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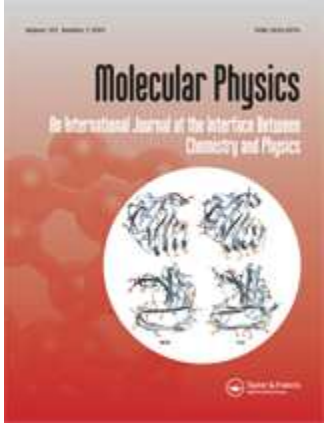

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A theoretical study of ZnH_2, a case of very strong Darling-Dennison resonance

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Abstract

The metastable linear ZnH_2 molecule in its $X\,^1\Sigma_g^+$ electronic ground state has been investigated by the coupled cluster method CCSD(T) in conjunction with a small-core pseudopotential for the zinc atom. Using three pieces of spectroscopic information for the most abundant isotopomer $^{64}ZnH_2$, an accurate near-equilibrium potential energy function (PEF) has been constructed and used in variational calculations of rovibrational energies and wave functions. The ν_1 and ν_2 band origins (in cm^{-1}) for $^{64}ZnH_2$ and $^{64}ZnD_2$ (in parentheses) are predicted at 1886.4(1349.7) and 635.1(459.8), respectively. $^{64}ZnH_2$ is characterized by strong Darling-Dennison and *l*-type rotational resonances. Various perturbations are analyzed in detail, partly making use of calculated expectation values of the vibrational quantum number $|l|$. Einstein coefficients of spontaneous emission are predicted for several transitions.

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1. Introduction

In a series of papers by Bernath and coworkers, three dihydrides of group 12 transition metals (ZnH_2, CdH_2 and HgH_2) have been studied by high-resolution infrared emission spectroscopy and a wealth of precise information on various rovibrational transitions of different isotopomers could be obtained [1-6]. The largest amount of spectroscopic data was collected for ZnH_2 isotopomers. For the most abundant species $^{64}ZnH_2$, as many as 14 different vibrational states (up to the third overtone of the antisymmetric stretching vibration ν_3) were accessible in the emission experiments and several molecular constants were determined through extensive analysis [5, 6].

Despite of the great success of the experimental work, there is still much room for predictions from theory. Following our recent work on HgH_2 [7] and CdH_2 [8], the present paper reports a thorough theoretical investigation of ZnH_2 in its linear electronic ground-state ($X\,^1\Sigma_g^+$). Previously published theoretical work dealing with spectroscopic properties for ZnH_2 is scarce and was restricted to the harmonic approximation in the calculation of vibrational wavenumbers [9, 10]. The present paper deals with the construction of an accurate potential energy surface up to energies of ca. 15 000 cm^{-1} above equilibrium, obtained from coupled cluster calculations in combination with a high-quality pseudopotential for the zinc atom and making use of a few pieces of spectroscopic information. Together with an ab initio electric dipole moment function, rovibrational term energies and wave functions as well as infrared intensities and Einstein coefficients of spontaneous emission have been calculated. Particular emphasis is given to the analysis of perturbations which were found in several emission bands [5, 6]. As we have shown recently for CdH_2 [8], theory may be very useful in the elucidation of the nature of perturbing states. In particular, it was demonstrated that rotational levels within the $(v_1,v_2^l,v_3) = (0,0^0,1)$ vibrational state of $^{114}CdH_2$ are perturbed by $(0,3^3,0)$e levels which, already for moderately large values of the rotational quantum number J, may undergo strong rotational *l*-type resonance interaction with the higher-lying $(0,3^1,0)$e levels. Likewise, the experimentally found perturbations of the $(0,1^1,1)$e levels were attributed to local interactions with $(0,4^2,0)$e levels. In addition, a rather complex picture of perturbations was established in the region of the Darling-Dennison resonance pair $(2,0^0,0)$ / $(0,0^0,2)$.

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2. Potential energy and electric dipole moment functions

The coupled cluster method CCSD(T) [11] in conjunction with a small-core energy-consistent pseudopotential (PP) for the zinc atom [12] was used for the calculation of a potential energy function (PEF) and an electric dipole moment function (EDMF) of zinc dihydride. The core of the central atom was chosen to be neon-like and thus corresponds to the 10-electron configuration $1s^2 2s^2 2p^6$. The 20 valence and outer-core electrons of the zinc atom were described by the Dunning-type basis set cc-pwCV5Z-PP as constructed by Peterson and Puzzarini [13], whereas the aug-cc-pV5Z basis set [14-16] was used for the hydrogen atoms. The complete basis set for ZnH_2 comprises 366 contracted Gaussian-type orbitals (cGTOs). All electronic structure calculations of the present work were carried out with the MOLPRO suite of programs [17, 18].

The equilibrium Zn-H distance of linear centrosymmetric ZnH_2 was calculated to be r_e (PP-CCSD(T)) = 1.51895 Å, with a corresponding total energy of -228.18065142 E_h. The theoretical r_e value may be compared with experimental values of r_e ($^{64}ZnH_2$) = 1.52413 Å and r_e ($^{64}ZnD_2$) = 1.52394 Å [5]. Analogous PP-CCSD(T) calculations for CdH_2 [8] and HgH_2 [7] yielded 1.66679 Å and 1.63695 Å, respectively.

On the basis of 386 symmetry-unique PP-CCSD(T) energy points, which cover an energy range of up to ca. 15 000 cm^{-1} above equilibrium, a PEF of the form

$$V - V_e = \sum_{ijk} C_{ijk}\, \tilde{r}_1^{\,i}\, \tilde{r}_2^{\,j}\, \theta^k \qquad (1)$$

was determined through weighted least-squares fitting. The weighting factor of each energy point was chosen to be $w_i = (E_i + \Delta)^{-2}$, the energy shift being taken as $\Delta = 0.00292\ E_h$ or 640 cm^{-1}. In equation (1), the two stretching coordinates $\tilde{r}_m$ (m = 1, 2) correspond to Morse-like coordinates of the form [19]

$$\tilde{r}_m = \{1 - \exp[-\beta(r_m - r_e)/r_e]\}/\beta \qquad (2)$$

The non-linear parameter β was determined to be 0.98. The angle θ measures the deviation of the H-Zn-H bond angle from the corresponding linear nuclear configuration.

The non-redundant linear parameters C_{ijk} of the analytical PP-CCSD(T) PEF are listed in Table 1. The table also includes a corrected PEF which makes use of three pieces of spectroscopic information for the most abundant isotopomer $^{64}ZnH_2$. Like in our previous

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work on HgH_2 and CdH_2 [7, 8], the ground-state rotational constant B_0 and the wavenumber of the antisymmetric stretching vibration ν_3 were employed. Owing to the fact that a larger body of experimental information exists for $^{64}ZnH_2$ in comparison with the heavier group 12 dihydrides, spectroscopic data on the bending vibration was used as well. We actually made use of the rovibrational term value with quantum numbers $v_2 = 3$, $l = 3$ and $J = 3$, as calculated from Table 5 of ref. [6] to be 1908.7 cm^{-1}. The three fit parameters of our corrected PEF are then r_e and two scaling factors f_1 and f_2, the former for the diagonal stretching part of the PEF and the latter for the diagonal bending part.

A comparison of calculated harmonic vibrational wavenumbers from previous [9, 10] and the present work is made in table 2. According to the present PP-CCSD(T) calculations and those with the corrected PEF, the difference ω_1 - ω_3 for $^{64}ZnH_2$ is very small. Therefore, strong vibrational anharmonic resonance of the Darling-Dennison type [20] is expected at the first overtone level of the two stretching vibrations. We prefer the specific term Darling-Dennison resonance over the term Fermi resonance, which is commonly used in a more general way for any vibrational anharmonic resonance. Experimentally, clear signatures of a strong Darling-Dennison resonance interaction were found in a number of emission bands of $^{64}ZnH_2$ [5, 6]. Approximate spectroscopically derived harmonic vibrational wavenumbers (see table 7 of ref. [5]) are given in the last line of table 2. Agreement with the present values from the corrected PEF is quite good, keeping in mind that experimental harmonic wavenumbers may depend sensitively on the data available for their determination. For $^{64}ZnD_2$, the difference in harmonic stretching vibrational wavenumbers is calculated to be -20 cm^{-1} and thus the resonance interaction should be significantly smaller.

PP-CCSD(T) electric dipole moments were calculated numerically by the finite field technique in an analogous way as for HgH_2 and CdH_2 [7, 8]. The expansion of the EDMF was carried out around the minimum of the corrected potential energy surface (r_e = 1.52416 Å). Like in our previous work [7, 8], the cartesian components of the dipole moment were transformed to the molecular Eckart frame. The resulting values of the parallel and perpendicular component, termed μ'' and $\mu^{\perp}$, were then least-squares fitted to the function

$$\mu^{\alpha} = \sum_{ijk} D_{ijk}^{\alpha} S_1^{\,i} S_3^{\,j} \theta^k \qquad (\alpha: \text{ parallel or perpendicular}) \qquad (3)$$

where S_1 and S_3 are symmetry coordinates, defined as $S_1 = 2^{-½} (r_1 + r_2 - 2r_e)$ and $S_3 = 2^{-½} (r_1 - r_2)$, respectively. For further details we refer to ref. [8]. In total, dipole moments were calculated at 153 non-redundant nuclear configurations and the two components were fitted with 18 and 23 terms, respectively. The EDMF parameters for $^{64}ZnH_2$ are listed in table 3. For

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other isotopomers, an appropriate transformation of the dipole moment components was carried out in the course of the calculation of dipole moment matrix elements over rovibrational basis functions.

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3. Rovibrational term energies and spectroscopic constants

3.1 Details of calculations

The computation of rovibrational term energies and wave functions is carried out by diagonalizing Watson's isomorphic rovibrational Hamiltonian for linear molecules [21] in a basis of harmonic oscillator/rigid rotor functions. A program written by one of us (P.S.) has been used for this purpose [22]. For the symmetric isotopomers, basis sets of 451 vibrational product functions are used for states with either g or u symmetry. They describe the vibrational term energies up to $v_3 = 4$ with an accuracy of 0.01 cm^{-1} or better. Provided that the chosen basis set is large enough to guarantee the desired numerical accuracy for term energies, theory has the advantage over experiment that, for a given range of the good quantum number J (standing for the total rotational angular momentum), the complete set of term values becomes available. This feature is very important for the analysis of perturbations since spectroscopy typically delivers data for just a few rovibrational levels of the perturbing vibrational state, whose nature may therefore be difficult to elucidate.

Comparison with the data from high-resolution IR emission spectroscopy [5, 6] is done at the stage of so-called spectroscopic constants, which were derived through least-squares fit to calculated rovibrational term energies. Rovibrational levels with zero vibrational angular momentum quantum number l were fitted by means of the formula:

$$E_v(J) = G_v + B_v\,[J(J+1)] - D_v\,[J(J+1)]^2. \qquad (4)$$

In equation 4, v stands collectively for all three vibrational quantum numbers v_1 to v_3, G_v denotes the vibrational term energy, B_v the rotational constant, and D_v the quartic centrifugal distortion constant. For states with $l \neq 0$, an effective Hamiltonian matrix is set up [23-25]. Its diagonal elements have the form:

$$\langle v,J,l \mid H_{eff} \mid v,J,l\rangle = G_v + B_v\,[J(J+1)-l^2] - D_v\,[J(J+1) - l^2]^2. \qquad (5)$$

The parameters G_v, B_v, and D_v now include contributions from vibrational angular momentum. In particular, G_v includes the additive term $g_{22}\,l^2$. The size of g_{22} plays an important role in the assignment of perturbations in the spectra of ZnH_2 and CdH_2 [6, 8].

The off-diagonal elements of the effective Hamiltonian are given by:

$$\langle v,J,l \mid H_{eff} \mid v,J,l \pm 2\rangle =$$

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$$¼[q_v + q_D(J+1)]\{[(v_2+l)^2-(l \pm 1)^2][J(J+1)-l(l \pm 1)][J(J+1)-(l \pm 1)(l \pm 2)]\}^{½}. \quad (6)$$

Here, the parameter q_v describes the vibrational dependence of *l*-type doubling and q_D its dependence on J. We employ the sign convention of Watson [26] for the *l*-type doubling constants which differs from that used by Bernath and coworkers [5, 6]. For a given value of the bending vibrational quantum number v_2, *l* may take $n = v_2+1$ different values from $-v_2$ up to v_2. The rotational quantum number J obeys the relationship $J \geq l$. Individual spectroscopic constants were obtained through diagonalisation of n x n effective Hamiltonian matrices in conjunction with least-squares fitting.

