD2 were about 50 and 20, respectively.

In addition to atomic and molecular emission lines, the spectra contained blackbody emission from the hot tube and absorption lines due to atmospheric water vapor. The black-body emission profile was subtracted from the spectra, in order to obtain flat baselines. Molecular emission lines due to vibration–rotation transitions of ZnH2, ZnD2, CO, ZnD and ZnD2 were identified. Line positions were measured using the WSPECTRA program written by M. Carleer (Université Libre de Bruxelles). Emission lines of CO appeared in the ZnH2 spectrum, and were used for absolute wavenumber calibration.45 The calibration factor for ZnD2 spectrum was determined using thirteen strong atomic lines common to the ZnH2 and ZnD2 spectra. The absolute accuracy of our calibrated line positions is better than 0.001 cm⁻¹. Assignment of the vibration–rotation bands was facilitated using a color Loomis-Wood program.

An overview of the ZnH2 spectrum is shown in Fig. 1. Zinc has five stable isotopes, and their terrestrial abundances are: 64Zn (48.6%), 66Zn (27.9%), 68Zn (4.1%), 69Zn (18.8%) and 70Zn (0.6%). Lines from different isotopes of zinc were completely resolved in both spectra, and their intensity ratios match those marked with stars are from 66ZnD2 and 68ZnD2. The weaker lines (unmarked) are from the hot bands of ZnD2.

3. Data analysis

3.1. Σ → Σ and Π → Π transitions

The total energy of a linear triatomic molecule in its ground electronic state can be separated into vibrational and rotational parts:

\[ E_{\text{vib-rot}} = G(v_1, v_2, v_3) + F_{\text{rot}}(J) \]  

The vibrational energy expression includes first-order harmonic and second-order anharmonic terms:46

\[ G(v_1, v_2, v_3) = \omega_1 (v_1 + \frac{1}{2}) + \omega_2 (v_2 + 1) + \omega_3 (v_3 + \frac{1}{2}) + x_{11} (v_1 + \frac{1}{2})^2 + x_{22} (v_2 + 1)^2 + x_{33} (v_3 + \frac{1}{2})^2 + g_{22} l^2 + g_{33} l (v_1 + \frac{3}{2}) (v_2 + 1) + x_{13} (v_1 + \frac{1}{2}) (v_3 + \frac{1}{2}) + x_{23} (v_2 + 1) (v_3 + \frac{1}{2}). \]  

(2)
In this equation, \( v_1, v_2 \) and \( v_3 \) are the vibrational quantum numbers for the symmetric stretching (\( \sigma_z \)), bending (\( \pi \)), and antisymmetric stretching (\( \sigma_x \)) modes, respectively, and \( l \) is the vibrational angular momentum quantum number. For the vibrational states with \( \Sigma(l = 0) \) or \( \Pi(l = 1) \) symmetry, the following expression was used for rotational energy levels:

\[
F_\Omega(J) = B(J(J + 1) - \frac{l^2}{2}) - D(J(J + 1) - \frac{l^2}{2})^2
+ H[J(J + 1) - \frac{l^2}{2}]^3 \pm \frac{1}{2} [q_J(J + 1) + q_0 J(J + 1)]^2.
\] (3)

\( B \) is the inertial rotational constant, \( D \) and \( H \) are centrifugal distortion constants, and \( J \) is the total angular momentum quantum number (including rotation). The rotational \( l \)-type doubling parameters, \( q \) and \( q_0 \), are zero for the \( \Sigma \) states, and the \(+(-)\) sign refers to \( e / f \) parity component of the \( \Pi \) states.\(^{47}\)

We used an experimental uncertainty of 0.001 cm\(^{-1}\) for lines from the 001 \( \rightarrow \) 000, 002 \( \rightarrow \) 001 and 011\(^{1}\) \( \rightarrow \) 010 bands of ZnH\(_2\) and ZnD\(_2\). Lines from the other hot bands were less intense, and were given an uncertainty of 0.002 cm\(^{-1}\).

The absolute rotational assignments of the 001 (\( \Sigma^+ \)) fundamental bands of ZnH\(_2\) and ZnD\(_2\) were easily obtained because we observed all the rotational lines near the band origins. The intensity alternations in adjacent rotational lines and small local perturbations at high \( J's \) of the 001 (\( \Sigma^+ \)) state of both ZnH\(_2\) and ZnD\(_2\) further confirmed our absolute \( J \) assignments. The local perturbations observed in the 001 level are caused by the nearby 030 level, because both theoretical calculations\(^{27}\) and matrix isolation experiments\(^{21,31}\) had found that the frequency of the antisymmetric stretching mode is close to three times the frequency of the bending mode, i.e., \( \nu_3 \approx 3 \nu_2 \). Rotational lines of the 001 (\( \Sigma^+ \)) \( \rightarrow \) 000 (\( \Sigma^+ \)) fundamental bands were fitted using the energy expression in eqn. (3), and the ground state vibrational energy was set to zero. For the perturbed rotational levels in the 001 (\( \Sigma^+ \)) state, i.e., \( J' > 15 \) for ZnH\(_2\) and \( J' > 20 \) for ZnD\(_2\), the total energies were fitted to term values. As a result, accurate rotational constants were obtained for the 000 ground states of ZnH\(_2\) and ZnD\(_2\), while the rotational constants of the 001 states can reproduce the data only for the lower \( J's \).

The rotational assignment of the 002 (\( \Sigma^+ \)) \( \rightarrow \) 001 (\( \Sigma^+ \)), 003 (\( \Sigma^- \)) \( \rightarrow \) 002 (\( \Sigma^+ \)) and 004 (\( \Sigma^- \)) \( \rightarrow \) 003 (\( \Sigma^- \)) hot bands were obtained consecutively using lower state combination differences. The 002 (\( \Sigma^+ \)) states of both ZnH\(_2\) and ZnD\(_2\) were globally perturbed by the nearby 200 (\( \Sigma^+ \)) states. The ab initio calculations of Greene et al.\(^{21}\) have predicted that \( \nu_1 \) and \( \nu_3 \) are nearly equal in frequency. The 001 and 100 levels have opposite \( g / u \) symmetry and do not interact with each other. However, the 002 and 200 levels both have \( \Sigma^+ \) symmetry and are strongly coupled by Fermi resonance. Due to the strong mixing of the 002 and 200 levels in ZnH\(_2\), rotational lines of the 200 (\( \Sigma^+ \)) \( \rightarrow \) 001 (\( \Sigma^+ \)) combination band of ZnH\(_2\) appeared in our spectrum, and were easily assigned using lower state combination differences. The energy expression in eqn. (3) was used for all these vibrational levels, and effective spectroscopic constants were determined for all the observed isotopologues. A complete list of the observed line positions and the outputs of our least-squares fitting program have been placed in Tables S1–S7, provided as electronic supplementary information (ESI).\(^{†}\) Effective spectroscopic constants for several vibrational states of ZnH\(_2\) and ZnD\(_2\) are presented in Tables 1 and 2, respectively, and those for the minor isotopologues are in Table S8. The total energies of high \( J \) levels of the 001 (\( \Sigma^+ \)) states were fitted as term values, and the values are presented in Tables S1–S7. The effect of Fermi resonance was neglected in determination of constants of Tables 1 and 2, but the effective constants reported in these tables can reproduce the data within the experimental uncertainty (0.001 or 0.002 cm\(^{-1}\)).

The second strongest bands in both ZnH\(_2\) and ZnD\(_2\) spectra had large \( l \)-type doubling, and were assigned as the 011\(^{1}\) (\( \Pi_u \)) \( \rightarrow \) 010\(^0\) (\( \Pi_u \)) hot bands. The absolute \( J \) assignment for these bands were obtained based on the intensity alternations and the fact that \( e \) and \( f \) parity components must have the same state.

