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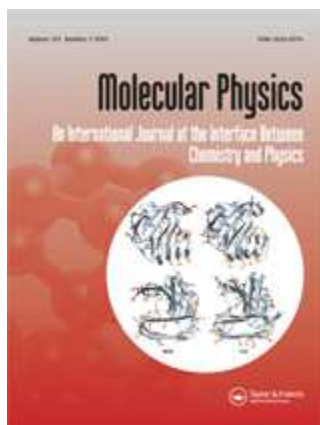
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Calculated spectroscopic properties of HgH₂

PETER BOTSCHWINA* and PETER SEBALD[#]

Institut für Physikalische Chemie, Universität Göttingen,
Tammannstraße 6, D-37077 Göttingen, Germany

[#] permanent address: Madenburgstraße 14, D-76865 Insheim, Germany

DETLEV FIGGEN and HERMANN STOLL

Institut für Theoretische Chemie, Universität Stuttgart,
Pfaffenwaldring 55, D-70569 Stuttgart, Germany

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*Email: pbotsch@gwdg.de

Abstract

Ab initio calculations of the coupled cluster and spin-orbit configuration type, in conjunction with a small-core pseudopotential for the mercury atom, have been employed to construct near-equilibrium potential energy and electric dipole moment functions for HgH₂. On that basis, rovibrational term energies and wavefunctions as well as transition dipole moments, absolute IR intensities and Einstein coefficients of spontaneous emission have been calculated variationally. Throughout, excellent agreement is obtained with recent experimental data from Fourier-transform infrared emission spectroscopy (A. Shayesteh, S. Yu, P. F. Bernath, *J. Phys. Chem. A*, **109**, 10280 (2005)). The gas-phase wavenumbers of the symmetric stretching and the bending vibrations of ²⁰²HgH₂ and ²⁰²HgD₂ (in parentheses) are predicted to be 2012.3 (1442.8) cm⁻¹ and 784.3 (564.1) cm⁻¹, respectively. Various predictions are made for ²⁰²HgHD, for which no high-resolution spectra have yet been published.

1. Introduction

Although the existence of solid mercury dihydride (HgH_2) has been known for more than half a century [1, 2], it was only recently that molecular HgH_2 could be investigated by means of high-resolution spectroscopy [3, 4]. Gaseous HgH_2 and its deuterated isotopomers were synthesized through the reaction of mercury vapour with molecular hydrogen or deuterium in the presence of a dc electrical discharge. The emission of molecules in excited rovibrational states was monitored by means of Fourier transform infrared (FTIR) spectroscopy within the spectral range of 1750-2200 cm^{-1} . Five different rovibrational bands could be analyzed for the isotopomers $^{202}\text{HgH}_2$, $^{200}\text{HgH}_2$, $^{202}\text{HgD}_2$ and $^{200}\text{HgD}_2$, allowing a wealth of spectroscopic constants to be determined with high precision. This material provides an almost ideal testing ground for high-level quantum chemical calculations, but still leaves much room for various predictions.

Earlier theoretical studies of spectroscopic properties of HgH_2 , carried out at the CIPSI, DFT(B3LYP), MP2 and CCSD(T) levels [5-8], were restricted to the harmonic approximation. Quite recently, a three-dimensional global potential energy surface for the electronic ground state of HgH_2 ($X^1\Sigma_g^+$) was constructed from more than 13,000 energy points as calculated by the internally contracted multireference configuration interaction method (MRCI) by Li, Xie and Guo [9]. Davidson's correction (termed MRCI+Q) was employed to approximately account for the effects of higher-order substitutions and the mercury atom was described by means of a pseudopotential (PP). The total valence basis comprised 210 contracted Gaussian-type orbitals (cGTOs). Three-dimensional spline interpolation was used to represent the PP/MRCI+Q potential energy surface, from which rotationless ($J = 0$) vibrational term energies and wavefunctions were computed by means of a direct product discrete variable representation (DVR). In comparison with the precise experimental results now available [4], the wavenumbers of the antisymmetric stretching vibrations (ν_3) of $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ were underestimated by 27.2 and 20.5 cm^{-1} , respectively.