As has been shown spectroscopically [5, 6], ZnH_2 and ZnD_2 are characterized by unusually large *l*-type doubling constants q_v, which give rise to strong rotational *l*–type resonances. As a consequence, *l* may loose it significance as a fairly good quantum number already for rather low values of J. On the other hand, the J-dependent expectation value of $|l|$ provides a very useful tool for the analysis of the perturbations to be studied in the present work. This quantity is easily calculated from the rovibrational wave functions since the rigid rotor part of a given basis function is associated with a well-defined *l* value.

Despite of the limitations described above, we continue to use *l* as a label in the assignment of rovibrational levels. At the lowest possible J values, *l* may still be considered to be a rather good quantum number. Increasing the J value by unity, there is mostly only a slight change in the vibrational part of the rovibrational wave function and we may thus use an overlap criterion for the assignment of neighbored rovibrational states. Occasionally, as a second criterion, the smooth variation of $<|l|>$ has been employed.

The calculated rovibrational wave functions together with the matrix elements of the EDMF over the basis functions were employed to calculate the squared transition dipole moments μ^2_{if} between rovibrational states, closely following the detailed description in ref. [27]. They may approximately be written as the product of three factors:

$$\mu^2_{if} \approx F_{HL}\, F_{HW}\, \mu^2_{vv'} \quad (7)$$

In equation 7, F_{HL} is the Hönl-London factor, F_{HW} is the Herman-Wallis factor, and $\mu_{vv'}$ is the transition dipole moment of the pure vibrational transition. For F_{HW} an expression of the form $[1+A_1m + A_2m^2]^2$ was used with m = -J and m = J+1 for P-branch and R-branch transitions, respectively [28]. Integrated molar absorption intensities of fundamental rovibrational bands were then calculated by the well-known formula [29]:

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$$A_{f0} = \frac{\pi N_A}{3\hbar c_0 \varepsilon_0} \bar{\nu}_{f0} \, | \mu_{f0} |^2 \qquad (8)$$

Here, N_A is Avogadro's number, ħ Planck's constant divided by 2π, c_0 the vacuum velocity of light, ε_0 the permitivity of vacuum, ν_{f0} the vibrational wavenumber and μ_{f0} the corresponding vibrational transition dipole moment.

3.2 States with l = 0

Table 4 lists calculated term energies of $^{64}ZnH_2$ and $^{64}ZnD_2$ for the 10 lowest excited vibrational states with l = 0. The table also includes those five wavenumbers which are accurately known from IR emission spectroscopy [4, 5]. The errors in the uncorrected PP-CCSD(T) calculations range between 6.2 cm^{-1} (for ν_3 of $^{64}ZnD_2$) and 22.5 cm^{-1} (for $2\nu_1$ of $^{64}ZnH_2$). The corrected PEF reproduces the experimental ν_3($^{64}ZnD_2$) within 0.3 cm^{-1} and overestimates the wavenumbers of the first overtones of the stretching vibrations of $^{64}ZnH_2$ by 3.0 and 1.8 cm^{-1}, while $2\nu_3$($^{64}ZnD_2$) is underestimated by 0.3 cm^{-1}. The energetic separation between the two components of the Darling-Dennison resonance pair which, like in ref. [5] are crudely termed (2,0^0,0) and (0,0^0,2), is calculated to be 58.1 cm^{-1} (corrected PEF). The corresponding experimental value is larger by only 1.2 cm^{-1}. For $^{64}ZnD_2$ we predict a smaller separation of 53.5 cm^{-1}. The wavenumber of the transition $(\nu_1+\nu_3) \rightarrow \nu_1$ of $^{64}ZnH_2$ is calculated to be 1828.0 cm^{-1}, in very good agreement with the experimental value of 1827.7 cm^{-1}. The noted accuracy should be sufficient to allow for a reliable analysis of the various perturbations to be discussed below.

Term energies of higher-lying stretching vibrational states of $^{64}ZnH_2$ and $^{64}ZnD_2$ up to the third overtones of the stretching vibrations are given in table 5. Agreement between the calculations with the corrected potential and experiment is still very good, the largest deviation amounting to 3.8 cm^{-1}.

Theoretical experimental rotational and centrifugal distortion constants for the vibrational ground state and the lowest 14 excited stretching vibrational states of $^{64}ZnH_2$ and $^{64}ZnD_2$ are listed in table 6. The theoretical values were obtained by fit to rovibrational levels up to J = 10, thereby avoiding any noticeable influence from perturbations and higher-order centrifugal distortion. According to the spectroscopic data of Bernath and coworkers [5] and our own fits, the sextic centrifugal distortion constant is as small as $H \approx 4 \cdot 10^{-10}$ cm^{-1} and makes up a negligible contribution to the rovibrational term values of less than 0.001 cm^{-1} at J = 10. The spectroscopic constants quoted in tables 1 and 2 of ref. [5] have been derived from different sets of J values which may explain part of the small differences from the present

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values. On the whole, the agreement between experimental and the present values must be considered to be very good.

Using the corrected PEF, the anharmonic wavenumbers for the stretching fundamentals of ^{64}ZnHD are predicted to be ν_1(~ ZnH stretch) = 1888.5 cm^{-1} and ν_3(~ ZnD stretch) = 1359.9 cm^{-1}. These values may be compared with IR absorptions observed in solid HD [10] at 1878.7 and 1352.6 cm^{-1}, respectively. The corresponding values obtained in an argon matrix are 1870.4 and 1346.2 cm^{-1} [9].

Isotopic shifts in the stretching vibrational term energies for each three isotopomers of ZnH_2 and ZnD_2 with heavier central atoms are listed in table 7. On the basis of the calculated shift in the antisymmetric stretching vibration, we predict ν_3(^{67}ZnD_2) = 1369.865 cm^{-1}, with an estimated uncertainty of 0.001 cm^{-1}. Like for CdH_2 [8], the effects of Darling-Dennison resonance are clearly discernible for the first overtones. In particular, the (2,0^0,0) states of ZnH_2 isotopomers experience calculated shifts between -0.656 and -1.294 cm^{-1} while the shifts in the symmetric stretching fundamentals are almost zero. On the whole, agreement between theoretical and experimental values is considered to be very good.

3.3 The lowest bending vibrational state

Table 8 lists theoretical and experimental values for the spectroscopic constants associated with the first excited bending vibrational state of ^{64}ZnH_2, ^{64}ZnD_2, and ^{64}ZnHD. The band origins for the symmetric isotopomers are calculated to be ν_2 (^{64}ZnH_2) = 635.1 cm^{-1} and ν_2 (^{64}ZnD_2) = 459.8 cm^{-1}. Directly measured gas-phase values are not yet available, but Wang and Andrews have published ν_2 values referring to rather inert media (solid hydrogen and neon). These are in the range 631.9-632.5 cm^{-1} and 456.0-456.4 cm^{-1} [10]. The corresponding data for less inert solid argon are 630.5 and 454.2 cm^{-1} [9]. For the asymmetric isotopomer ^{64}ZnHD we predict ν_2 = 555.1 cm^{-1}.

Throughout, the calculated spectroscopic constants (B_v, D_v, q_v and q_D) for ^{64}ZnH_2 and ^{64}ZnD_2 are in very good agreement with the experimental values [5]. In particular, the *l*-type doubling constants q_V almost coincide with the experimental values. Consequently, we expect high accuracy for the predicted values of ^{64}ZnHD, as well.

3.4 States with large rotational l-type resonances

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In the experiments of Bernath and coworkers [5, 6], the vibrational states $(0,2^2,1)$ and $(0,2^0,1)$ were populated, from which emission to $(0,2^2,0)$ and $(0,2^0,0)$ could be observed for both $^{64}ZnH_2$ and $^{64}ZnD_2$. Owing to the exceptionally large *l*-type doubling constants for both isotopomers, rotational *l*-type resonance is quite pronounced. Results of the present calculations along with spectroscopically derived values (see table 3 of ref. [6]) are given in table 9. We present two sets of calculated spectroscopic parameters, obtained either from a fit with a maximum rotational quantum number $J_{max} = 10$ or with $J_{max} = 20$. For all eight B_v and D_v values considered, the latter set provides better agreement with the noted experimental values. This is not too surprising, since J values up to $J' = 22$ were employed in the least-squares fitting of observed line positions. Excellent agreement with experiment is observed for the two q_v values. The small term q_D shows a strong dependence on J_{max} in the case of the *l*-type resonance pair $(0,2^l,1)$ with $l = 0, 2$, which goes along with a strong change in D_v. In this special case of *l*–type resonance ($v_2 = 2$, $l = 0, 2$), q_v and q_D are determined by e parity levels only. Thus, a fit of f parity levels alone must yield spectroscopic constants G_v, B_v, and D_v numerically identical to those resulting from a fit of e parity levels using eq. 5 and 6. The fit with $J_{max} = 20$ shows this consistency much better than a fit with $J_{max} = 10$. From the calculated G_v values we obtain a difference of $G(0,2^2,1) - G(0,2^2,0) = 1864.74$ cm^{-1}, in almost perfect agreement with the experimental value of 1864.55 cm^{-1} [6]. The agreement in the g_{22} values is slightly worse than expected, but we are a bit sceptical whether calculated and experimentally derived data are strictly comparable.

Table 10 compares calculated and experimental data for $^{64}ZnD_2$; in this case the former refer to $J_{max} = 20$. Agreement between the two sets of data is about as good as for $^{64}ZnH_2$. The calculated difference in G_v values of states $(0,2^2,1)$ and $(0,2^2,0)$ agrees with experiment within 0.3 cm^{-1}, which gives further support to the type of corrections we applied to the PP-CCSD(T) potential energy function.

Spectroscopic constants for the second overtones of the bending vibration of $^{64}ZnH_2$ and $^{64}ZnD_2$ are listed in table 11. The "experimental" values given in parentheses have not been measured directly, but were derived through extrapolation. Nevertheless, agreement with the theoretical values is quite good.

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4. Analysis of some perturbations

4.1 Local perturbations in the ν_3 bands of $^{64}ZnH_2$ and $^{64}ZnD_2$

For both $^{64}ZnH_2$ and $^{64}ZnD_2$, IR emission spectra show perturbations in the $(0,0^0,1)$ vibrational states [5, 6]. Rotational levels of $^{64}ZnH_2$ with J ≤ 17 are shifted towards higher wavenumbers, whereas levels with J ≥ 18 are shifted downwards. For $^{64}ZnD_2$, levels with J ≤ 22 are shifted up and those with J ≥ 23 are shifted down. The magnitudes of these perturbations were measured to be small, with the largest shifts amounting to only 0.04 cm^{-1}. The present calculations with the corrected PEF allow for an easy interpretation of the observed perturbations. As suggested by the experimentalists [5, 6], the second overtone of the bending vibration (v_2 = 3) plays a decisive role. Table 12 lists the relevant rovibrational term values for rotational quantum numbers up to J = 30. A more illustrative graphical representation showing relative values with respect to $(0,0^0,1)$e levels is given in figure 1. In this figure and the following ones, the relative energies of rovibrational levels within an assigned series are connected by polygons, such that crossings may occur between different series. As an inset, the figure also includes the expectation values of $|l|$ over the rovibrational wave functions as a function of J. In agreement with the experimental findings, the curves for the $(0,0^0,1)$e and $(0,3^1,0)$e levels cross between J = 17 and J = 18. As is clearly shown by the inset, l is a reasonably good quantum number only for low values of J. In the vicinity of the crossing, the graph of $<|l|>$ for the $(0,0^0,1)$e levels is characterized by a small hump with a maximum between J = 17 and 18, making this quantity a sensitive indicator of the local perturbation.

Results for $^{64}ZnD_2$ are given in table 13 and figure 2. According to the present calculations, the crossing point occurs between J = 21 and J = 22, still in very good agreement with experiment. The inset shows that the perturbation is practically restricted to a single J value and thus of extremely local nature.

Compared with $^{64}ZnH_2$, $^{114}CdH_2$ exhibits noteworthy differences (see figure 5 of ref. [8]. For the latter dihydride, our calculations predicted crossing with the $(0,3^3,0)$e levels between J = 14 and J = 15. A plot of the $<|l|>$ values of the interacting states is provided as supplementary online material (figure SF1).

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4.2 The interacting system $(0,1^1,1)/(0,4^l,0)$ of $^{64}ZnH_2$ and $^{64}ZnD_2$ (l = 0,2,4)

The second strongest bands in the IR emission spectra of $^{64}ZnH_2$ and $^{64}ZnD_2$ were assigned as the $(0,1^1,1) \rightarrow (0,1^1,0)$ hot bands [5]. For both isotopomers, small local perturbations in higher J levels of the upper vibrational state were observed. The perturbations were claimed to be "caused by the nearby 040 vibrational level", but no detailed analysis was given.