### Table 1  Effective spectroscopic constants (in cm\(^{-1}\)) for the \( \Sigma \) and \( \Pi \) vibrational states of ZnH\(_2\)

<table>
<thead>
<tr>
<th>State</th>
<th>( G_{\Omega} - G_{\text{000}} )</th>
<th>( B )</th>
<th>( D/10^{-5} )</th>
<th>( H/10^{-10} )</th>
<th>( q/10^{-2} )</th>
<th>( q_0/10^{-6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>000 (( \Sigma^+ ))</td>
<td>0.0</td>
<td>3.548 2143(86)(^{a})</td>
<td>4.9225(25)</td>
<td>4.27(22)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>001 (( \Sigma^+ ))</td>
<td>1889.433 10(24)</td>
<td>3.506 5650(83)</td>
<td>4.9001(23)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>002 (( \Sigma^+ ))</td>
<td>3772.292 98(33)</td>
<td>3.457 8091(65)</td>
<td>4.7293(10)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 (( \Sigma^+ ))</td>
<td>3712.969 42(60)</td>
<td>3.451 2141(15)</td>
<td>5.0353(57)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>003 (( \Sigma^- ))</td>
<td>5605.283 50(56)</td>
<td>3.419 5915(88)</td>
<td>4.8433(19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>004 (( \Sigma^- ))</td>
<td>7422.500 30(75)</td>
<td>3.372 528(12)</td>
<td>4.6507(31)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>010(^0) (( \Pi_u ))</td>
<td>( \nu_2 )</td>
<td>3.542 900(10)</td>
<td>4.9850(18)</td>
<td>(-5.9464(21))</td>
<td>2.920(35)</td>
<td></td>
</tr>
<tr>
<td>011(^1) (( \Pi_u ))</td>
<td>1876.966 90(24) + ( \nu_2 )</td>
<td>3.501 569(11)</td>
<td>4.9792(21)</td>
<td>(-5.8509(21))</td>
<td>2.784(41)</td>
<td></td>
</tr>
<tr>
<td>100 (( \Sigma^+ ))</td>
<td>( \nu_1 )</td>
<td>3.496 356(27)</td>
<td>4.8994(77)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>101 (( \Sigma^+ ))</td>
<td>1827.656 21(46) + ( \nu_1 )</td>
<td>3.454 273(27)</td>
<td>4.9231(77)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) The numbers in parentheses are one standard deviation statistical uncertainties in the last quoted digits.\(^{†}\) The effective constants of the 001 state can accurately reproduce the \( J = 0 \) to 15 rotational energy levels (see the text).\(^{\text{†}}\) The effect of Fermi resonance between the 002 and 200 states was neglected in determination of these constants (see the text).\(^{\text{†}}\) The wavenumbers of \( \nu_1 \) and \( \nu_2 \) could not be determined from our data. The neon matrix value (ref. 9) for \( \nu_2 \) is 632.5 cm\(^{-1}\), and \( \nu_1 \) is almost equal to \( \nu_2 \).
Table 2  Effective spectroscopic constants (in cm$^{-1}$) for the $\Sigma$ and $\Pi$ vibrational states of $^{64}$ZnD$_2$

<table>
<thead>
<tr>
<th>State</th>
<th>$G_{001} - G_{100}$</th>
<th>$B$</th>
<th>$D/10^{-5}$</th>
<th>$H/10^{-10}$</th>
<th>$q/10^{-2}$</th>
<th>$q_{SD}/10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>000 ($\Sigma_+^-$)</td>
<td>0.0</td>
<td>1.783 4239(67)*</td>
<td>1.227(11)</td>
<td>0.452(54)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>001 ($\Sigma_+^+$)</td>
<td>1371.631 34(22)</td>
<td>1.767 9889(64)</td>
<td>1.220 73(93)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>002 ($\Sigma_+^+$)</td>
<td>2732.322 41(32)</td>
<td>1.752 1750(56)</td>
<td>1.215 09(56)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>003 ($\Sigma_+^+$)</td>
<td>4076.865 17(57)</td>
<td>1.736 6911(64)</td>
<td>1.218 86(68)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>01'0 ($\Pi_0$)</td>
<td>$\nu_3$</td>
<td>1.781 7330(48)</td>
<td>1.237 46(38)</td>
<td>$-0.0744(10)$</td>
<td>0.491(8)</td>
<td></td>
</tr>
<tr>
<td>01'1 ($\Pi_1$)</td>
<td>1364.992 38(19) + $\nu_2$</td>
<td>1.766 3714(50)</td>
<td>1.234 01(48)</td>
<td>$-0.0538(10)$</td>
<td>0.466(9)</td>
<td></td>
</tr>
<tr>
<td>01'2 ($\Pi_2$)</td>
<td>2719.380 19(44) + $\nu_2$</td>
<td>1.750 5663(57)</td>
<td>1.229 74(60)</td>
<td>$-0.0353(10)$</td>
<td>0.467(10)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The numbers in parentheses are one standard deviation statistical uncertainties in the last quoted digits. $^*$ The effective constants of the 001 state can accurately reproduce the $J = 0$ to 20 rotational energy levels (see the text). $^\ddagger$ The effect of Fermi resonance between the 002 and 200 states was neglected in determining these constants (see the text). $^\ddagger$ The wavenumbers of $\nu_1$ and $\nu_2$ could not be determined from our data. The neon matrix value (ref. 9) for $\nu_2$ is 456.4 cm$^{-1}$, and $\nu_1$ is about 30 cm$^{-1}$ smaller than $\nu_3$.

3.2. Rotational $l$-type resonance

The 02'1 ($\Delta_\lambda \rightarrow 02'0$ ($\Delta_\lambda$) hot bands of $^{64}$ZnH$_2$ and $^{64}$ZnD$_2$ were rotationally assigned using the $\nu_2$ values determined in the previous section. The $f$ parity of the levels of the $\Delta$ states ($l = 2$) were not perturbed, and a simple energy level expression similar to eqn. (3) was used to fit this sub-band:

$$E_\lambda^f = G_A + B_A [J(J + 1) - \Delta_A] [J(J + 1) - \Delta_f]$$

(7)

However, the $\Delta$ state levels with $e$ parity are shifted to higher energies due to an interaction with the nearby $\Sigma^+$ states ($e$ parity). The vibrational energies of the 02'0 ($\Sigma_+^+$) and 02'1 ($\Sigma_+^+$) states are slightly smaller than those of 02'0 ($\Delta_\lambda$) and 02'1 ($\Delta_\lambda$) states, respectively, and the difference is equal to 4$g_{SD}$ (see eqn. (2)). The interaction between $\Sigma^+$ ($e$) and $\Delta$ ($e$) states of a degenerate vibrational level is due to rotational $l$-type resonance.21 Following Maki and Lide,22 we used a 2 $\times$ 2 Hamiltonian matrix to fit the $\Sigma^+$ ($e$) and $\Delta$ ($e$) states energy levels:

$$H = \begin{pmatrix} E_{\Sigma}^e & \sqrt{2W_{20}} \\ \sqrt{2W_{20}} & E_{\Delta}^e \end{pmatrix}$$

(8)

In this equation, $E_{\Sigma}^e$ is the same as that in eqn. (7), and the other two matrix elements are given by the following equations in which $x = J(J + 1)$:

$$E_{\Delta}^e = (G_A - 4g_{SD}) + B_{\Delta} (J(J + 1) - D_{\Delta}) [J(J + 1)]^2$$