The present paper aims to extend and **significantly** improve the previous theoretical work **for the lower-lying vibrational states up to $3\nu_1$ (second overtone of the symmetric stretching vibration)**. In particular, molecular rotation is taken into account and transition dipole moments and intensities of rovibrational transitions have been calculated. Higher accuracy is achieved **in the present calculations by the following means: a) use of a coupled cluster variant accounting for connected triple substitutions (however limited in application compared to ref. 9 because of its single-reference character), b) considerably larger basis sets than used in the earlier work, and c) the use of a modern pseudopotential for the mercury atom as well as explicit consideration of spin-orbit interaction.**

2. Details of calculations

High-level ab initio calculations of the coupled cluster (CC) and spin-orbit configuration interaction (SO-CI) type have been performed for the title molecule. Relativistic effects (both scalar-relativistic ones and SO contributions) have been included into the Hamiltonian by means of a small-core energy-consistent pseudopotential for the Hg atom [10]. For the description of valence orbitals, Dunning-type correlation-consistent polarized valence n-tuple zeta basis sets (cc-pVnZ) have been used, together with appropriate augmentations by diffuse functions (aug-cc-pVnZ) and functions of relevance for Hg outer-core (5sp) correlation (cc-pwCVnZ) [11-13].

The potential energy surface was first explored at the scalar-relativistic level, using the SO averaged pseudopotential in CC calculations with singles and doubles and perturbative triples (CCSD(T)) [14]. The cc-pwCV5Z [11] and aug-cc-pV5Z basis sets were applied for Hg and H, respectively, comprising a total of 344 contracted Gaussian-type orbitals (cGTOs). All explicitly treated electrons were correlated, including the Hg 5sp outer core. The ab initio program package MOLPRO [15, 16] was used in these calculations.

In a second step, we determined SO corrections to a selected number of the points of the scalar-relativistic potential energy surface as follows. We performed double-group SO-CI calculations with and without the SO part of the Hg pseudopotential. The cc-pwCVQZ [11] and cc-pVQZ [12] basis sets were used for Hg and H, respectively; for technical reasons, we had to leave out the h functions for Hg. Again, all valence and outer-core electrons were correlated. The SO-CI describes the second-order SO effects for HgH₂, together with electron correlation effects, by including all single and double excitations from the closed-shell singlet ground state with spin symmetries up to quintet. The SO energy contribution determined this way at the experimental equilibrium geometry [4] is -0.1386 E_h, i.e., less than 0.1% of the scalar-relativistic CISD energy. Including the SO part of the pseudopotential changes the weight of the reference function in the CISD wavefunction from 0.90 to 0.89. These small changes a-posteriori justify the incremental scheme used for the SO effects in the present work. The program package COLUMBUS [17, 18] was used for these calculations.

Three different analytical potential energy functions (PEFs) were established in the present work, all of which have the following form:

$$V - V(\tilde{r}_e) = \sum_{ijk} C_{ijk} \tilde{R}_1^i \tilde{R}_2^j \theta^k \quad (1)$$

In equation (1) the angle θ measures the deviation from linearity and \tilde{R}_i ($i = 1, 2$) is a Morse-like coordinate defined as follows [19]:

$$\tilde{R}_i = \{1 - \exp[-\beta(r_i - \tilde{r}_e)] / \tilde{r}_e\} / \beta \quad (2)$$

In equation (2), r_i ($i = 1, 2$) denote the two Hg-H distances. The definition of the dimensionless coordinate \tilde{R}_i involves two non-linear parameters, termed β and \tilde{r}_e . The first one is a common fitting parameter which was roughly optimized in a preliminary fit and then held fixed at a value of $\beta = 1.36$ in all following calculations. Preferably, the second parameter \tilde{r}_e should be the equilibrium Hg-H distance corresponding to the minimum of the analytical PEF under discussion. For linear HgH₂ a suitable approximate value is easily available through a one-dimensional fit to just a few energy values. Inserting the resulting \tilde{r}_e value into the chosen three-dimensional fit function according to equations (1) and (2), small linear terms C_{100} and C_{010} (both equal due to symmetry) will result. The fit function has thus to be transformed to those Hg-H distances r_i ($i = 1, 2$) which correspond to the PEF minimum, both termed r_e . The latter should provide an improvement over the initial \tilde{r}_e value and an iterative process may be started by setting $\tilde{r}_e = r_e$ and insertion into equation (2), followed by a new least-squares fit. In the present applications, the iterative process converged in 1-2 iterations to a numerical accuracy in r_e of ca. 10^{-6} Å. We may therefore safely set $\tilde{r}_e = r_e$ at the end.