Figure 3 of the present paper makes an attempt to elucidate the nature of the perturbations for $^{64}ZnH_2$; the corresponding rovibrational term values are provided as supplementary online material (S1). Levels of both e and f parity are considered in the figure, but since e and f levels do not interact with each other, the e and f levels of the reference state $(0,1^1,1)$ form a common zero horizontal line. Three different crossings are observed. Between J = 7 and J = 8, $(0,4^0,0)$e levels cross the e levels of the reference state. Quite interestingly, this crossing has only a tiny effect on the expectation values of $|l|$ for J = 7 and 8. For higher J values a crossing occurs both within the e level and the f level manifold. For the latter, the crossing is predicted between J = 20 and J = 21 and for the former between J = 22 and J = 23. In both cases, the inset of the figure shows pronounced signatures in the $<|l|>$ graphs.

A similar situation is predicted for $^{64}ZnD_2$. Crossing between e levels of $(0,1^1,1)$ and $(0,4^0,0)$ occurs between J = 10 and J = 11, again without noticeable change in $<|l|>$. For the f and e levels of $(0,4^2,0)$, the crossings are shifted to J values of 24-25 and 27-28, respectively. A table with rovibrational term values and a figure may be found with the supplementary online material (table S2 and figure SF2).

4.3 An extremely local perturbation in the $(1,0^0,1)$ state

For both $^{64}ZnH_2$ and $^{64}ZnD_2$, the hot band $(1,0^0,1) \rightarrow (1,0^0,0)$ could be observed in the IR emission spectra [5]. The present analysis for $^{64}ZnH_2$ (see figure 4) shows an extremely local perturbation which exclusively affects two rovibrational levels with a common J = 17, the perturbing state being described as $(1,3^3,0)$e. The sharpness of the peaks in $<|l|>$ at J = 17 is probably somewhat exaggerated in our calculations. Actually, already a shift of the $(1,3^3,0)$e curve by 1 cm^{-1} with respect to the reference line $(1,0^0,1)$e reduces the peak heights by about a factor of 2. Results for $^{64}ZnD_2$ may be found in the supplementary online material (figure SF3).

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4.4 The Darling-Dennison resonance system (2,0^0,0)/(0,0^0,2) and associated local perturbations

In our previous paper on CdH_2 isotopomers, we predicted that $^{114}CdH_2$ shows a rather complex series of local perturbations in the region of the first Darling-Dennison resonance system (see figure 8 of ref. [8]). The situation for $^{64}ZnH_2$ is at least as complicated. Figure 5 of the present paper draws the relevant rovibrational term values with respect to the upper component of the Darling-Dennison resonance system. Their numerical values referring to the absolutely lowest rovibrational state of $^{64}ZnH_2$ are provided as supplementary online material. Like for $^{114}CdH_2$, the interacting levels belong to two classes, either (0, 6^l,0)e levels with l = 0-4 or (0,3^l,1)e levels with l = 1 or 3.

To a first approximation, Darling-Dennison resonance is considered to be independent of J. According to figure 5, this is fulfilled reasonably well only for low values of J, while for J > 10 we calculate a significant lowering of the relative rovibrational term values for the lower component of the Darling-Dennison resonance system. For low values of J, the (2,0^0,0)e levels are very close to the (0,6^2,0)e levels. Actually, they almost coincide for J = 3-5 and J = 12. The situation for the (2,0^0,0)e levels changes at J = 16 through interaction with (0,3^3,1)e. At this J value, the expectation value of $|l|$ rises to 0.167 while the adjacent levels with J = 15 and 17 have low expectation values of 0.019 and 0.050, respectively.

The graphs of the (0,3^3,1)e and the (0,6^2,0)e levels cross between J = 13 and J = 14 without any significant effect on either rovibrational wavenumbers or expectation values of $|l|$. On the other hand, significant interaction appears to occur between (0,3^1,1)e and (0,6^2,0)e levels at J = 23.

Finally, the upper component of the Darling-Dennison resonance system experiences crossings with (0,6^0,0)e levels close to J = 15, with (0,6^2,0)e levels close to J = 27 and with (0,3^1,0)e levels between J = 28 and J = 29.

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5. IR intensities and Einstein coefficients of spontaneous emission

Calculated transition dipole moments and molar IR intensities of absorption for several transitions of three isotopomers of zinc dihydride are listed in table 14. Owing to a strong dependence of the perpendicular component of the electric dipole moment on the bending angle (note the large coefficient $D^{\perp}_{001}$ in table 3), the bending vibration of $^{64}ZnH_2$ has the largest transition dipole moment among the fundamentals. Despite of the low value of the ν_2 band origin (see table 8), the ν_2 band is still strongest when comparison is made at the stage of the A values as calculated by equation 8. The familiar double-harmonic approximation works very well in the prediction of absolute IR intensities of the fundamentals as was found for mercury and cadmium dihydride in our earlier work [7, 8]. Darling-Dennison resonance in $^{64}ZnH_2$ manifests itself in a rather large transition dipole moment for the transition $(2,0^0,0) \leftarrow (0,0^0,1)$, the corresponding value for $^{64}ZnD_2$ being smaller by a factor of 2.6.

Einstein coefficients of spontaneous emission are important for the quantitative analysis of emission spectra. Predicted values for a number of vibrational transitions of $^{64}ZnH_2$ and $^{64}ZnD_2$ are given in table 15. Like for $^{114}CdH_2$ [8], Darling-Dennison resonance leads to comparably large values for the transitions $(0,0^0,1) \leftarrow (0,0^0,2)$, $(0,0^0,1) \leftarrow (2,0^0,0)$ and $(0,0^0,0) \leftarrow (0,0^0,1)$, while a rather different situation holds for $^{64}ZnD_2$.

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6. Conclusions

The coupled cluster method CCSD(T) in combination with a small-core pseudopotential for the zinc atom has been employed in the calculation of near-equilibrium potential energy and electric dipole moment surfaces for the electronic ground state of zinc dihydride. A significant improvement of the PEF has been achieved through the use of three pieces of spectroscopic information for $^{64}ZnH_2$, namely the ground-state rotational constant, the vibrational wavenumber ν_3 and the rovibrational term value with quantum numbers $v_2 = 3$ and $J = l = 3$. The refined PEF appears to be accurate enough to allow for the assignment of various local perturbations in both $^{64}ZnH_2$ and $^{64}ZnD_2$.

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Table 1. Non-redundant parameters of analytical potential energy functions for ZnH_2.[a]

i	j	k	PP-CCSD(T)[b]	corrected[c]
2	0	0	0.6010526	0.5991468
3	0	0	-0.7383551	-0.7377748
4	0	0	0.5656775	0.5643549
5	0	0	-0.3913471	-0.3935801
6	0	0	0.0858438	0.0866934
0	0	2	0.0333275	0.0329642
0	0	4	-0.0051292	-0.0050650
0	0	6	0.0151447	0.0150704
0	0	8	-0.0365025	-0.0363448
0	0	10	0.0492862	0.0490732
0	0	12	-0.0334860	-0.0333413
0	0	14	0.0089711	0.0089323
1	1	0	0.0189037	0.0180215
2	1	0	-0.0646753	-0.0639260
3	1	0	0.0288622	0.0276816
2	2	0	0.0676449	0.0659762
4	1	0	-0.0448696	-0.0461443
3	2	0	-0.0803108	-0.0818558
5	1	0	-0.0415051	-0.0415051
4	2	0	-0.0820563	-0.0820563
3	3	0	-0.0407448	-0.0407448
1	0	2	-0.0321497	-0.0320507
1	1	2	0.0329954	0.0331844
2	0	2	-0.0021720	-0.0020589
2	1	2	0.0140266	0.0135320
3	0	2	0.0065939	0.0061945
2	2	2	-0.0323112	-0.0323112
3	1	2	-0.0265266	-0.0265266
4	0	2	-0.0224780	-0.0224780
1	0	4	0.0061707	0.0061246
1	1	4	-0.0046776	-0.0046776
2	0	4	-0.0043628	-0.0043866
3	0	4	-0.0023131	-0.0023131
1	0	6	-0.0012977	-0.0012977

[a] Throughout, the non-linear parameter β has a value of 0.98. The mathematical forms of the PEFs are described in equations (1) and (2).

[b] r_e = 1.51895 Å.

[c] r_e = 1.52416 Å.

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Table 2. Harmonic vibrational wavenumbers (in cm^{-1}) for $^{64}ZnH_2$ and $^{64}ZnD_2$.[a]

Method and basis	ref.[b]	$^{64}ZnH_2$			$^{64}ZnD_2$		
		ω_1	ω_2	ω_3	ω_1	ω_2	ω_3
PP-MP2 / A[c]	[9]	2031	678	2039	1437	487	1464
PP-MP2 / B[d]	[9]	2021	684	2001	-	-	-
PP-CCSD(T) / A[c]	[9]	1939	631	1955	1372	453	1404
PP-CCSD(T) /B[d]	[9]	1926	637	1921	1362	458	1379
B3LYP / 6-311++G (3df, 3pd)	[10]	1929.9	645.3	1917.8	1385.8	463.4	1356.6
PP-CCSD(T) / 366 cGTOs	*	1971.4	662.1	1970.8	1394.4	475.5	1415.1
corrected PEF	*	1960.7	655.7	1961.6	1386.9	470.8	1408.6
experimental	[5]	1958	656	1959.7	1385	474	1404.9

[a] According to common spectroscopic convention ω_1, ω_2, and ω_3 refer to symmetric stretching, bending, and antisymmetric stretching vibrations, respectively.

[b] Results from the present work are marked with an asterisk.

[c] Basis: [6s, 5p, 3d / 2s, 1p].

[d] Basis: [8s, 6p, 5d, 2f / 7s, 2p].

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Table 3. PP-CCSD(T) electric dipole moment function (EDMF) for ZnH_2.[a]

i	j	k	$D^{\parallel}_{ijk}$	i	j	k	$D^{\perp}_{ijk}$
0	1	0	0.54472	0	0	1	-0.81720
0	3	0	-0.01583	0	0	3	-0.01654
0	5	0	0.00175	0	0	5	0.01615
1	1	0	0.13467	0	0	7	-0.00128
1	3	0	-0.01020	1	0	1	-0.13300
1	5	0	0.00468	1	0	3	0.03761
2	1	0	-0.10662	1	0	5	-0.00795
2	3	0	-0.01022	2	0	1	0.03075
0	1	2	0.07559	2	0	3	0.00368
0	1	4	0.01257	2	0	5	0.00405
0	3	2	-0.01214	3	0	1	0.01084
0	3	4	-0.00029	3	0	3	-0.00099
0	5	2	0.00096	4	0	1	0.00318
1	1	2	0.01519	0	2	1	0.04123
2	1	2	-0.06277	0	4	1	0.00203
1	1	4	-0.00277	0	2	3	0.00790
2	1	4	-0.00363	0	4	3	-0.00178
1	3	2	0.01637	0	2	5	0.00088
				1	2	1	0.00059
				2	2	1	0.01782
				1	2	3	0.01238
				3	2	1	-0.00596
				1	2	5	0.00437

[a] The EDMF is expanded around r_e = 1.52416 Å (minimum of corrected PEF).

All EDMF terms (for definition see eq 3) are given in ea_0.

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Table 4. Term energies (in cm^{-1}) of 10 lowest excited vibrational states (l = 0) for $^{64}ZnH_2$ and $^{64}ZnD_2$.

	$^{64}ZnH_2$			$^{64}ZnD_2$		
(v_1, v_2, v_3)	PP-CCSD(T)	corr.	exp.	PP-CCSD(T)	corr.	exp.
(0, 2, 0)	1272.0	1260.7		922.5	914.3	
(1, 0, 0)	1896.7	1886.4		1357.0	1349.7	
(0, 0, 1)	1898.5	1889.4	1889.4	1377.8	1371.3	1371.6
(0, 4, 0)	2523.3	2500.9		1833.1	1816.8	
(0, 2, 1)	3145.9	3125.6		2287.2	2272.5	
(1, 2, 0)	3148.8	3127.2		2269.7	2254.2	
(1, 0, 1)	3733.6	3714.4		2703.6	2689.8	
(2, 0, 0)[b]	3735.5	3716.0	3713.0	2693.0	2678.5	
(0, 0, 2)[b]	3793.3	3774.1	3772.3	2745.2	2732.0	2732.3
(0, 6, 0)	3756.2	3723.0		2733.1	2708.9	
ZPE[a]	2598.0	2582.4		1862.0	1850.8	

[a] Zero-point vibrational energy.

[b] Darling-Dennison resonance pair.