(9)

$$W_{20} = \frac{1}{\sqrt{2}} (q + q_{SD}) [x(x - 2)]^{1/2}$$

(10)

For both $^{64}$ZnH$_2$ and $^{64}$ZnD$_2$ molecules, the 02'2 ($\Delta_\lambda \rightarrow 02'0$ ($\Delta_\lambda$) and 02'1 ($\Sigma_+^+$) $\rightarrow 02'0$ ($\Sigma_+^+$) hot bands were fitted simultaneously using eqns. (7)–(10), and the constants of Tables 3 and 4 were obtained. Like the other hot bands, the unknown vibrational energies of the lower states, i.e., $G(02'0)$, were set to zero and the band origins, $(G(02'1) - G(02'0))$, were determined. The $l$-type doubling constants ($q$ and $q_{SD}$) of the 020 level are very close to those of the 01'0 ($\Pi_0$) state, and the off-diagonal matrix element of eqn. (8) changes from zero (at $J = 0$ and 1) to about $-27$ cm$^{-1}$ for $^{64}$ZnH$_2$ (at $J = 21$) and $-15$ cm$^{-1}$ for $^{64}$ZnD$_2$ (at $J = 27$). We also found that the fitted values of $B_{\Delta}$ and $D_{\Delta}$ in Tables 3 and 4 remain unchanged if we fit only the $\Delta$ states $f$ levels. For the minor isotopologues, $^{66}$ZnH$_2$ and $^{66}$ZnD$_2$, only the $f$ component of the 02'1 ($\Delta_\lambda$) $\rightarrow 02'0$ ($\Delta_\lambda$) band was found and analyzed using eqn. (7), and the constants are listed in Table 58.$^d$

The $g_{SD}$ constants for the 020 vibrational levels of $^{64}$ZnH$_2$ and $^{64}$ZnD$_2$ were found to be 5.381(6) cm$^{-1}$ and 2.649(5) cm$^{-1}$,
respectively. In our previous work on BeH₂ and BeD₂, 42 we determined the g_{22} constants by calculating the difference between the 02^3(Σ_g^+) and 02^3(Δ_u) vibrational energies and dividing it by a factor of 4. Since we had used an effective energy level expression without the $C$ term for the Λ states of BeH₂ and BeD₂, instead of eqn. (7), the $[B_0]^2$ term had been added to the vibrational energies of the Λ states. Therefore, the effective g_{22} constants of 2.050(1) cm⁻¹ and 0.150(2) cm⁻¹ reported for BeH₂ and BeD₂ in ref. 42 are in fact equal to $[g_{22} - B_0]^2$ and should not be directly compared with those of $^{64}$ZnH₂ and $^{64}$ZnD₂. If one uses eqn. (7) for BeH₂ and BeD₂, the resultant g_{22} values will be 6.772(1) cm⁻¹ and 2.524(2) cm⁻¹, respectively.

3.3. Local perturbations

For both $^{64}$ZnH₂ and $^{64}$ZnD₂ molecules, high rotational levels of the 001 (Σ_u) state are perturbed by the nearby 030 (Π_u) and 030 (Π_u) states. Rotational levels of the 001 (Σ_u) state of ZnH₂ with J ≤ 17 are shifted towards higher energies, whereas the J ≥ 18 levels are shifted towards lower energies. Similarly, the rotational levels of the 001 (Σ_u) state of ZnD₂ with J ≤ 22 were shifted up and the J ≥ 23 levels were shifted down. The magnitudes of these perturbations were small, and the largest energy shifts were about 0.04 cm⁻¹, observed right at the crossing point (J = 17 for ZnH₂ and J = 22 for ZnD₂). The perturbation pattern observed in both ZnH₂ and ZnD₂ clearly indicates that the perturbing state has a larger effective B_{0} value. We estimated the effective B_{0} values of the 030 (Π_u) and 030 (Π_u) states using the B_{0} values of the 000, 010, 020, and 020 states. The 030 (Π_u) and 030 (Π_u) states have e and f parity components, but only the e parity levels can interact with the 001 (Σ_u) rotational levels. Due to the large rotational l-type doubling in the 030 (Π_u) state, the effective B_{0} value of its e parity component becomes considerably smaller than that of the 001 (Σ_u) state. Therefore, in both ZnH₂ and ZnD₂, the 030 (Π_u) state is responsible for the observed perturbations in the 001 (Σ_u) state. We constructed a 3 x 3 Hamiltonian matrix for the e parity levels of 001 (Σ_u), 030 (Π_u), and 030 (Π_u) states. The 030 (Π_u) state was included in the matrix because it interacts with the 030 (Π_u) state through rotational l-type resonance, 52 and thus has an indirect effect on the state of interest (001, Σ_u). The vibrational energy difference between the 030 and 030 states is equal to 8g_{22} (see eqn. (2)). Makì and Lide 52 have derived the Hamiltonian matrix for rotational l-type resonance between Π and Φ states. After parity transformation and including the Σ_u (e) state, we obtained the following 3 x 3 Hamiltonian matrix for the e states:

$$H = \begin{pmatrix} E_{001} & -W_{001} & 0 \\ -W_{001} & E_{001} & W_{001} \\ 0 & W_{001} & E_{001} + W_{001} \end{pmatrix}. \quad (11)$$

The matrix element connecting the Σ_u and Π_u states was fixed to zero because we knew that the Φ_u state is causing the perturbation in the 001 (Σ_u) state. The following expressions, in which J = J + 1, were used for the above matrix elements:

$$E_{001} = G_{001} + B_{001}(J(J + 1) - D_{001}(J + 1)^2) + H_{001}(J + 1)^3 \quad (12)$$

$$E_{001} = G_{001} + B_{001}[J(J + 1) - D_{001}(J + 1) - D_{001}(J + 1)^3] \quad (13)$$

$$W_{11} = q_x + q_3x \quad (15)$$

$$W_{03} = K_{03}[x(x - 2)(x - 6)]^{1/2} \quad (17)$$

The J-dependence of W_{03}, which connects the Σ and Φ states, was determined by applying the J^{3/2} operator (in the molecular frame) to the Σ state basis function. The purpose of this perturbation analysis was to obtain the unperturbed constants for the 001 (Σ_u) state, and to estimate the vibrational energy of the 030 (Π_u) state.

All rotational lines of the 001 → 000, 002 → 001, and 200 → 001 bands were fitted using the Hamiltonian matrix in eqn. (11) for the 001 levels, while the constants of 000, 002, and 200 states were fixed to the values reported in Tables 1 and 2. Rotational constants (B, D) and the l-type doubling constants (q_x, q_3x) of the 030 (Π_u) and 030 (Π_u) states were fixed to the values estimated by extrapolating the 000, 010, 020, and 020 constants. The following expression was used to estimate the B_{0} values as accurately as possible:

$$B_{0} = B_n - \frac{1}{2}(v + \frac{1}{2}) - \frac{3}{2}(v + 1) - \frac{3}{2}(v + \frac{1}{2}) + \frac{1}{2}(v + 1)^2 + \frac{3}{2}(v + \frac{1}{2})^2$$

$$+ \frac{1}{2}(v + 1)^2 + \frac{3}{2}(v + \frac{1}{2}) + \frac{1}{2}(v + 1)$$

$$+ \frac{1}{2}(v + 1)(v + \frac{1}{2}) \quad (18)$$

\[\text{Table 3 Spectroscopic constants (in cm}^{-1}\text{) for the observed rotational l-type resonance in }^{64}\text{ZnH}_2\]