In the construction of the first analytical PEF, termed PP/CCSD(T), 218 non-redundant energy points were employed. These cover a range of nuclear coordinate space which extends up to ca. $10,000 \text{ cm}^{-1}$ above the minimum; this portion of the potential energy surface appears to lie well within the regime where single-reference CCSD(T) is valid. At the end of the iterative process, a fit with 32 non-redundant linear coefficients C_{ijk} (zero linear terms not counted) yielded a standard deviation of $6.4 \cdot 10^{-7} E_h$. The minimum of the fit function was determined to be $r_e = \tilde{r}_e = 1.636948$ Å.

Over the range of nuclear configurations considered, the spin-orbit corrections show only a slight dependence on the change in the Hg-H bond lengths and a still smaller dependence on the H-Hg-H bond angle. Consequently, a smaller grid of points turned out to be sufficient. A total of 87 non-redundant SO contributions was employed, which were least squares fitted in the same way as the CCSD(T) energies (standard deviation: $3.4 \cdot 10^{-7} E_h$), but taking only 14 non-redundant linear parameters into account. Addition of the analytical forms for PEF PP/CCSD(T) and SO correction and readjustment to the resulting energy minimum leads to PEF "PP/CCSD(T)+SO", with

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minimum at $r_e = \tilde{r}_e = 1.63448 \text{ \AA}$. Further improvement of the latter PEF is based on variational calculations of rovibrational states as described below. Two pieces of experimental information are employed which are easily accessible in many cases. These are the experimental ground-state rotational constant B_{000} of the most abundant isotopomer $^{202}\text{HgH}_2$ and the (rotationless) wavenumber of the antisymmetric stretching vibration (ν_3) of the same isotopic species. These two sources of information were employed in an iterative least-squares procedure to adjust the fit parameter r_e , mainly determined by B_{000} (exp.), and to determine a common scaling factor for the diagonal stretch-only parts of the corrected PEF, termed “PP/CCSD(T)+SO+corr” in the following. Non-linear and linear parameters of all three different PEFs are given in table 1. By definition, the corrected PEF reproduces the experimental values for B_{000} ($^{200}\text{HgH}_2$) and ν_3 ($^{202}\text{HgH}_2$) [4] in converged variational calculations of rovibrational states.

Making use of the PEFs described above, rovibrational term energies and wavefunctions were calculated variationally by diagonalizing Watson’s isomorphic rovibrational Hamiltonian for linear molecules [20] in a basis of harmonic oscillator/rigid rotor functions. These calculations were carried out with a program written by one of us [21]. Utilizing g/u-symmetry for the symmetrical isotopomers HgH_2 and HgD_2 , a product basis of 451 functions yields the term energies of vibrational states up to $3\nu_1$ with a numerical accuracy of 0.01 cm^{-1} or better. In the calculations for HHgD , a basis set of 924 functions was employed in order to achieve the same sort of accuracy. The total size of the rovibrational Hamiltonian matrix is about J-times the size of the pure vibrational basis, where J is the rotational quantum number.

The empirically corrected PEF was used in the calculation of rovibrational levels which were considered up to $J = 25$. For states with quantum number $l = 0$, rotational constants B_v and quartic centrifugal distortion constants D_v were determined by least-squares fit according to the formula:

$$E_v = \nu_0 + B_v J(J+1) - D_v [J(J+1)]^2 \quad (3)$$

Here, E_v is the calculated rovibrational term energy of the vibrational state under consideration and ν_0 denotes the band origin. For states with $l \neq 0$, the following formula was employed:

$$E^e + E^f = \nu_0 + B_v [J(J+1) - l^2] - D_v [J(J+1) - l^2]^2 \quad (4)$$

In equation [4], E^e and E^f denote the rovibrational term energy of the vibrational level under consideration in the so called e-block and f-block, respectively. The l-type doubling constants q_v and q_J were obtained through least-squares fit with an expression on the form:

$$E^e - E^f = q_v J(J+1) + q_J [J(J+1)]^2 \quad (5)$$

In order to compute transition dipole moments and intensities of rovibrational transitions, the variation of the electric dipole moment with the nuclear coordinates has to be known. An analytical electric dipole moment function (EDMF) has been constructed on the basis of PP/CCSD(T) calculations with the 344 cGTO basis set (see above). Individual dipole moment values were obtained as sums of Hartree-Fock contributions (computed as expectation values) and CCSD(T) correlation contributions, the latter calculated as energy derivatives using electric field strengths of ± 0.0002 a.u.. The expansion of the EDMF was carried out around the minimum of the corrected potential energy surface ($r_e = 1.633405$ Å; cf. table 1). The originally calculated components of the dipole moment, termed μ_z and μ_x , were then transformed to the molecular Eckart frame [22]. The resulting components, termed μ^{\parallel} and μ^{\perp} , were least-squares fitted independently by an analytical function of the form:

$$\mu_{\alpha} = \sum_{ijk} D_{ijk}^{\alpha} S_1^i S_3^j \theta^k \quad (\alpha : \text{parallel or perpendicular}) \quad (6)$$

S_1 and S_3 are symmetry co-ordinates defined as $S_1 = 2^{-1/2} (r_1 + r_2 - 2r_e)$ and $S_3 = 2^{-1/2} (r_1 - r_2)$, respectively. The parallel component of the dipole moment is of σ_u symmetry, while the perpendicular component is of π_u symmetry. Therefore, the former is fitted with only odd values of j and even values of k , whereas the latter component is fitted with even values of j and odd values of k . There are no restrictions on the index i . In total, dipole moments were calculated at 90 nuclear configurations and the two components were fitted with 25 and 19 terms, respectively. The parameters of the EDMF for $^{202}\text{HgH}_2$, i.e., coefficients D_{ijk}^{\parallel} and D_{ijk}^{\perp} , are listed in table 2. Since the definition of the molecular Eckart frame depends on the nuclidic masses, a transformation of the dipole moment components has to be undertaken in the course of the calculation of dipole moment matrix elements over rovibrational basis functions, in particular for the asymmetric isotopomer $^{202}\text{HgHD}$.

Rovibrational wavefunctions and dipole moment matrix elements were used to calculate squared transition dipole moments, termed R^2 , closely following the detailed description of ref. [23]. Taking the square root of R^2 values divided by the appropriate Hönl-London factor gives the

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2 transition dipole moment of the rovibrational transition of interest. For a given rovibrational band,
3 either of parallel or perpendicular type, (rotationless) vibrational transition dipole moments may
4 then be extracted by making use of formulae derived by Watson [24]. Finally, absolute IR
5 absorption intensities of complete rovibrational bands, corresponding to transitions from the
6 vibrational ground-state $|0\rangle$ to a final state $|f\rangle$, were approximately calculated by the well-known
7 formula (see, e.g., [25]):
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$$A_{f0} = \frac{\pi N_A}{3\hbar c_0 \epsilon_0} \tilde{\nu}_{f0} |\mu_{f0}|^2 \quad (7)$$

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20 Here, N_A is Avogadro's constant, \hbar Planck's constant divided by 2π , c_0 the vacuum velocity of
21 light, ϵ_0 the permittivity of vacuum, $\tilde{\nu}_{f0}$ the vibrational wavenumber and μ_{f0} the corresponding
22 vibrational transition moment.
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3. Results and discussion

Rotationless vibrational term energies for $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$, as obtained from the previous work [9] and the three PEFs of the present paper (cf. table1), are listed in Table 3. All vibrational states with $l = 0$ up to the second overtone of the symmetric stretching vibration ($3\nu_1$) are included. Experimental values, available for ν_3 , $2\nu_3$ and $3\nu_3$ of both isotopomers, are given in parentheses. Compared with the results of Li et al. [9], the present PP/CCSD(T) calculations reduce the errors in the term energies of the $n\nu_3$ series by a factor of 2. Explicit inclusion of SO effects yield errors for the ν_3 fundamentals of $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ of only 2.5 and 2.3 cm^{-1} , respectively, which constitutes an improvement by an order of magnitude with respect to the results of the previous work [9]. PEF PP/CCSD(T)+SO also does a very good job for the overtones $2\nu_3$ and $3\nu_3$ of both isotopomers, deviations from the experimental values not exceeding 3.7 cm^{-1} . The empirically corrected potential PP/CCSD(T)+SO+corr produces data for the $n\nu_3$ series of $^{202}\text{HgD}_2$ in excellent agreement with experiment (largest deviation: 0.9 cm^{-1}), keeping in mind that the corrections to the potential involve no experimental data for this isotopomer. For the wavenumbers of the symmetric stretching vibrations of $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ it is expected to yield values which are accurate to better than 1 cm^{-1} . Further comparison with experiment is possible for the differences between the term energies of states (1,0,1) and (0,0,1). Calculated values for $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ are 1843.1 and 1340.2 cm^{-1} , respectively, whereas the corresponding experimental values are 1842.0 and 1340.1 cm^{-1} [4].