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Table 5. Term energies (in cm^{-1}) for higher-lying stretching vibrational states of $^{64}ZnH_2$ and $^{64}ZnD_2$.[a]

(v_1, v_2, v_3)	$^{64}ZnH_2$	$^{64}ZnD_2$
(2, 0, 1)	5482.6	3980.8
(1, 0, 2)	5483.2	4033.9
(3, 0, 0)	5591.3	3980.8
(0, 0, 3)	5607.0 (5605.3)	4076.6 (4076.9)
(3, 0, 1)	7191.3	5252.0
(2, 0, 2)	7191.4	5251.4
(1, 0, 3)	7361.6	5351.8
(4, 0, 0)	7362.1	5323.1
(0, 0, 4)	7426.3 (7422.5)	5407.1

[a] Calculations with the corrected PEF. Experimental values [5] are given in parentheses.

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Table 6. Effective rotational and centrifugal distortion constants (in cm^{-1}) for stretching vibrational states.[a]

	$^{64}ZnH_2$		$^{64}ZnD_2$	
(v_1, v_2, v_3)	B_v	$D_v/10^{-5}$	B_v	$D_v/10^{-5}$
(0,0,0)	3.54821	4.914	1.78291	1.219
	(3.54821)	(4.923)[b]	(1.78342)	(1.227)
(1,0,0)	3.49650	4.880	1.76467	1.220
	(3.49636)	(4.899)	(1.76511)	(1.222)
(0,0,1)	3.50684	4.916	1.76761	1.225
	(3.50657)	(4.900)[b]	(1.76799)	(1.221)
(1,0,1)	3.45467	4.893	1.74925	1.220
	(3.45427)	(4.932)	(1.74959)	(1.228)
(2,0,0)	3.45234	5.047	1.74682	1.219
	(3.45124)	(5.035)		
(0,0,2)	3.45765	4.720	1.75185	1.218
	(3.45781)	(4.729)	(1.75218)	(1.215)
(2,0,1)	3.40540	4.931	1.72987	1.226
(1,0,2)	3.40559	4.970	1.73214	1.202
(3,0,0)	3.40010	4.755	1.72987	1.226
(0,0,3)	3.42020	4.858	1.73648	1.219
	(3.41959)	(4.843)	(1.73669)	(1.216)
(3,0,1)	3.35642	4.952	1.71352	1.220
(2,0,2)	3.35658	4.952	1.71315	1.225
(1,0,3)	3.36362	4.835	1.71725	1.213
(4,0,0)	3.35307	5.068	1.71259	1.200
(0,0,4)	3.37233	4.588	1.72089	1.215
	(3.37253)	(4.657)		

[a] From variational calculations with the corrected PEF. Experimental values (see tables 1 and 2 of ref. [5]) are given in parentheses. The calculated B_v and D_v values result from fits with equation 4 considering J values up to 10.

[b] Fits of spectroscopic data (see S1.1 of ref. [5]) with $J \leq 16$ yield $4.910 \cdot 10^{-5}$ and $4.905 \cdot 10^{-5}$ cm^{-1} for states $(0,0^0,0)$ and $(0,0^0,1)$, respectively.

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Table 7. Isotopic shifts (in cm^{-1}) in term energies of stretching vibrational states.[a]

Isotopomer	$(1,0^0,0)$	$(0,0^0,1)$		$(1,0^0,1)$	$(2,0^0,0)$		$(0,0^0,2)$		$(0,0^0,3)$	
	theor.	theor.	exp.	theor.	theor.	exp.	theor.	exp.	theor.	exp.
$^{66}ZnH_2$	0.000	-0.837	-0.837	-0.823	-0.656	-0.598	-0.978	-1.031	-2.111	-2.123
$^{67}ZnH_2$	0.001	-1.239	-1.239	-1.217	-0.978		-1.438		-3.120	
$^{68}ZnH_2$	0.001	-1.627	-1.626	-1.599	-1.294	-1.182	-1.879	-1.983	-4.095	-4.121
$^{66}ZnD_2$	-0.001	-1.194	-1.194	-1.181	-0.190		-2.158	-2.176	-3.287	-3.295
$^{67}ZnD_2$	-0.001	-1.766		-1.747	-0.287		-3.187		-4.859	
$^{68}ZnD_2$	-0.001	-2.320	-2.320	-2.294	-0.385		-4.178	-4.215	-6.378	

[a] Shifts are quoted with respect to $^{64}ZnH_2$ or $^{64}ZnD_2$. Theoretical values refer to calculations with the corrected PEF, which makes use of the experimental value for $\nu_3(^{64}ZnH_2)$.

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Table 8. Theoretical and experimental spectroscopic constants for the lowest bending vibrational state.[a]

	G_v[b]	B_v	$D_J/10^{-5}$	$q_v/10^{-2}$	$q_D/10^{-6}$
$^{64}ZnH_2$	635.1	3.54294 (3.54290)	5.008 (4.985)	5.949 (5.946)	-2.966 (-2.920)
$^{64}ZnD_2$	459.8	1.78126 (1.78173)	1.244 (1.237)	2.075 (2.074)	-0.506 (-0.491)
$^{64}ZnHD$	555.1	2.38154	2.457	3.096	-1.126

[a] From variational calculations with the corrected PEF. Spectroscopic constants result from fits according to equations 5 and 6 considering J up to 10. Experimental values [5] are given in parentheses.

[b] All G_v values include *l*-dependent contributions.

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Table 9. Spectroscopic constants (in cm^{-1}) for rotational *l*-type resonances in $^{64}ZnH_2$.[a]

State	J_{max}	G_v	B_v	$D_v/10^{-5}$	g_{22}	$q_v/10^{-2}$	$q_D/10^{-6}$
$(0,2^0,0)$	10	1260.7	3.53920	5.123			
	20	1260.7	3.53914	5.093			
			(3.53909)	(5.099)			
$(0,2^2,0)$	10e	1267.7	3.53781	5.105	1.744	5.98	-3.06
	10f	1267.7	3.53781	5.105			
	20e	1267.7	3.53775	5.075	1.744	5.97	-2.98
	20f	1267.7	3.53775	5.075			
			(3.53775)	(5.083)	(1.645)	(5.97)	(-2.95)
$(0,2^0,1)$	10	3125.6	3.49833	4.924			
	20	2125.6	3.49832	5.080			
			(3.49806)	(5.095)			
$(0,2^2,1)$	10e	3132.4	3.49711	5.213	1.706	5.89	-4.44
	10f	3132.4	3.49708	5.198			
	20e	3132.4	3.49693	5.063	1.706	5.88	-2.83
	20f	3132.4	3.49693	5.063			
			(3.49676)	(5.086)	(1.604)	(5.88)	(-2.81)

[a] From variational calculations with the corrected PEF. Spectroscopic constants result from fits according to equations 5 and 6. For details of the fits see the text. Experimental values [6] are given in parentheses.

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Table 10. Spectroscopic constants (in cm^{-1}) for rotational *l*-type resonances in $^{64}ZnD_2$.[a]

State	G_v	B_v	$D_v/10^{-5}$	g_{22}	$q_v/10^{-2}$	$q_D/10^{-6}$
$(0,2^0,0)$	914.3	1.77998 (1.78039)	1.260 (1.251)			
$(0,2^2,0)$	918.2	1.77961 (1.78017)	1.258 (1.263)	0.984 (0.908)	2.08 (2.08)	-0.51 (-0.45)
$(0,2^0,1)$	2272.5	1.76480 (1.76510)	1.260 (1.248)			
$(0,2^2,1)$	2276.3	1.76442 (1.76488)	1.257 (1.259)	0.969 (0.892)	2.06 (2.06)	-0.50 (-0.43)

[a] From variational calculations with the corrected PEF. Spectroscopic constants result from fits with equations 5 and 6 and J up to 20. Experimental values [6] are given in parentheses.

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Table 11. Spectroscopic constants (in cm^{-1}) for second overtones of the bending vibrations of $^{64}ZnH_2$ and $^{64}ZnD_2$.[a]

Isotopomer	State	J_{max}	G_v	B_v	$D_v/10^{-5}$	g_{22}	$q_v/10^{-2}$	$q_D/10^{-6}$
$^{64}ZnH_2$	$(0,3^1,0)$	10	1884.9	3.53551	5.241			
		20	1884.9	3.53543	5.205			
				(3.53544)	(5.249)			
	$(0,3^3,0)$	10	1898.1	3.53277	5.205	1.659	6.01	-3.15
		20	1898.1	3.53268	5.162	1.659	6.01	-3.05
			(1898.1)	(3.53277)	(5.217)	(1.64)	(6.00)	(-2.98)
$^{64}ZnD_2$	$(0,3^1,0)$	20	1367.8	1.77872	1.280			
				(1.77917)	(1.280)			
	$(0,3^3,0)$	20	1375.3	1.77801	1.277	0.934	2.09	-0.53
			(1374.7)	(1.77875)	(1.302)	(0.91)	(2.08)	(-0.40)

[a] From variational calculations with the corrected PEF. Spectroscopic constants result from fits with equations 5 and 6. Experimental data from table 5 of ref. [6] are given in parentheses.

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Table 12. Rovibrational levels (in cm^{-1}) for $^{64}ZnH_2$.[a]

J	$(0,0^0,1)e$	$(0,3^1,0)e$	$(0,3^3,0)e$
0	1889.430		
1	1896.443	1888.269	
2	1910.469	1902.170	
3	1931.505	1923.029	1908.717
4	1959.547	1950.858	1936.935
5	1994.591	1985.675	1972.160
6	2036.631	2027.505	2014.355
7	2085.659	2076.382	2063.465
8	2141.668	2132.347	2119.440
9	2204.648	2195.440	2182.217
10	2274.588	2265.694	2251.743
11	2351.477	2343.119	2327.981
12	2435.302	2427.707	2410.914
13	2526.049	2519.433	2500.538
14	2623.702	2618.262	2596.857
15	2728.246	2724.159	2699.870
16	2839.664	2837.087	2809.579
17	2957.947	2957.005	2925.977
18	3083.008	3083.948	3049.055
19	3214.939	3217.772	3178.801
20	3353.650	3358.517	3315.199
21	3499.128	3506.141	3458.231
22	3651.348	3660.616	3607.878
23	3810.287	3821.910	3764.117
24	3975.918	3989.993	3926.924
25	4148.213	4164.834	4096.275
26	4327.144	4346.400	4272.144
27	4512.682	4534.658	4454.501
28	4704.795	4729.574	4643.320
29	4903.452	4931.115	4838.568
30	5108.620	5139.243	5040.216

[a] From variational calculations with the corrected PEF.

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Table 13. Rovibrational levels (in cm^{-1}) for $^{64}ZnD_2$.[a]

J	$(0,0^0,1)e$	$(0,3^1,0)e$	$(0,3^3,0)e$
0	1371.265		
1	1374.800	1369.560	
2	1381.870	1376.590	
3	1392.475	1387.139	1380.625
4	1406.613	1401.209	1394.838
5	1424.283	1418.804	1412.591
6	1445.483	1439.930	1433.876
7	1470.213	1464.597	1458.679
8	1498.470	1492.816	1486.987
9	1530.251	1524.599	1518.780
10	1565.554	1559.959	1554.040
11	1604.376	1598.908	1592.752
12	1646.714	1641.451	1634.901
13	1692.565	1687.589	1680.481
14	1741.923	1737.317	1729.487
15	1794.787	1790.626	1781.922
16	1851.150	1847.507	1837.785
17	1911.008	1907.948	1897.077
18	1974.357	1971.940	1959.799
19	2041.191	2039.473	2025.950
20	2111.505	2110.538	2095.526
21	2185.301	2185.117	2168.526
22	2262.542	2263.233	2244.945
23	2343.259	2344.841	2324.778
24	2427.430	2429.946	2408.021
25	2515.048	2518.542	2494.667
26	2606.107	2610.618	2584.710
27	2700.598	2706.167	2678.144
28	2798.514	2805.179	2774.961
29	2899.847	2907.645	2875.153
30	3004.589	3013.556	2978.714

[a] From variational calculations with the corrected PEF.

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Table 14. Transition dipole moments μ (in D) and integrated molar absorption intensities A (km mol^{-1}).

Transition		$^{64}ZnH_2$	$^{64}ZnD_2$	$^{64}ZnHD$
$(1,0^0,0) \leftarrow (0,0^0,0)$	μ	0[a]	0[a]	0.147
	A[b]			73.5
				(73.4)
$(0,1^1,0) \leftarrow (0,0^0,0)$	μ	0.449	0.379	0.419
	A[b]	321.6	165.9	243.7
		(319.8)	(164.9)	(242.4)
$(0,0^0,1) \leftarrow (0,0^0,0)$	μ	0.250	0.211	0.178
	A[b]	295.0	152.5	150.0
		(294.0)	(151.6)	(149.4)
$(0,0^0,2) \leftarrow (0,0^0,1)$	μ	0.273	0.287	0.255
$(0,0^0,3 \leftarrow (0,0^0,2)$	μ	0.375	0.357	
$(0,0^0,4 \leftarrow (0,0^0,3)$	μ	0.437	0.415	
$(2,0^0,0 \leftarrow (0,0^0,1)$	μ	0.229	0.087	0.000
$(2,0^0,0 \leftarrow (1,0^0,0)$	μ	0[a]	0[a]	0.209
$(0,0^0,3 \leftarrow (2,0^0,0)$	μ	0.165	0.042	
$(0,1^1,1 \leftarrow (0,1^1,0)$	μ	0.251	0.211	0.146

[a] Zero by symmetry.