<table>
<thead>
<tr>
<th>State</th>
<th>B</th>
<th>D/10^{-5}</th>
<th>g_{22}</th>
<th>q/10^{-2}</th>
<th>q_{0}/10^{-6}</th>
<th>G(02^{1}) - G(02^{0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>020</td>
<td>02^{3}(\Delta)</td>
<td>3.537 760(24)</td>
<td>5.0845(41)</td>
<td>5.3811(59)</td>
<td>-5.9478(58)</td>
<td>2.6066(97)</td>
</tr>
<tr>
<td></td>
<td>02^{0}(Σ_g^+)</td>
<td>3.530 000(51)</td>
<td>5.079(11)</td>
<td>5.3386(58)</td>
<td>-5.8508(57)</td>
<td>2.467(93)</td>
</tr>
<tr>
<td>021</td>
<td>02^{3}(\Delta)</td>
<td>3.496 783(25)</td>
<td>5.0906(44)</td>
<td>5.3386(58)</td>
<td>-5.8508(57)</td>
<td>2.467(93)</td>
</tr>
<tr>
<td></td>
<td>02^{1}(Σ_g^+)</td>
<td>3.497 946(49)</td>
<td>5.071(11)</td>
<td>5.3386(58)</td>
<td>-5.8508(57)</td>
<td>2.467(93)</td>
</tr>
</tbody>
</table>

\[\text{Table 4 Spectroscopic constants (in cm}^{-1}\text{) for the observed rotational l-type resonance in }^{64}\text{ZnD}_2\]

<table>
<thead>
<tr>
<th>State</th>
<th>B</th>
<th>D/10^{-5}</th>
<th>g_{22}</th>
<th>q/10^{-2}</th>
<th>q_{0}/10^{-6}</th>
<th>G(02^{1}) - G(02^{0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>020</td>
<td>02^{3}(\Delta)</td>
<td>1.780 183(18)</td>
<td>1.2633(20)</td>
<td>2.6491(47)</td>
<td>-2.0765(27)</td>
<td>0.440(24)</td>
</tr>
<tr>
<td></td>
<td>02^{0}(Σ_g^+)</td>
<td>1.780 306(31)</td>
<td>1.2502(34)</td>
<td>2.6491(47)</td>
<td>-2.0765(27)</td>
<td>0.440(24)</td>
</tr>
<tr>
<td>021</td>
<td>02^{3}(\Delta)</td>
<td>1.764 886(19)</td>
<td>1.2597(22)</td>
<td>2.6340(47)</td>
<td>-2.0560(27)</td>
<td>0.423(23)</td>
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<tr>
<td></td>
<td>02^{1}(Σ_g^+)</td>
<td>1.765 081(31)</td>
<td>1.2472(34)</td>
<td>2.6340(47)</td>
<td>-2.0560(27)</td>
<td>0.423(23)</td>
</tr>
</tbody>
</table>

\[\text{Table 4 Spectroscopic constants (in cm}^{-1}\text{) for the observed rotational l-type resonance in }^{64}\text{ZnD}_2\]

\[\text{Table 3 Spectroscopic constants (in cm}^{-1}\text{) for the observed rotational l-type resonance in }^{64}\text{ZnH}_2\]

\[\text{Table 4 Spectroscopic constants (in cm}^{-1}\text{) for the observed rotational l-type resonance in }^{64}\text{ZnD}_2\]
were obtained using the 000, 01 10, 02 00 and 02 20 modes. For the minor isotopologues of ZnH$_2$ and ZnD$_2$, the squares fitting resulted in determination of 0310 states of 64ZnH$_2$ and 64ZnD$_2$. A quadratic expression analogous to eqn. (18) was used to calculate the 03 30 states, because they have opposite g/u symmetry. However, the 002 and 200 states have the same symmetry (Σ$^+$), and are strongly coupled due to Fermi resonance. We clearly observed the effects of this resonance in our ZnH$_2$ spectrum: (a) The zinc isotope shift in the 002 (Σ$^+$) → 001 (Σ$^-$) band of ZnH$_2$ was unusually small compared to all regular bands (see Fig. 4), which is an indication of mixing between 002 and 200 states; (b) The vibrational band origin of the 002 (Σ$^+$) → 001 (Σ$^-$) band of ZnH$_2$ was unusually high, which indicates that the rotational levels of the 002 (Σ$^+$) state are systematically shifted towards higher energies; (c) The B$_\text{r}$ value of the 002 (Σ$^+$) state was slightly different from the value predicted by x$_3$, which indicates that this state is mixed with another state with a different B$_\text{r}$ value; d) The 200 (Σ$^+$) → 001 (Σ$^-$) combination band that should be very weak in the absence of resonance appeared in our ZnH$_2$ spectrum, and it had a small zinc isotope shift in the opposite direction of those of all other bands.

The above expression is preferred to eqn. (4), since it includes higher order terms. The constants [2;22;14; and [3;23; + 7;24; + 7;25;] were obtained using the 000, 01 10, 02 00 and 02 20 B$_{\text{r}}$ values, and were used to calculate the B$_{\text{r}}$ constants of the 003 and 03 30 states of 64ZnH$_2$ and 64ZnD$_2$. A quadratic expression analogous to eqn. (18) was used to calculate the B$_{\text{r}}$ constants.

The vibrational constants g$_{22}$ and g$_{32}$ for the perturbing states (030 and 033) were fixed to the extrapolated values (see the text). The numbers in parentheses are one standard deviation statistical uncertainties in the last quoted digits.

### Table 5

<table>
<thead>
<tr>
<th>Constant$^a$</th>
<th>64ZnH$_2$</th>
<th>64ZnD$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(030)$^0$</td>
<td>3.532 80</td>
<td>1.778 78</td>
</tr>
<tr>
<td>B(033)$^0$</td>
<td>3.535 27</td>
<td>1.779 17</td>
</tr>
<tr>
<td>10$^D$B(030)</td>
<td>5.221</td>
<td>1.305</td>
</tr>
<tr>
<td>10$^D$B(033)</td>
<td>5.949</td>
<td>2.079</td>
</tr>
<tr>
<td>10$^D$g$_{030}$</td>
<td>2.29</td>
<td>0.388</td>
</tr>
<tr>
<td>g$_{32}$</td>
<td>5.3811</td>
<td>2.6941</td>
</tr>
<tr>
<td>G(030) – G(000)</td>
<td>1906.1992</td>
<td>1378.3604</td>
</tr>
</tbody>
</table>

$^a$ The constants reported in this table can reproduce all the observed rotational energy levels of the 001 (Σ$^+$) states within their experimental uncertainties. $^b$ The constants B, D, q, g, and g$_{22}$ for the perturbing states (030 and 033) were fixed to the extrapolated values (see the text). The numbers in parentheses are one standard deviation statistical uncertainties in the last quoted digits.

The Σ–Φ interaction constants (K$_{\Sigma\Phi}$) were determined to be 3.456(13) × 10$^{-5}$ cm$^{-1}$ and 1.672(14) × 10$^{-5}$ cm$^{-1}$ for 64ZnH$_2$ and 64ZnD$_2$, respectively. The off-diagonal matrix element W$_{03}$ is zero for J < 3, and it increases rapidly with J. At the highest observed rotational levels of 64ZnH$_2$ (J = 28) and 64ZnD$_2$ (J = 35), W$_{03}$ is about 0.8 cm$^{-1}$ and 0.3 cm$^{-1}$, respectively. Although the vibrational energies of the 03 30 states (G$_{03}$) of 64ZnH$_2$ and 64ZnD$_2$ have statistical uncertainties of ~0.01 cm$^{-1}$ in Table 5, we estimate an absolute accuracy of about 0.5 cm$^{-1}$ for these energies, because several constants in our fits were fixed to the extrapolated values. The outputs of the least-squares fits and the corresponding constants for 64ZnH$_2$, 64ZnD$_2$, 66ZnD$_2$, and 68ZnD$_2$ have been placed in Table S9.