[b] Values calculated within the double harmonic approximation are given in parentheses.

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Table 15. Einstein coefficients of spontaneous emission (in s^{-1})

Transition	$^{64}ZnH_2$	$^{64}ZnD_2$
$(0,1^1,1) \leftarrow (0,1^1,0)$	131	35
$(0,0^0,0) \leftarrow (0,0^0,1)$	132	36
$(0,0^0,1) \leftarrow (0,0^0,2)$	157	65
$(0,0^0,2) \leftarrow (0,0^0,3)$	271	97
$(0,0^0,3) \leftarrow (0,0^0,4)$	361	127
$(0,0^0,1) \leftarrow (2,0^0,0)$	100	5
$(2,0^0,0) \leftarrow (0,0^0,3)$	58	2
$(1,0^0,0) \leftarrow (1,0^0,1)$	122	32

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Figure Captions

Figure 1: Relative energies of e parity levels for $(0,3^1,0)$ and $(0,3^3,0)$ states of $^{64}ZnH_2$, taken with respect to $(0,0^0,1)$ e levels. The inset shows the expectation values of $|l|$.

Figure 2: Relative energies of e parity levels for $(0,3^1,0)$ and $(0,3^3,0)$ states of $^{64}ZnD_2$, taken with respect to $(0,0^0,1)$ e levels. The inset shows the expectation values of $|l|$.

Figure 3: Relative energies and expectation values of $|l|$ for state $(0,1^1,1)$ and perturbing states.

Figure 4: Analysis of the strong local perturbation in the $(1,0^0,1)$ state of $^{64}ZnH_2$.

Figure 5: Perturbations in the range of the first Darling-Dennison resonance system $(2,0^0,0)/(0,0^0,2)$ of $^{64}ZnH_2$.

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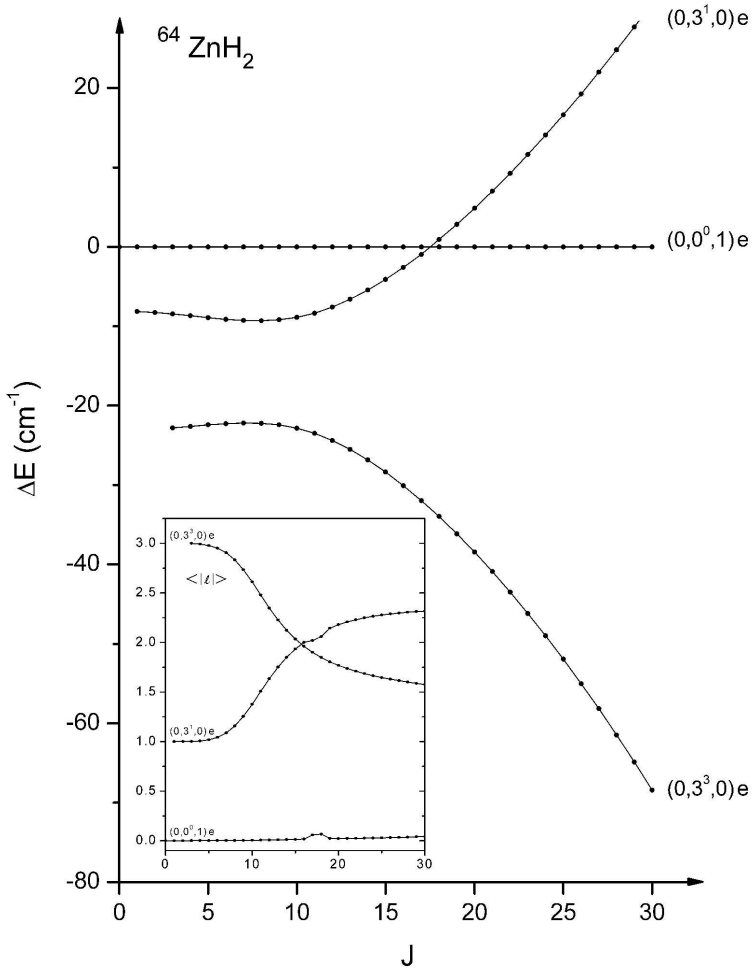

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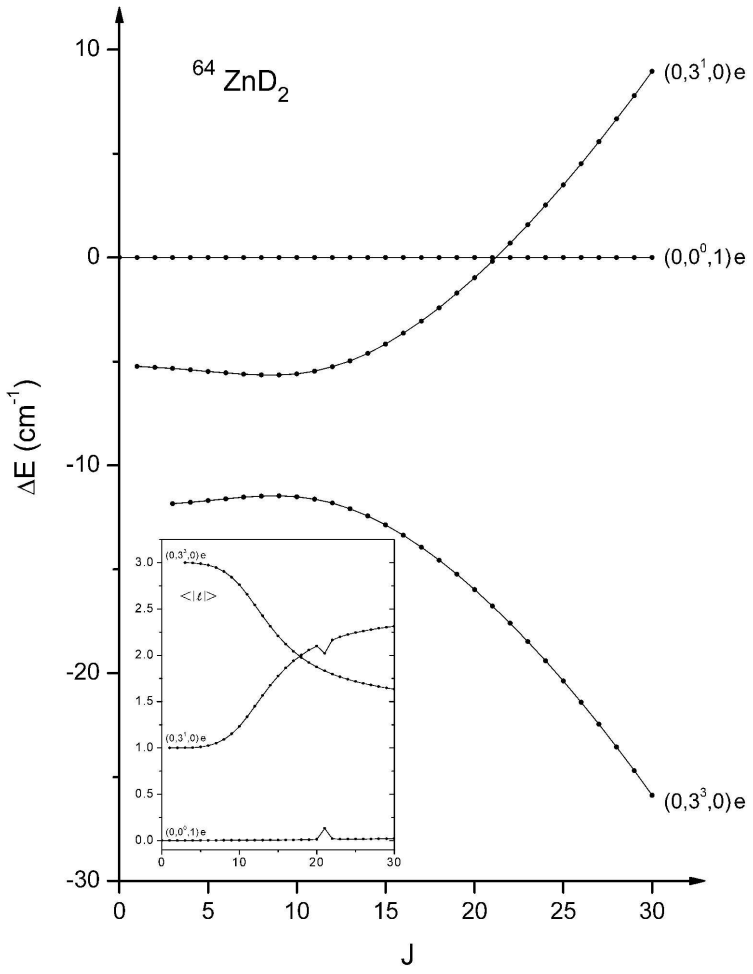

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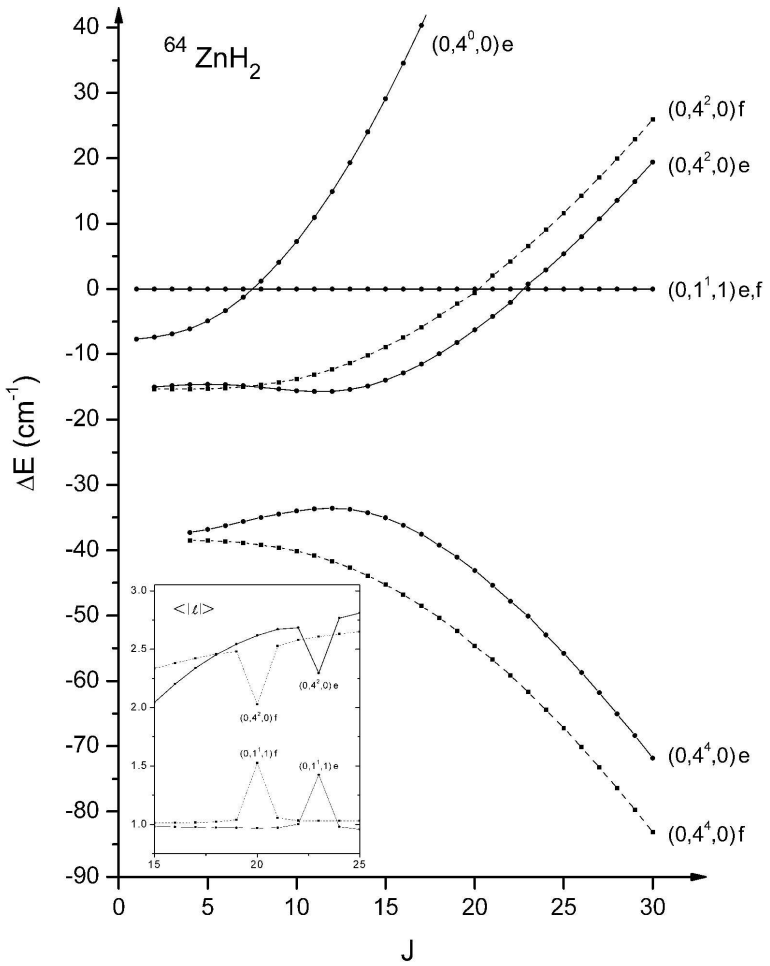

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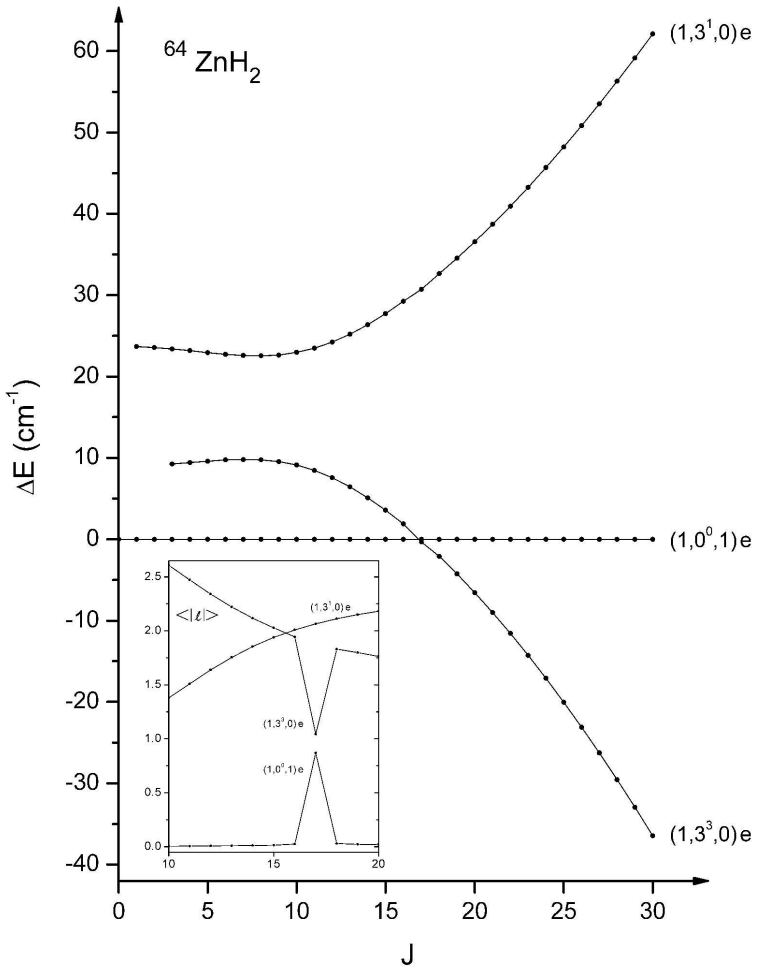

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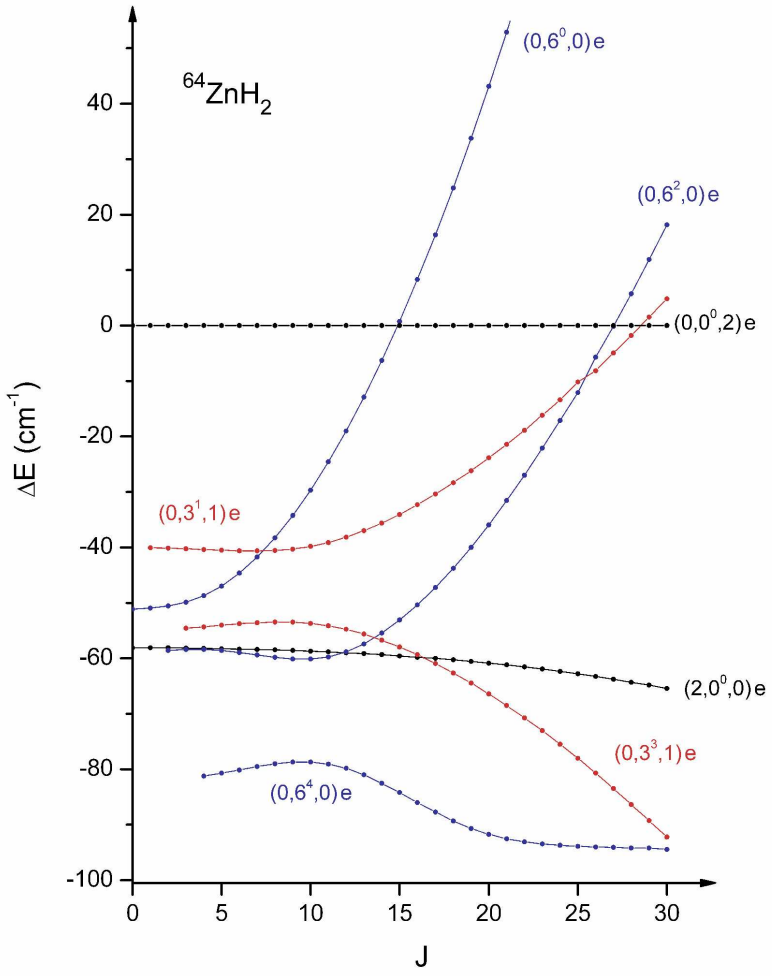

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Supplementary Online Material

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A theoretical study of ZnH_2, a case of very large Darling-Dennison resonance

5 tables and 3 figures

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Table S1: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{64}ZnH_2$.[a]

J	$(0,4^0,0)e$	$(0,4^2,0)e$	$(0,4^2,0)f$	$(0,4^4,0)e$	$(0,4^4,0)f$	$(0,1^1,1)e$	$(0,1^1,1)f$
0	2500.870						
1	2507.936					2515.593	2515.710
2	2522.102	2514.446	2514.481			2529.482	2529.833
3	2543.430	2535.500	2535.669			2550.313	2551.015
4	2572.001	2563.444	2563.931	2540.778	2540.778	2578.082	2579.251
5	2607.883	2598.214	2599.278	2575.995	2575.996	2612.785	2614.538
6	2651.112	2639.782	2641.720	2618.199	2618.204	2654.416	2656.868
7	2701.689	2688.155	2691.269	2667.357	2667.373	2702.970	2706.235
8	2759.610	2743.364	2747.939	2723.428	2723.473	2758.424	2762.629
9	2824.829	2805.452	2811.738	2786.360	2786.475	2820.794	2826.041
10	2897.337	2874.471	2882.675	2856.091	2856.348	2890.054	2896.459
11	2977.109	2950.478	2960.750	2932.549	2933.064	2966.194	2973.872
12	3064.123	3033.531	3045.960	3015.655	3016.600	3049.203	3058.266
13	3158.359	3123.675	3138.296	3105.338	3106.934	3139.066	3149.626
14	3259.793	3220.936	3237.743	3201.546	3204.048	3235.768	3247.936
15	3368.403	3325.306	3344.281	3304.256	3307.927	3339.293	3353.179
16	3484.166	3436.754	3457.887	3413.466	3418.554	3449.624	3465.338
17	3607.057	3555.233	3578.537	3529.186	3535.915	3566.742	3584.392
18	3737.050	3680.694	3706.200	3651.427	3659.993	3690.629	3710.324
19	3874.119	3813.088	3840.842	3780.197	3790.773	3821.263	3843.120
20	4018.235	3952.368	3982.289	3915.498	3928.236	3958.624	3982.899
21	4169.371	4098.491	4131.086	4057.324	4072.363	4102.692	4129.062
22	4327.494	4251.404	4286.509	4205.666	4223.131	4253.458	4282.277
23	4492.576	4411.363	4448.814	4360.510	4380.520	4410.602	4442.231
24	4664.582	4577.661	4617.956	4521.839	4544.504	4574.773	4608.907
25	4843.480	4750.797	4793.901	4689.630	4715.059	4745.408	4782.279
26	5029.235	4930.613	4976.612	4863.862	4892.157	4922.604	4962.318
27	5221.811	5117.066	5166.055	5044.510	5075.769	5106.338	5148.993
28	5421.171	5310.119	5362.193	5231.546	5265.867	5296.582	5342.273
29	5627.279	5509.736	5564.990	5424.943	5462.419	5493.306	5542.123
30	5840.094	5715.881	5774.408	5624.670	5665.394	5696.477	5748.512

[a] From variational calculations with the corrected PEF.

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Table S2: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{64}ZnD_2$.[a]

J	$(0,4^0,0)e$	$(0,4^2,0)e$	$(0,4^2,0)f$	$(0,4^4,0)e$	$(0,4^4,0)f$	$(0,1^1,1)e$	$(0,1^1,1)f$
0	1816.788						
1	1820.344					1826.277	1826.318
2	1827.464	1823.994	1824.003			1833.299	1833.423
3	1838.166	1834.622	1834.667			1843.833	1844.079
4	1852.473	1848.757	1848.889	1838.344	1838.344	1857.876	1858.286
5	1870.409	1866.375	1866.672	1856.093	1856.093	1875.427	1876.043
6	1891.991	1887.462	1888.019	1877.376	1877.377	1896.485	1897.348
7	1917.230	1912.012	1912.933	1902.186	1902.189	1921.049	1922.198
8	1946.123	1940.028	1941.419	1930.513	1930.520	1949.116	1950.593
9	1978.667	1971.520	1973.480	1962.344	1962.363	1980.684	1982.530
10	2014.854	2006.501	2009.121	1997.664	1997.707	2015.751	2018.005
11	2054.681	2044.986	2048.343	2036.456	2036.543	2054.310	2057.016
12	2098.136	2086.993	2091.149	2078.698	2078.864	2096.365	2099.560
13	2145.216	2132.540	2137.538	2124.366	2124.661	2141.908	2145.632
14	2195.914	2181.644	2187.510	2173.438	2173.928	2190.935	2195.229
15	2250.225	2234.319	2241.060	2225.893	2226.659	2243.443	2248.347
16	2308.143	2290.571	2298.186	2281.715	2282.849	2299.428	2304.982
17	2369.661	2350.399	2358.882	2340.900	2342.492	2358.884	2365.127
18	2434.773	2413.794	2423.142	2403.444	2405.586	2421.808	2428.779
19	2503.472	2480.743	2490.959	2469.352	2472.125	2488.193	2495.931
20	2575.751	2551.232	2562.325	2538.626	2542.105	2558.034	2566.579
21	2651.604	2625.246	2637.232	2611.272	2615.522	2631.326	2640.716
22	2731.022	2702.770	2715.673	2687.289	2692.370	2708.062	2718.336
23	2813.998	2783.793	2797.639	2766.679	2772.645	2788.236	2799.433
24	2900.524	2868.301	2883.117	2849.441	2856.341	2871.841	2884.003
25	2990.592	2956.284	2972.181	2935.571	2943.451	2958.872	2971.957
26	3084.193	3047.731	3064.622	3025.066	3033.970	3049.321	3063.490
27	3181.318	3142.619	3160.599	3117.920	3127.891	3143.192	3158.421
28	3281.958	3241.012	3260.060	3214.129	3225.206	3240.406	3256.789
29	3386.104	3342.781	3362.994	3313.685	3325.908	3341.072	3358.586
30	3493.746	3447.986	3469.389	3416.583	3429.989	3445.113	3463.805

[a] From variational calculations with the corrected PEF.

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Table S3: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{64}ZnH_2$.[a]

J	$(1,0^0,1)e$	$(1,3^1,0)e$	$(1,3^3,0)e$
0	3714.377		
1	3721.286	3744.979	
2	3735.103	3758.670	
3	3755.826	3779.215	3765.072
4	3783.451	3806.625	3792.869
5	3817.973	3840.919	3827.566
6	3859.387	3882.121	3869.126
7	3907.685	3930.266	3917.501
8	3962.860	3985.395	3972.632
9	4024.901	4047.548	4034.460
10	4093.799	4116.757	4102.932
11	4169.541	4193.032	4178.012
12	4252.116	4276.364	4259.685
13	4341.507	4366.728	4347.946
14	4437.701	4464.089	4442.800
15	4540.680	4568.413	4544.248
16	4650.424	4679.664	4652.293
17	4767.089	4797.811	4766.753
18	4890.184	4922.821	4888.092
19	5020.119	5054.664	5015.867
20	5156.746	5193.312	5150.187
21	5300.040	5338.735	5291.039
22	5449.974	5490.903	5438.401
23	5606.524	5649.787	5592.254
24	5769.664	5815.356	5752.574
25	5939.366	5987.579	5919.336
26	6115.600	6166.425	6092.513
27	6298.339	6351.860	6272.079
28	6487.551	6543.852	6458.004
29	6683.205	6742.364	6650.259
30	6885.267	6947.363	6848.813

[a] From variational calculations with the corrected PEF.

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Table S4: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{64}ZnD_2$.[a]

J	$(1,0^0,1)e$	$(1,3^1,0)e$	$(1,3^3,0)e$
0	2689.844		
1	2693.342	2704.662	
2	2700.339	2711.620	
3	2710.833	2722.058	2715.591
4	2724.824	2735.981	2729.656
5	2742.310	2753.393	2747.225
6	2763.291	2774.299	2768.288
7	2787.763	2798.709	2792.834
8	2815.726	2826.634	2820.846
9	2847.177	2858.087	2852.308
10	2882.113	2893.080	2887.201
11	2920.532	2931.624	2925.508
12	2962.430	2973.726	2967.217
13	3007.803	3019.385	3012.319
14	3056.648	3068.598	3060.813
15	3108.961	3121.354	3112.699
16	3164.737	3177.645	3167.976
17	3223.972	3237.460	3226.648
18	3286.661	3300.788	3288.712
19	3352.798	3367.621	3354.170
20	3422.376	3437.949	3423.019
21	3495.415	3511.763	3495.230
22	3571.850	3589.055	3570.862
23	3651.722	3669.816	3649.858
24	3735.014	3754.038	3732.227
25	3821.717	3841.713	3817.963
26	3911.824	3932.832	3907.060
27	4005.327	4027.387	3999.512
28	4102.220	4125.369	4095.311
29	4202.493	4226.769	4194.449
30	4306.138	4331.577	4296.920

[a] From variational calculations with the corrected PEF.

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TABLE S5: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{64}ZnH_2$ in the region of the first Darling-Dennison resonance system.[a]

J	$(2,0^0,0)e$	$(0,6^0,0)e$	$(0,6^2,0)e$	$(0,6^4,0)e$	$(0,6^6,0)e$	$(0,3^1,1)e$	$(0,3^3,1)e$	$(0,0,2)e$
0	3716.032	3723.028						3774.118
1	3722.937	3730.088				3740.989		3781.033
2	3736.745	3744.274	3736.284			3754.732		3794.862
3	3757.453	3765.708	3757.192			3775.355	3761.049	3815.603
4	3785.059	3794.526	3784.862	3761.997		3802.868	3788.946	3843.252
5	3819.557	3830.814	3819.236	3797.106		3837.289	3823.769	3877.805
6	3860.942	3874.594	3860.330	3839.149	3799.794	3878.643	3865.483	3919.256
7	3909.205	3925.835	3908.216	3888.068	3848.931	3926.973	3914.040	3967.598
8	3964.339	3984.570	3962.995	3943.784	3904.994	3982.260	3969.384	4022.824
9	4026.334	4050.688	4024.789	4006.196	3967.945	4044.627	4031.457	4084.924
10	4095.179	4124.208	4093.735	4075.184	4037.742	4114.063	4100.204	4153.888
11	4170.862	4205.104	4169.954	4150.643	4114.339	4190.585	4175.589	4229.705
12	4253.369	4293.353	4253.515	4232.518	4197.682	4274.186	4257.594	4312.362
13	4342.687	4388.933	4344.414	4320.824	4287.710	4364.842	4346.223	4401.847
14	4438.798	4491.820	4442.683	4415.629	4384.354	4462.520	4441.402	4498.143
15	4541.685	4601.990	4548.119	4517.027	4487.530	4567.185	4543.276	4601.236
16	4651.308	4719.418	4660.754	4625.122	4597.143	4678.803	4651.771	4711.108
17	4767.758	4844.075	4780.518	4740.018	4713.087	4797.339	4766.787	4827.742
18	4890.861	4975.934	4907.360	4861.807	4835.254	4922.764	4888.472	4951.118
19	5020.672	5114.966	5041.236	4990.555	4963.558	5055.047	5016.736	5081.216
20	5157.161	5261.139	5182.106	5126.282	5097.950	5194.158	5151.573	5218.014
21	5300.305	5414.422	5329.928	5268.961	5238.424	5340.070	5292.964	5361.492
22	5450.078	5574.781	5484.660	5418.530	5385.006	5492.756	5440.890	5511.623
23	5606.455	5742.181	5646.258	5574.911	5537.731	5652.194	5595.329	5668.385
24	5769.408	5916.588	5814.652	5738.026	5696.631	5818.382	5756.258	5831.752
25	5938.910	6097.964	5989.612	5907.807	5861.729	5991.482	5923.653	6001.696
26	6114.931	6286.271	6172.492	6084.191	6033.034	6170.069	6097.488	6178.191
27	6297.442	6481.471	6361.062	6267.122	6210.549	6356.287	6277.736	6361.218
28	6486.412	6683.522	6556.463	6456.547	6394.264	6548.941	6464.373	6550.729
29	6681.809	6892.384	6758.527	6652.407	6584.166	6748.182	6657.383	6746.635
30	6883.599	7108.013	6967.206	6854.570	6780.237	6953.838	6856.824	6949.047

[a] From variational calculations with the corrected PEF.