A few rotational lines of the 01 11 (Π$^-$) states of both ZnH$_2$ and ZnD$_2$ were perturbed by the nearby 04 00 vibrational level, which has 04 00 (Σ$^+$), 04 00 (Π$^+$), and 04 00 (Π$^-$) states. In this case, it was not clear which states were causing the perturbations observed in e and f parity components of the 01 11 (Π$^-$) state. We tried to perform a similar perturbation fit for this state by estimating the constants of the 04 00 level, but we were unable to fit the e and f parity components together.

### 3.4. Fermi resonance

*Ab initio* calculations at the MP2, CCSD(T) and DFT(B3LYP) levels of theory showed that the vibrational frequencies of the symmetric stretching (ω$_1$) and antisymmetric stretching (ω$_2$) modes are very close to each other in both ZnH$_2$ and ZnD$_2$. In case of ZnD$_2$, ω$_2$ was predicted to be larger than ω$_1$ by about 30 cm$^{-1}$. This energy separation is smaller for ZnH$_2$, and in fact the results of MP2, CCSD(T) and DFT(B3LYP) calculations were inconsistent in determining which vibrational mode has the higher frequency. The highest level calculation to date, CCSD(T) with a relatively large basis set, predicted that ω$_2$ is slightly larger than ω$_1$ for ZnH$_2$.

There is no interaction between the 100 (Σ$^+$) and 001 (Σ$^-$) states, because they have opposite g/u symmetry. However, the 002 and 200 states have the same symmetry (Σ$^+$), and are strongly coupled due to Fermi resonance. We clearly observed the effects of this resonance in our ZnH$_2$ spectrum: (a) The zinc isotope shift in the 002 (Σ$^+$) → 001 (Σ$^-$) band of ZnH$_2$ was unusually small compared to all regular bands (see Fig. 4), which is an indication of mixing between 002 and 200 states; (b) The vibrational band origin of the 002 (Σ$^+$) → 001 (Σ$^-$) band of ZnH$_2$ was unusually high, which indicates that the rotational levels of the 002 (Σ$^+$) state are systematically shifted towards higher energies; (c) The B$_{\text{r}}$ value of the 002 (Σ$^+$) state was slightly different from the value predicted by x$_3$, which indicates that this state is mixed with another state with a different B$_{\text{r}}$ value; d) The 200 (Σ$^+$) → 001 (Σ$^-$) combination band that should be very weak in the absence of resonance appeared in our ZnH$_2$ spectrum, and it had a small zinc isotope shift in the opposite direction of those of all other bands.

The 002 (Σ$^+$) and 200 (Σ$^-$) states of ZnH$_2$ are pushed apart due to Fermi resonance. More precisely, rotational levels of the 002 (Σ$^+$) state are shifted towards higher energies, and those of the 200 (Σ$^-$) state are shifted towards lower energies by exactly the same amount. Therefore, for each value of J, the sum of their energies remains unchanged. It is straightforward to show that the sum of vibrational energies ($G_{\Sigma^+} = G_{\text{iso}} + G_{\text{aniso}}$) rotational constants [B$_{\text{sum}} = B_{\text{002}} + B_{\text{200}}$], and centrifugal distortion constants [D$_{\text{sum}} = D_{\text{002}} + D_{\text{200}}$] also remain unchanged. The effective G$_{\Sigma^+}$, B$_{\Sigma^+}$ and D$_{\Sigma^+}$ constants of the 002 (Σ$^+$) and 200 (Σ$^-$) states of 64ZnH$_2$ (Table 1) were used to

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*Fig. 4* An expanded view of the ZnH$_2$ spectrum showing the zinc isotope shifts in two R-branch lines. The zinc isotope shifts in the 002 → 001 hot band are unusually small, due to the coupling between 002 and 200 states (Fermi resonance).
calculate these sums. We performed a Fermi resonance fit for these states using the following 2 × 2 Hamiltonian matrix, which is similar to the one used for the 100 (Σ_g^+) and 020 (Σ_g^−) states of the CO_2 molecule: 46,47

\[
H = \begin{pmatrix}
E_0^B(002) & -K_{00} \\
-K_{00} & E_0^G(200)
\end{pmatrix}.
\]  

(19)

The diagonal elements in the above matrix are simple energy expressions for the Σ states with G_{000}, B_{000} and D_{000} constants, and K_{000} is the perturbation matrix element that has no J-dependence. All rotational lines of the 002 → 001, 200 → 001 and 003 → 200 bands of ZnH_2 were fitted using the Hamiltonian matrix in eqn. (19) for the 002 and 200 states, and the constants of 001 and 003 states were fixed to the previously determined values (Tables 5 and 1, respectively). The sums of G_{000}, B_{000} and D_{000} constants for the 002 (Σ_g^+) and 200 (Σ_g^−) states, i.e., G_{sum}, B_{sum} and D_{sum}, were also fixed to the values calculated from Table 1. In order to determine the off-diagonal matrix element (K_{000}) and the unperturbed constants for these states, we had to fix at least one more parameter in our fit. We chose to fix the D_{2000} constant to the extrapolated value, i.e., D_{2000} = 2200 → 0000, because the 000 (Σ_g^+) and 100 (Σ_u^+) states are not perturbed, and their D_{000} constants are reliable. Since no rotational line with J > 16 was observed for the 100 (Σ_g^+) and 200 (Σ_g^−) states, we fitted only the low-J lines of the 001 → 000 band to obtain a comparable D_{000} appropriate for extrapolation (see Table S1†). The constant D_{2000} was then calculated to be 4.8891 × 10^{-2} cm^{-1}, and was held fixed in the least-squares fitting. Only three parameters, i.e., G_{000}, B_{000} and K_{000}, were allowed to vary in the fit, and the results are presented in Table 6. The constants of the 002 (Σ_g^+) state were then calculated by subtracting G_{000}, B_{000} and D_{000} from G_{sum}, B_{sum} and D_{sum}, respectively. The constants of Table 6 can reproduce all the observed energy levels of the 002 and 200 states within their experimental uncertainties (0.001 or 0.002 cm^{-1}). The outputs of the least-squares fitting program and the corresponding constants for 64ZnH_2 and 66ZnH_2 are in Table S10.† The off-diagonal matrix element (K_{000}) was determined to be 28.168(7) cm^{-1}. The unperturbed G_{000} constant in Table 6 is about 19 cm^{-1} larger than G_{2000} but this energy separation increases to about 59 cm^{-1} (Table 1) due to the off-diagonal matrix element (K_{000}). Although the unperturbed G_{000} constant of 64ZnH_2 has an uncertainty of ≈ 0.02 cm^{-1} in the fit (Table 6), we estimate an absolute accuracy of about 0.5 cm^{-1} for G_{000} and G_{2000}, because the D_{2000} constant in our fit was fixed to an extrapolated value.