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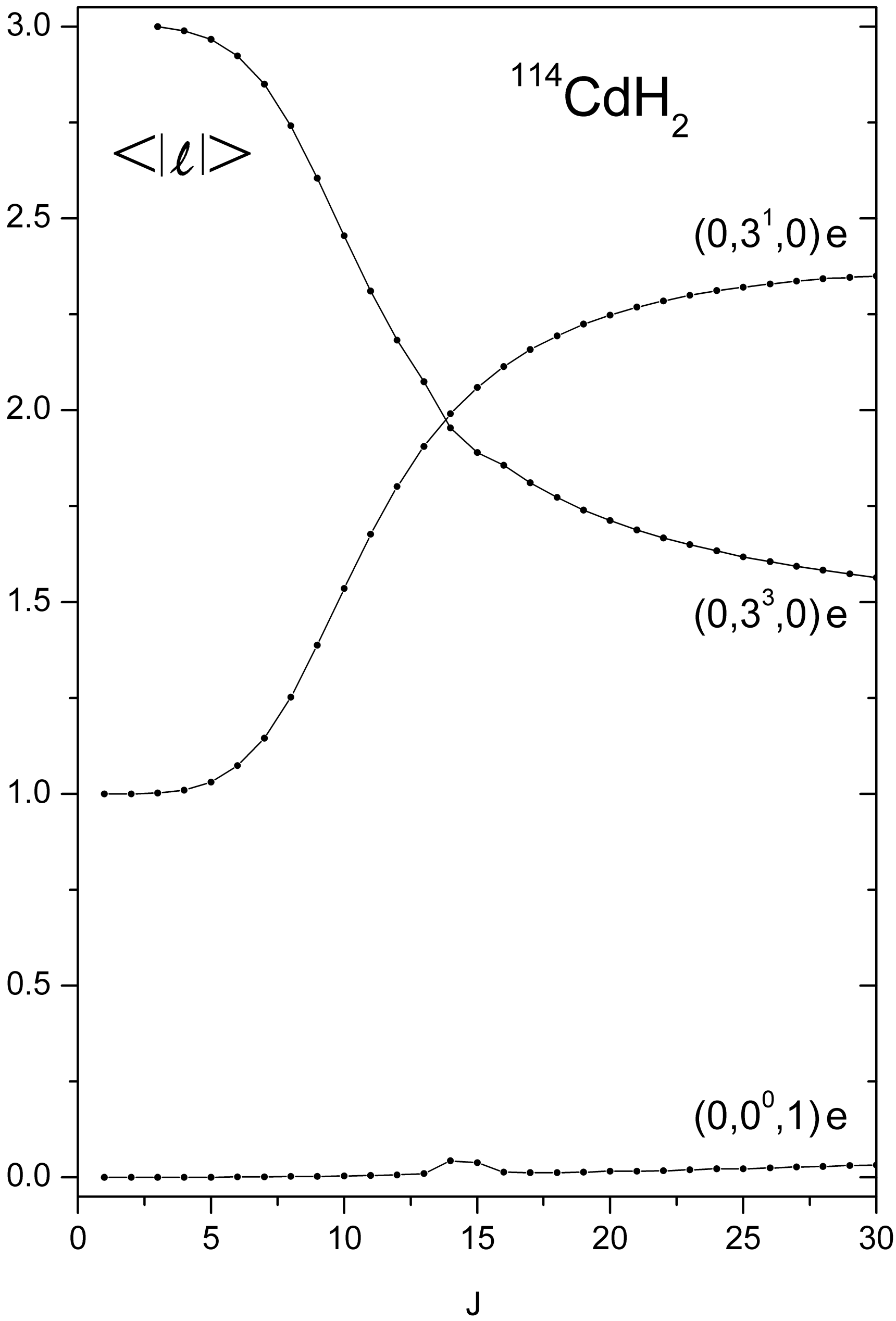
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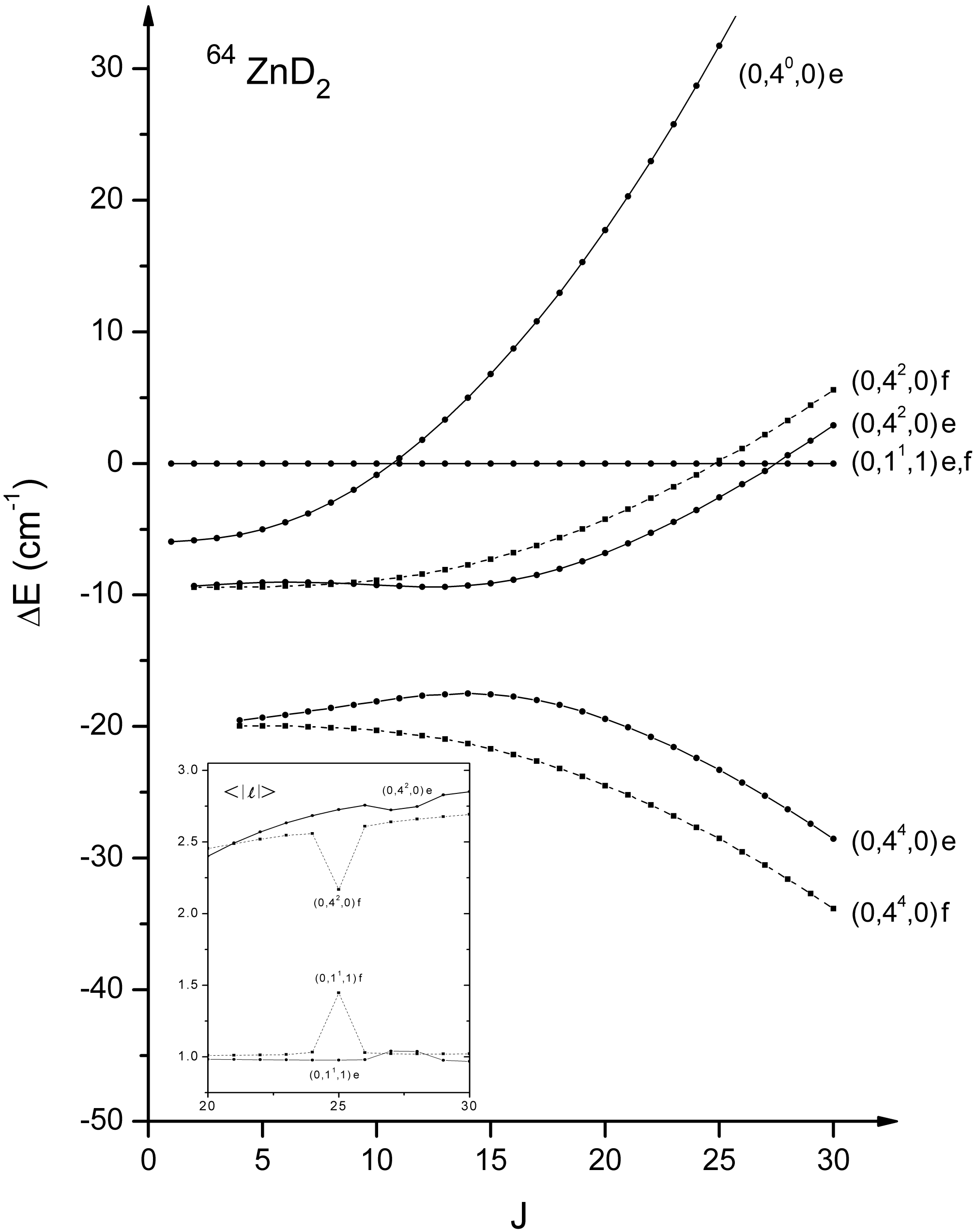
(0,3¹,0)e
(0,3³,0)e
(0,0⁰,1)e
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
5
10
15
20
25
30
J

SF1


$^{64}ZnD_2$
$(0,4^0,0)e$
$(0,4^2,0)f$
$(0,4^2,0)e$
$(0,1^1,1)e,f$
$(0,4^4,0)e$
$(0,4^4,0)f$
$\Delta E\ (cm^{-1})$
J
30
20
10
0
-10
-20
-30
-40
-50
0
5
10
15
20
25
30
$<|\ell|>$
$(0,4^2,0)e$
$(0,4^2,0)f$
$(0,1^1,1)f$
$(0,1^1,1)e$
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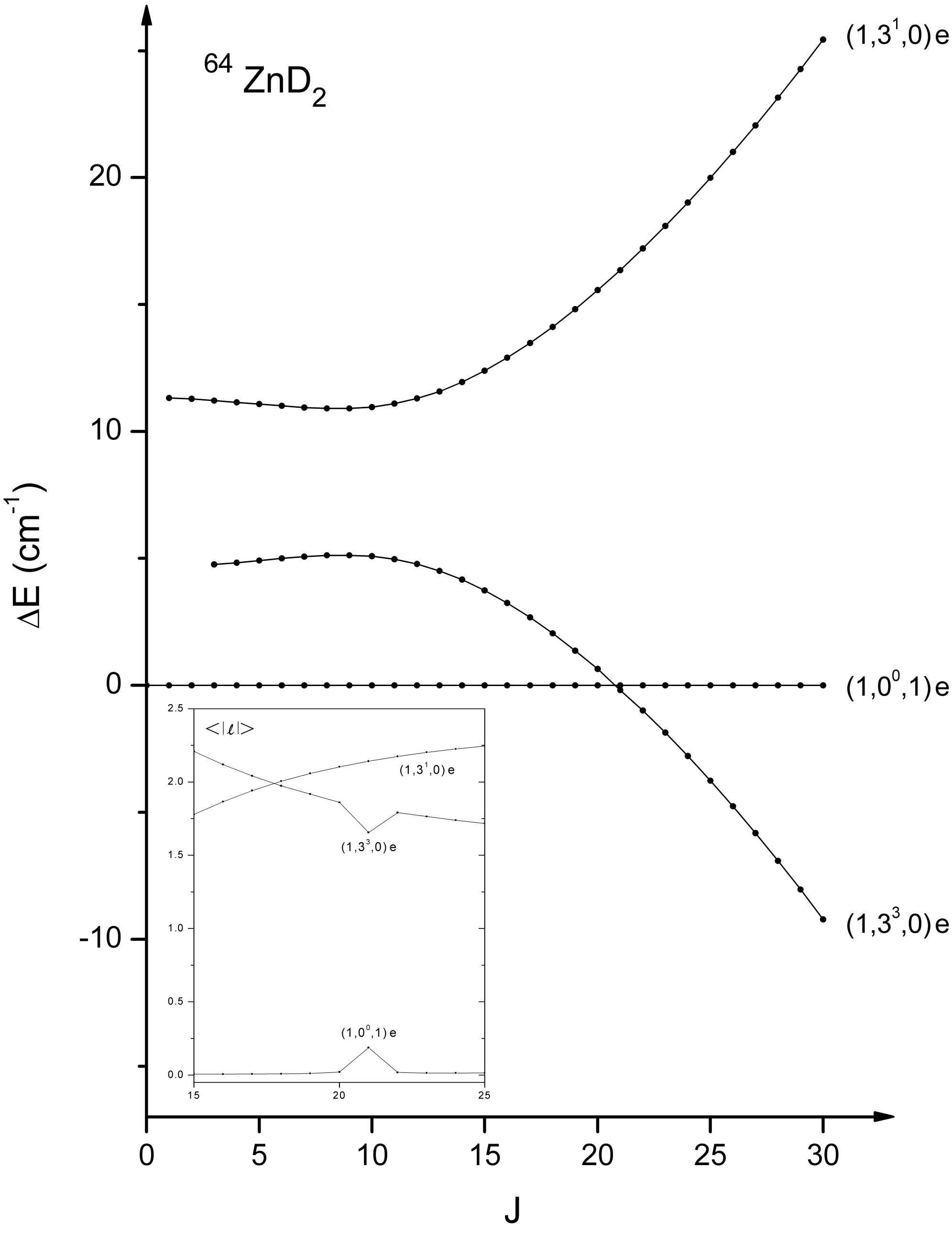
2.0
1.5
1.0
20
25
30

SF2



SF3

Supplementary Online Material

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A theoretical study of ZnH_2, a case of very large Darling-Dennison resonance

5 tables and 3 figures

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Table S1: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{64}ZnH_2$.[a]

J	$(0,4^0,0)e$	$(0,4^2,0)e$	$(0,4^2,0)f$	$(0,4^4,0)e$	$(0,4^4,0)f$	$(0,1^1,1)e$	$(0,1^1,1)f$
0	2500.870						
1	2507.936					2515.593	2515.710
2	2522.102	2514.446	2514.481			2529.482	2529.833
3	2543.430	2535.500	2535.669			2550.313	2551.015
4	2572.001	2563.444	2563.931	2540.778	2540.778	2578.082	2579.251
5	2607.883	2598.214	2599.278	2575.995	2575.996	2612.785	2614.538
6	2651.112	2639.782	2641.720	2618.199	2618.204	2654.416	2656.868
7	2701.689	2688.155	2691.269	2667.357	2667.373	2702.970	2706.235
8	2759.610	2743.364	2747.939	2723.428	2723.473	2758.424	2762.629
9	2824.829	2805.452	2811.738	2786.360	2786.475	2820.794	2826.041
10	2897.337	2874.471	2882.675	2856.091	2856.348	2890.054	2896.459
11	2977.109	2950.478	2960.750	2932.549	2933.064	2966.194	2973.872
12	3064.123	3033.531	3045.960	3015.655	3016.600	3049.203	3058.266
13	3158.359	3123.675	3138.296	3105.338	3106.934	3139.066	3149.626
14	3259.793	3220.936	3237.743	3201.546	3204.048	3235.768	3247.936
15	3368.403	3325.306	3344.281	3304.256	3307.927	3339.293	3353.179
16	3484.166	3436.754	3457.887	3413.466	3418.554	3449.624	3465.338
17	3607.057	3555.233	3578.537	3529.186	3535.915	3566.742	3584.392
18	3737.050	3680.694	3706.200	3651.427	3659.993	3690.629	3710.324
19	3874.119	3813.088	3840.842	3780.197	3790.773	3821.263	3843.120
20	4018.235	3952.368	3982.289	3915.498	3928.236	3958.624	3982.899
21	4169.371	4098.491	4131.086	4057.324	4072.363	4102.692	4129.062
22	4327.494	4251.404	4286.509	4205.666	4223.131	4253.458	4282.277
23	4492.576	4411.363	4448.814	4360.510	4380.520	4410.602	4442.231
24	4664.582	4577.661	4617.956	4521.839	4544.504	4574.773	4608.907
25	4843.480	4750.797	4793.901	4689.630	4715.059	4745.408	4782.279
26	5029.235	4930.613	4976.612	4863.862	4892.157	4922.604	4962.318
27	5221.811	5117.066	5166.055	5044.510	5075.769	5106.338	5148.993
28	5421.171	5310.119	5362.193	5231.546	5265.867	5296.582	5342.273
29	5627.279	5509.736	5564.990	5424.943	5462.419	5493.306	5542.123
30	5840.094	5715.881	5774.408	5624.670	5665.394	5696.477	5748.512

[a] From variational calculations with the corrected PEF.

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Table S2: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{64}ZnD_2$.[a]

J	$(0,4^0,0)e$	$(0,4^2,0)e$	$(0,4^2,0)f$	$(0,4^4,0)e$	$(0,4^4,0)f$	$(0,1^1,1)e$	$(0,1^1,1)f$
0	1816.788						
1	1820.344					1826.277	1826.318
2	1827.464	1823.994	1824.003			1833.299	1833.423
3	1838.166	1834.622	1834.667			1843.833	1844.079
4	1852.473	1848.757	1848.889	1838.344	1838.344	1857.876	1858.286
5	1870.409	1866.375	1866.672	1856.093	1856.093	1875.427	1876.043
6	1891.991	1887.462	1888.019	1877.376	1877.377	1896.485	1897.348
7	1917.230	1912.012	1912.933	1902.186	1902.189	1921.049	1922.198
8	1946.123	1940.028	1941.419	1930.513	1930.520	1949.116	1950.593
9	1978.667	1971.520	1973.480	1962.344	1962.363	1980.684	1982.530
10	2014.854	2006.501	2009.121	1997.664	1997.707	2015.751	2018.005
11	2054.681	2044.986	2048.343	2036.456	2036.543	2054.310	2057.016
12	2098.136	2086.993	2091.149	2078.698	2078.864	2096.365	2099.560
13	2145.216	2132.540	2137.538	2124.366	2124.661	2141.908	2145.632
14	2195.914	2181.644	2187.510	2173.438	2173.928	2190.935	2195.229
15	2250.225	2234.319	2241.060	2225.893	2226.659	2243.443	2248.347
16	2308.143	2290.571	2298.186	2281.715	2282.849	2299.428	2304.982
17	2369.661	2350.399	2358.882	2340.900	2342.492	2358.884	2365.127
18	2434.773	2413.794	2423.142	2403.444	2405.586	2421.808	2428.779
19	2503.472	2480.743	2490.959	2469.352	2472.125	2488.193	2495.931
20	2575.751	2551.232	2562.325	2538.626	2542.105	2558.034	2566.579
21	2651.604	2625.246	2637.232	2611.272	2615.522	2631.326	2640.716
22	2731.022	2702.770	2715.673	2687.289	2692.370	2708.062	2718.336
23	2813.998	2783.793	2797.639	2766.679	2772.645	2788.236	2799.433
24	2900.524	2868.301	2883.117	2849.441	2856.341	2871.841	2884.003
25	2990.592	2956.284	2972.181	2935.571	2943.451	2958.872	2971.957
26	3084.193	3047.731	3064.622	3025.066	3033.970	3049.321	3063.490
27	3181.318	3142.619	3160.599	3117.920	3127.891	3143.192	3158.421
28	3281.958	3241.012	3260.060	3214.129	3225.206	3240.406	3256.789
29	3386.104	3342.781	3362.994	3313.685	3325.908	3341.072	3358.586
30	3493.746	3447.986	3469.389	3416.583	3429.989	3445.113	3463.805

[a] From variational calculations with the corrected PEF.

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Table S3: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{64}ZnH_2$.[a]

J	$(1,0^0,1)e$	$(1,3^1,0)e$	$(1,3^3,0)e$
0	3714.377		
1	3721.286	3744.979	
2	3735.103	3758.670	
3	3755.826	3779.215	3765.072
4	3783.451	3806.625	3792.869
5	3817.973	3840.919	3827.566
6	3859.387	3882.121	3869.126
7	3907.685	3930.266	3917.501
8	3962.860	3985.395	3972.632
9	4024.901	4047.548	4034.460
10	4093.799	4116.757	4102.932
11	4169.541	4193.032	4178.012
12	4252.116	4276.364	4259.685
13	4341.507	4366.728	4347.946
14	4437.701	4464.089	4442.800
15	4540.680	4568.413	4544.248
16	4650.424	4679.664	4652.293
17	4767.089	4797.811	4766.753
18	4890.184	4922.821	4888.092
19	5020.119	5054.664	5015.867
20	5156.746	5193.312	5150.187
21	5300.040	5338.735	5291.039
22	5449.974	5490.903	5438.401
23	5606.524	5649.787	5592.254
24	5769.664	5815.356	5752.574
25	5939.366	5987.579	5919.336
26	6115.600	6166.425	6092.513
27	6298.339	6351.860	6272.079
28	6487.551	6543.852	6458.004
29	6683.205	6742.364	6650.259
30	6885.267	6947.363	6848.813

[a] From variational calculations with the corrected PEF.

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Table S4: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{64}ZnD_2$.[a]

J	$(1,0^0,1)e$	$(1,3^1,0)e$	$(1,3^3,0)e$
0	2689.844		
1	2693.342	2704.662	
2	2700.339	2711.620	
3	2710.833	2722.058	2715.591
4	2724.824	2735.981	2729.656
5	2742.310	2753.393	2747.225
6	2763.291	2774.299	2768.288
7	2787.763	2798.709	2792.834
8	2815.726	2826.634	2820.846
9	2847.177	2858.087	2852.308
10	2882.113	2893.080	2887.201
11	2920.532	2931.624	2925.508
12	2962.430	2973.726	2967.217
13	3007.803	3019.385	3012.319
14	3056.648	3068.598	3060.813
15	3108.961	3121.354	3112.699
16	3164.737	3177.645	3167.976
17	3223.972	3237.460	3226.648
18	3286.661	3300.788	3288.712
19	3352.798	3367.621	3354.170
20	3422.376	3437.949	3423.019
21	3495.415	3511.763	3495.230
22	3571.850	3589.055	3570.862
23	3651.722	3669.816	3649.858
24	3735.014	3754.038	3732.227
25	3821.717	3841.713	3817.963
26	3911.824	3932.832	3907.060
27	4005.327	4027.387	3999.512
28	4102.220	4125.369	4095.311
29	4202.493	4226.769	4194.449
30	4306.138	4331.577	4296.920

[a] From variational calculations with the corrected PEF.

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TABLE S5: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{64}ZnH_2$ in the region of the first Darling-Dennison resonance system.[a]

J	$(2,0^0,0)e$	$(0,6^0,0)e$	$(0,6^2,0)e$	$(0,6^4,0)e$	$(0,6^6,0)e$	$(0,3^1,1)e$	$(0,3^3,1)e$	$(0,0,2)e$
0	3716.032	3723.028						3774.118
1	3722.937	3730.088				3740.989		3781.033
2	3736.745	3744.274	3736.284			3754.732		3794.862
3	3757.453	3765.708	3757.192			3775.355	3761.049	3815.603
4	3785.059	3794.526	3784.862	3761.997		3802.868	3788.946	3843.252
5	3819.557	3830.814	3819.236	3797.106		3837.289	3823.769	3877.805
6	3860.942	3874.594	3860.330	3839.149	3799.794	3878.643	3865.483	3919.256
7	3909.205	3925.835	3908.216	3888.068	3848.931	3926.973	3914.040	3967.598
8	3964.339	3984.570	3962.995	3943.784	3904.994	3982.260	3969.384	4022.824
9	4026.334	4050.688	4024.789	4006.196	3967.945	4044.627	4031.457	4084.924
10	4095.179	4124.208	4093.735	4075.184	4037.742	4114.063	4100.204	4153.888
11	4170.862	4205.104	4169.954	4150.643	4114.339	4190.585	4175.589	4229.705
12	4253.369	4293.353	4253.515	4232.518	4197.682	4274.186	4257.594	4312.362
13	4342.687	4388.933	4344.414	4320.824	4287.710	4364.842	4346.223	4401.847
14	4438.798	4491.820	4442.683	4415.629	4384.354	4462.520	4441.402	4498.143
15	4541.685	4601.990	4548.119	4517.027	4487.530	4567.185	4543.276	4601.236
16	4651.308	4719.418	4660.754	4625.122	4597.143	4678.803	4651.771	4711.108
17	4767.758	4844.075	4780.518	4740.018	4713.087	4797.339	4766.787	4827.742
18	4890.861	4975.934	4907.360	4861.807	4835.254	4922.764	4888.472	4951.118
19	5020.672	5114.966	5041.236	4990.555	4963.558	5055.047	5016.736	5081.216
20	5157.161	5261.139	5182.106	5126.282	5097.950	5194.158	5151.573	5218.014
21	5300.305	5414.422	5329.928	5268.961	5238.424	5340.070	5292.964	5361.492
22	5450.078	5574.781	5484.660	5418.530	5385.006	5492.756	5440.890	5511.623
23	5606.455	5742.181	5646.258	5574.911	5537.731	5652.194	5595.329	5668.385
24	5769.408	5916.588	5814.652	5738.026	5696.631	5818.382	5756.258	5831.752
25	5938.910	6097.964	5989.612	5907.807	5861.729	5991.482	5923.653	6001.696
26	6114.931	6286.271	6172.492	6084.191	6033.034	6170.069	6097.488	6178.191
27	6297.442	6481.471	6361.062	6267.122	6210.549	6356.287	6277.736	6361.218
28	6486.412	6683.522	6556.463	6456.547	6394.264	6548.941	6464.373	6550.729
29	6681.809	6892.384	6758.527	6652.407	6584.166	6748.182	6657.383	6746.635
30	6883.599	7108.013	6967.206	6854.570	6780.237	6953.838	6856.824	6949.047

[a] From variational calculations with the corrected PEF.

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