The constants of Table 6 can be used to calculate the eigenfunctions for the 002 (Σ_g^+) and 200 (Σ_g^−) states from their basis functions, and to quantify the extent of mixing between the two states. The eigenfunctions of the perturbed states are related to their unperturbed eigenfunctions by the following equations: 46,47

\[
1002^\prime,J) = c_11002,J) - c_2200,J) \tag{20}
\]

\[
1200^\prime,J) = c_21002,J) + c_1200,J) \tag{21}
\]

In these equations, c_1 and c_2 are equal to cos θ and sin θ, respectively, and of course c_1^2 + c_2^2 = 1. For each value of J, the mixing coefficients c_1^2 and c_2^2 can be calculated using the following equation, 46 which relates θ to the matrix elements of eqn. (19):

\[
tan2θ = \frac{2K_{000}}{E_0^B(002) - E_0^G(200)}.
\]

(22)

The mixing coefficients c_1^2 and c_2^2 were determined for J = 0 to 15 levels of the 002 (Σ_g^+) and 200 (Σ_g^−) states of 64ZnH_2. The extent of mixing decreases very slowly with increasing J; for example, there is a 66%–34% mixture at J = 0, and a 69%–31% mixture at J = 15. Similar calculations for 64ZnH_2 and 68ZnH_2 showed mixing almost to the same extent (see Table S11†). Therefore, the observed 002 (Σ_g^+) state of ZnH_2 can be considered approximately as a 2/3 : 1/3 mixture of the unperturbed 002 and 200 states, and vice versa.

Another way to quantify the mixing between these states is to consider the zinc isotope shifts for the 002 (Σ_g^+) → 001 (Σ_u^+) band. For the unperturbed bands of ZnH_2 in the ν_5 region, i.e., ν_1, ν_2, ν_3 + 1, we observed 64Zn:66Zn isotope shift is about 0.8 cm^{-1}. In other words, c_2 for 66ZnH_2 is larger than that of 64ZnH_2 by about 0.8 cm^{-1}. On the other hand, c_1 has no dependence on the mass of zinc atoms within the harmonic oscillator approximation. Therefore, the 64Zn:66Zn isotope shifts for the 002 (Σ_g^+) → 001 (Σ_u^+) and 200 (Σ_g^−) → 001 (Σ_u^+) bands are expected to be +0.8 and −0.8 cm^{-1}, respectively, in the absence of Fermi resonance. The observed 64Zn:66Zn isotope shift of the 002 (Σ_g^+) → 001 (Σ_u^+) band of ZnH_2 was about +0.2 cm^{-1}, which indicates that the observed 002 (Σ_g^+) state is approximately a 62%–38% mixture of the unperturbed 002 and 200 states, consistent with the more accurate results obtained from eqns. (20)–(22). The energy separation between ν_1 and ν_0 of ZnD_2 is larger than that of ZnH_2, 21 and the Fermi resonance effects in ZnD_2 were not as severe as in ZnH_2. We did not observe the 002 (Σ_g^+) → 001 (Σ_u^+) combination band for ZnD_2, because the extent of mixing between the 200 and 002 states is relatively small. In this case, the observed 64Zn:66Zn isotope shift was about 1.2 cm^{-1} for the unperturbed bands in the ν_5 region, and about 1.0 cm^{-1} for the 002 (Σ_g^+) → 001 (Σ_u^+) band. Based on the isotope shifts, we estimate that the observed 002 (Σ_g^+) state of ZnD_2 is approximately a 92%–8% mixture of the unperturbed 002 and 200 states. There is yet another way to estimate the mixing coefficients for the 002 and 200 states of ZnD_2. The effective B_{002} constant of 64ZnD_2 (observed) is related to the unperturbed B'_{002} and B''_{000} constants by the following equation: 47

\[
B'_{002}\text{(obs.)} \approx c_1^2 B'_{002} + c_2^2 B''_{000}.
\]

(23)

The unperturbed B'_{002} and B''_{000} constants of 64ZnD_2 were estimated using ν_1 and ν_2, respectively, and the effective B_{002} constant was taken from Table 2. The mixing coefficients, c_1^2 and c_2^2, were found to be 93% and 7%, respectively, consistent with the ones calculated from zinc isotope shifts.

<table>
<thead>
<tr>
<th>State</th>
<th>G_{00} - G_{000}</th>
<th>B</th>
<th>D/10^4</th>
<th>K_{00} (Σ,Σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[002 + 200]^2</td>
<td>7485.262 40^a</td>
<td>6.909 050^b</td>
<td>9.7646^c</td>
<td></td>
</tr>
<tr>
<td>002 (Σ_u^−)^d</td>
<td>3751.928^e</td>
<td>3.464 920^f</td>
<td>4.8755^g</td>
<td>28.1680(73)^f</td>
</tr>
<tr>
<td>002 (Σ_u^−)^d</td>
<td>3733.334(24)^h</td>
<td>3.444 130(16)^i</td>
<td>4.8891^j</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Sum of the effective constants for the 200 and 002 states, calculated directly from Table 1 and held fixed in the least-squares fitting (see the text). \(^{b}\) These constants were determined by least-squares fitting. The numbers in parentheses are 1σ uncertainties in the last quoted digits. \(^{c}\) D_{2000} was calculated using D_{000} and D_{000} constants, and held fixed in the fit (see the text). \(^{d}\) The unperturbed constants of the 002 state were finally calculated by subtracting G_{000}, B_{000} and D_{000} from G_{sum}, B_{sum} and D_{sum}, respectively (see the text).
3.5. Determination of bond lengths

The $B_{000}$ constants of $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$, taken from Tables 1 and 2, were used to determine the $r_0$ bond lengths directly from the moment of inertia equation. The $r_0$ values obtained for $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$ are 1.535 274(2) Å and 1.531 846(3) Å, respectively. Their difference is in the fourth significant figure, and is due to the fact that the 000 ground state of $\text{ZnD}_2$ lies lower than that of $\text{ZnH}_2$ on the potential energy surface.

The vibration–rotation interaction constants ($x_1$, $x_2$, and $x_3$ in eqn. (4)) were determined by taking the differences between the ground state rotational constant ($B_{000}$) and the $B_k$ values of the 100, 01 0, and 001 states, respectively. The equilibrium rotational constant ($B_e$) was then calculated for both $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$ using their $B_{000}$ values and the three $x$'s. The equilibrium constants of $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$ determined in this study are listed in Table 7, and those for the minor isotopologues are in Table S12. Although eqn. (18) for $B_{012}$ is more accurate than eqn. (4), we did not use it for calculation of $B_e$, because our experimental data are not sufficient for determination of some higher order constants in eqn. (18), i.e., $\gamma_{12}$ for both isotopologues and $\gamma_{11}$ for $^{64}\text{ZnD}_2$. The equilibrium centrifugal distortion constant ($D_e$) was calculated in a similar way, using a linear equation analogous to eqn. (4) for the $D_0$ and $D_1$ values.

Using the $B_k$ values of 3.600 269(31) cm$^{-1}$ and 1.801 985(25) cm$^{-1}$ for $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$, respectively, we obtained the equilibrium bond distances ($r_0$) of these isotopologues independently. The $r_0$ values were determined to be 1.524 13(1) Å and 1.523 94(1) Å for $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$, respectively. The difference in the $r_0$ values of $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$ is very small (only about 0.01%), but still considerably larger than the statistical uncertainties. This discrepancy appears to be due to the breakdown of Born–Oppenheimer approximation or the exclusion of higher order $\gamma$ constants in determination of $B_e$. In order to examine the contribution of $\gamma$ constants in this discrepancy, we recalculated the $B_k$ constants of $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$, this time from eqn. (18), by fixing the $\gamma_{12}$ constant of $^{64}\text{ZnD}_2$ to the mass-scaled value and setting the unknown $\gamma_{11}$ constants to zero. The new $r_0$ values turned out to be 1.524 062(2) Å and 1.523 863(3) Å for $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$, respectively, and their difference is still about 0.01%. Therefore, we believe that the main reason for this discrepancy is the breakdown of Born–Oppenheimer approximation.

In polyatomic molecules for which the available spectroscopic data are not sufficient to determine the equilibrium bond lengths, it is common to calculate the $r_0$ structure by using the moments of inertia of isotopically substituted molecules.54–57 For example, in our earlier paper on CdH$_2$ and CdD$_2$, we could not determine $B_e$ and $r_0$ due to the lack of data, and we used the $B_{000}$ values of CdH$_2$ and CdD$_2$ together to obtain the $r_0$ bond length.37 We have determined both $r_0$ and $r_e$ for the $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$ molecules independently, and an average $r_0$ bond length is not necessary. We calculated $r_0$ for this molecule only to compare it with the $r_0$ and $r_e$ values. The following equation was used to estimate the $r_0$ bond length:56

$$ \frac{1}{r_0^2} - \frac{1}{r_e^2} = 2C(\mu_0 - \mu_1). $$

(24)

In this equation, $r_0^2$ and $r_e^2$ are the moments of inertia calculated from the $B_{000}$ values of $^{64}\text{ZnD}_2$ and $^{64}\text{ZnH}_2$, respectively, and $\mu_0$ and $\mu_1$ are the atomic masses for deuterium and hydrogen. The $r_e$ bond length calculated from eqn. (24) is 1.528 41 Å, which lies between the $r_0$ and $r_e$ values, qualitatively consistent with the predictions of Watson57 for the relative magnitudes of $r_0$, $r_e$, and $r_0$.

We also performed ab initio calculations for the bond length of gaseous $\text{ZnH}_2$ using the Gaussian 03 program.56 The 6-311++G(3df, 3pd) basis set was used at the HF, DFT(B3LYP), MP2, MP3, MP4(SDQ), CISD, CCD and QCISD levels of theory, and the computed $r_e$ values were in the range of 1.516 Å to 1.574 Å. The MP4(SDQ) method predicted 1.530 Å for $r_e$, which was the closest value to the experimental equilibrium bond lengths. The results of these calculations are presented in Table S13.

3.6. Vibrational analysis

A few anharmonicity constants in eqn. (2) were directly calculated from our experimental band origins. The $x_{13}$ constant was obtained for $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$ by taking the difference between the 101 to 100 and 001 to 000 band origins. Similarly, $x_{23}$ constants were calculated by taking the difference between the 011 to 010 and 010 to 001 band origins. Furthermore, the difference between the 002 to 001 and 001 to 000 band origins is equal to $2x_{13}$ (see eqn. (2)), but the 002 state is perturbed by Fermi resonance. We used the unperturbed $G_{002}$ (from Table 6) to calculate this difference for $^{64}\text{ZnH}_2$ and to obtain the $x_{13}$ constant. In the case of $^{64}\text{ZnD}_2$, we had to use the slightly perturbed $G_{002}$ from Table 2, and the calculated $x_{13}$ constant is not reliable. All the hot bands of $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$ had smaller origins compared to the $x_{13}$ fundamental bands, and thus the $x_{13}$, $x_{23}$, and $x_{33}$ constants have negative values (see Table 7).

The equilibrium vibrational frequency of the antisymmetric stretching mode ($\omega_{33}$) was calculated simply by

$$ \nu_3 \text{ (obs.)} = G_{000} - G_{001} = \nu_3 + 1/2x_{13} + x_{23} + 2x_{33}, $$

(25)

which is derived from eqn. (2). The $\omega_{33}$ values for $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$ turned out to be 1959.72 cm$^{-1}$ and 1404.87 cm$^{-1}$, respectively, the latter being uncertain by about 5 cm$^{-1}$ due to the error in determination of $x_{13}$ for $^{64}\text{ZnD}_2$. The equilibrium vibrational frequency of the symmetric stretching mode ($\omega_{13}$) was estimated using Kratzer’s equation, which applies to diatomic and symmetric linear triatomic molecules:57

$$ \omega_{13} = \frac{4\omega_{33}^2}{\omega_{33}}. $$

(26)

Using the $B_e$ and $D_e$ constants of Table 7, we estimated $\omega_{13}$ to be 1958 cm$^{-1}$ and 1385 cm$^{-1}$ for $^{64}\text{ZnH}_2$ and $^{64}\text{ZnD}_2$, respectively. Our results indicate that $\omega_{13}$ is larger than $\omega_{33}$ for both $\text{ZnH}_2$ and $\text{ZnD}_2$, and their difference is larger in $\text{ZnD}_2$. The
The $\nu_2$ values estimated from eqn. (27) are 656 cm$^{-1}$ and 474 cm$^{-1}$ for $^{64}$ZnH$_2$ and $^{66}$ZnD$_2$, respectively, and the latter has a larger uncertainty due to the small error in calculation of $\nu_2$ for $^{66}$ZnD$_2$.

We also computed the harmonic vibrational frequencies of all isotopologues of ZnH$_2$ with the Gaussian 03 program, using HF, MP2 and DFT(B3LYP) methods with the 6-311+G(3df,3pd) basis set, and the results are shown in Table S13.† The values of 1915, 643 and 1927 cm$^{-1}$ were obtained for $\nu_1$ ($\sigma_g$), $\nu_2$ ($\pi_g$), and $\omega$ ($\sigma_u$) of $^{64}$ZnH$_2$, respectively, using the DFT(B3LYP) method. The corresponding frequencies for $^{64}$ZnD$_2$ were computed to be 1355, 462 and 1384 cm$^{-1}$, respectively, using the same method. These numbers differ slightly from the ones reported in ref. 9 because we used a tighter convergence criterion in the Gaussian 03 program.

The other constants in eqn. (2), i.e., $\kappa_1$, $\kappa_2$ and $\kappa_3$, could not be determined from our data, and therefore, the absolute vibrational energies of the 100 ($\Sigma_g^+$), 010 ($\Pi_u$) and 020 ($\Delta_u$) states are not known with experimental accuracy. However, the vibrational energies of the 200 ($\Sigma_u^+$) state of ZnH$_2$ and the 030 ($\Phi_g$) state of both ZnH$_2$ and ZnD$_2$ (Tables 5 and 6) have reasonable accuracies, and may be used to estimate roughly the vibrational energies of the 100, 010 and 020 states.

4. Discussion

4.1. Isotope effects

For a symmetric linear triatomic molecule such as ZnH$_2$, the vibrational frequencies of different isotopologues are related by the following equations:

$$\frac{\nu_i'}{\nu_i} = \frac{m_i}{m_i'} \left( \frac{1}{\alpha} \right)^{\frac{1}{2}}$$

$$\frac{\omega_1}{\omega_2} = \frac{m_1}{m_2} \left( \frac{m_2}{m_1} \right)^{\frac{1}{2}} = \frac{Z_2}{Z_1}$$

In these equations, $m_i$ and $m_i'$ are atomic masses of hydrogen (or deuterium) and zinc, respectively, and $M$ is the total mass of the molecule. We observed the $\nu_1$ fundamentals for several isotopologues of ZnH$_2$, and we also estimated $\nu_2$ and $\nu_3$ for $^{64}$ZnH$_2$, $^{64}$ZnD$_2$, $^{68}$ZnH$_2$, $^{68}$ZnD$_2$ and $^{64}$ZnD$_2$. The observed $^{64}$Zn: $^{68}$Zn isotope shift for the $\nu_1$ fundamental band of ZnH$_2$ is 0.837 cm$^{-1}$, which corresponds to a ratio of 1.00044 between the $\nu_1$ fundamentals of $^{64}$ZnH$_2$ and $^{68}$ZnH$_2$. The ratio predicted by eqn. (28) is 1.00046, and the discrepancy is in the sixth significant figure. Similarly, the observed $^{64}$Zn: $^{68}$Zn isotope shift for the $\nu_5$ fundamental band of ZnD$_2$ is 1.194 cm$^{-1}$, corresponding to a ratio of 1.00087 between the $\nu_5$ fundamentals of $^{64}$ZnD$_2$ and $^{68}$ZnD$_2$, whereas a ratio of 1.00090 is predicted by eqn. (29). The observed ratio between the $\nu_1$ fundamentals of $^{64}$ZnH$_2$ and $^{64}$ZnD$_2$ (Table 5) is 1.3775 and the predicted ratio from eqn. (29) is 1.3926. If we use the estimated $\nu_2$ frequencies from Table 7 instead, the agreement becomes better and a ratio of 1.3950 is obtained. The observed $^H$ : $^D$ isotopic ratios for $\nu_1$ and $\nu_2$ (Table 7) are 1.4136 and 1.3849, respectively, and the predicted ratios from eqns. (28) and (29) are 1.4137 and 1.3926, respectively.

Simple isotopic relations exist for the $\nu_1$, $\nu_2$ and $\nu_3$ constants of symmetric linear triatomic molecules. These constants are not sensitive to the mass of central atom, and in the case of ZnH$_2$ they should change only when hydrogen is substituted with deuterium. The mass dependences of $B_e$ and $C_i$ are given in eqns. (5) and (6), and the mass dependence of $D_e$ is easily obtained by combining eqns. (5), (26) and (28). The observed ratios between the $B_e$, $C_i$ and $D_e$ constants of $^{64}$ZnH$_2$ and $^{64}$ZnD$_2$ are 1.9979, 2.8313 and 3.9912, respectively, whereas the predicted ratios are 1.9985, 2.8252 and 3.9939, respectively. The other constant for which a relatively simple mass dependence can be found is the $\nu_1$-type doubling constant ($q$). This constant is related to $B_e$, $\omega_2$ and $\omega_3$ constants via eqn. (27), and its mass dependence is obtained by combining eqns. (5), (27) and (29). The observed ratio between $q_{\nu_1}$ constants of $^{64}$ZnH$_2$ and $^{64}$ZnD$_2$ is 2.8665 and the predicted ratio is 2.8680. Overall, the observed isotope effects are consistent with the theoretical predictions. The $r_e$ values for all the isotopologues should be the same if the Born–Oppenheimer approximation is exact. We found that $r_e$ values are the same for different isotopes of zinc, within their experimental uncertainties. However, the $r_e$ values of $^{64}$ZnH$_2$ and $^{64}$ZnD$_2$ (Table 7) differ in the fifth significant figure, and this is mainly due to the breakdown of the Born–Oppenheimer approximation.

4.2. Relative stability of gaseous ZnH$_2$

Gaseous ZnH$_2$ has been predicted to have a slightly higher energy than the ground state Zn (g) + H$_2$ (g), and there is a large barrier to insertion for ground state Zn atoms into the H–H bond. However, when zinc atoms are excited to the metastable $^3$P state in the presence of an electrical discharge, they can insert into the H–H bond, leading to an exothermic production of gaseous ZnH$_2$. Breaking the first Zn–H bond in ZnH$_2$ requires a significant amount of energy, while the second bond (ZnH) can be broken by a small fraction of that energy. We used a combination of experimental and theoretical data to calculate these bond energies:

$$ZnH_2 (g) \rightarrow ZnH (g) + H (g).$$

$$ZnH (g) \rightarrow Zn (g) + H (g).$$

The best $ab initio$ theoretical value for the heat of formation of gaseous ZnH$_2$ from zinc vapor and molecular hydrogen$^{27}$ is +7.6 kcal mol$^{-1}$, and the experimental values for dissociation energies of H$_2$ and ZnH are 103.3 and 19.6 kcal mol$^{-1}$, respectively.$^{60}$ Therefore, the dissociation energy of the first Zn–H bond in ZnH$_2$ is estimated to be 76.1 kcal mol$^{-1}$, nearly four times larger than that of the second bond. The relative energies of gaseous MH and MH$_2$ molecules (M = Zn, Be and Mg) are compared in a simple diagram in Fig. 5. The best $ab initio$ theoretical values for the heats of formation of

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**Fig. 5** A diagram showing the relative energies of gaseous metal monohydrides and dihydrides. For each metal (M), the energy of the ground state M (g) + H$_2$ (g) was taken as zero.
gaseous \( \text{BeH}_2 \) and \( \text{MgH}_2 \) from metal vapor and molecular hydrogen are \(-37.6\) and \(+3.6\) kcal mol\(^{-1}\), respectively.\(^{61,62}\) On the other hand, the experimental dissociation energies of \( \text{BeH} \) and \( \text{MgH} \) are 46.9 and 29.3 kcal mol\(^{-1}\), respectively (see Fig. 5).\(^{63,64}\) Therefore, the dissociation energies of the first metal-hydrogen bond in gaseous \( \text{BeH}_2 \) and \( \text{MgH}_2 \) are estimated to be 94.0 and 70.4 kcal mol\(^{-1}\), respectively. Based on the energies required to break the first metal-hydrogen bonds, \( \text{BeH}_2 \rightarrow \text{BeH} + \text{H} \) (g), the order of stability is \( \text{BeH}_2 > \text{ZnH}_2 > \text{MgH}_2 \). It turns out that gaseous \( \text{CdH}_2 \) and \( \text{HgH}_2 \) (group 12) similarly lie between \( \text{BeH}_2 \) and \( \text{MgH}_2 \) in this series.\(^{65,66}\) The other dihydrides of group 2 elements, i.e., \( \text{CaH}_2, \text{SrH}_2 \) and \( \text{BaH}_2 \), have not been detected in the gas phase yet, and our efforts to generate these molecules have been unsuccessful.

5. Conclusions

High resolution infrared emission spectra of gaseous \( \text{ZnH}_2 \) and \( \text{ZnD}_2 \) in the \( \nu_3 \) region were analyzed. The \( \nu_3 \) fundamentals of the most abundant isotopologues, \( ^{64}\text{ZnH}_2 \) and \( ^{64}\text{ZnD}_2 \), were observed at 1889.433 cm\(^{-1}\) and 1371.631 cm\(^{-1}\), respectively, and the band origins for the minor isotopes of zinc appeared at slightly lower wavenumbers, consistent with the theoretical predictions. In addition to the \( \nu_3 \) fundamental bands of \( ^{64}\text{ZnH}_2 \), \( ^{68}\text{ZnH}_2 \), \( ^{62}\text{ZnH}_2 \), \( ^{62}\text{ZnD}_2 \) and \( ^{68}\text{ZnD}_2 \), several hot bands involving \( \nu_1 \) and \( \nu_2 \) were assigned and analyzed. Spectroscopic constants were obtained for each observed vibrational level by fitting the data to analytic energy level expressions. Rotational \( \Lambda \)-type doubling and \( \Lambda \)-type resonance, local perturbations, and Fermi resonances were observed in the vibration-rotation bands of both \( \text{ZnH}_2 \) and \( \text{ZnD}_2 \), and equilibrium vibrational frequencies (\( \omega_1 \), \( \omega_2 \) and \( \omega_3 \)) were estimated. Using the rotational constants of the 000, 100, 010 and 001 vibrational levels, the equilibrium rotational constants \( B_0 \) of \( ^{64}\text{ZnH}_2 \) and \( ^{64}\text{ZnD}_2 \) were determined to be 3.600 269(31) cm\(^{-1}\) and 1.801 985(25) cm\(^{-1}\), respectively, and the associated equilibrium bond lengths \( r_e \) were found to be 1.524 13(1) \( \text{Å} \) and 1.523 94(1) \( \text{Å} \), respectively. The difference between the \( r_e \) values of \( ^{64}\text{ZnH}_2 \) and \( ^{64}\text{ZnD}_2 \) is about 0.01%, and is mainly due to the breakdown of the Born-Oppenheimer approximation.

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