Since no gas-phase high-resolution spectroscopic studies have yet been published for $^{202}\text{HgHD}$, the theoretical values collected in table 4 stand as predictions. Like for the symmetrical isotopomers (cf. table 3), the results based on the empirically corrected potential from the present work are expected to provide a significant enhancement in accuracy over the results of earlier calculations [9]. In particular, the calculated band origins of the two IR active stretching vibrations at $\nu_1 = 1966.9\text{ cm}^{-1}$ (\sim Hg-H stretch) and $\nu_3 = 1405.8$ (\sim Hg-D stretch) should be in error by only about 1 cm^{-1} . These values may be compared with $\text{H}_2/\text{D}_2/\text{Ar}$ matrix-isolation IR data of 1947 and 1392 cm^{-1} [26] and more recent IR data for HgHD in solid neon of 1966.9 and 1405.9 cm^{-1} [8]. The absolute IR intensities of the two stretching vibrations of $^{202}\text{HgHD}$ are predicted to be $A(\nu_1) = 172.1$ (172.2) km mol^{-1} and $A(\nu_3) = 115.3$ (120.1) km mol^{-1} , where the corresponding values as obtained within the familiar double harmonic (DH) approximation (harmonic force field and linear dipole moment function) are given in parentheses. The present DH intensities may be compared with earlier values of 167 and 142 km mol^{-1} (MP2) and 209 and 146 km mol^{-1} (DFT/B3LYP) [8].

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Rotational and centrifugal distortion constants for seven vibrational states of four different symmetric isotopomers with $l = 0$ are listed in Table 5. The changes in the rotational constants occurring upon vibrational excitation are reproduced well by the present calculations. For the ν_3 series of $^{202}\text{HgH}_2$, these are (in cm^{-1}) -0.02898 (-0.02983), -0.05990 (-0.06173) and -0.09618 (-0.09975), where experimental values are given in parentheses. The computed values thus account for 96-97 % of their experimental counterparts. Even better agreement with experiment is obtained for excitation of one quantum of the symmetric stretching vibration ν_1 , with the reduction in the rotational constant calculated to be 0.04755 (exp.: 0.04789) cm^{-1} . Simultaneous excitation of both one quantum of symmetric and antisymmetric stretching vibration reduces the ground-state rotational constant by 0.07713 cm^{-1} (calc.) and 0.07837 cm^{-1} (exp.). For isotopomer $^{202}\text{HgHD}$, the ground-state and excited state rotational constants B_{000} , B_{100} and B_{001} are predicted to be (in cm^{-1}) 2.06723, 2.04916 and 2.04426. The corresponding quartic centrifugal distortion constants are (in 10^{-5}cm^{-1}): 1.402, 1.389 and 1.394. Spectroscopic constants for other vibrational states are available from the authors upon request.

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Gas-phase IR absorption spectra in the region of the stretching fundamentals for $^{202}\text{HgH}_2$, $^{202}\text{HgD}_2$ and $^{202}\text{HgHD}$ are displayed in figure 1. For the symmetric isotopomers, the different statistical weights for H and D were taken into account and result in a characteristic alternation of the line intensities. The absolute IR intensities of the antisymmetric stretching vibrations of $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ are calculated to be 388.3 (388.4) and 196.3 (196.2) km mol^{-1} , respectively, DH values being given in parentheses. The rather high intensities may be considered as spectroscopic indicators of a relatively high polarity of the Hg-H bonds and thus of substantial hydride character of the terminal hydrogen atoms. Earlier theoretical DH values [8] are 411 and 208 km mol^{-1} (MP2) and 472 as well as 238 km mol^{-1} (DFT/B3LYP), both in reasonable agreement with the present values.

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A comparison of calculated and experimental spectroscopic constants for two states with $l = 1$, again for four different symmetric isotopomers, is made in table 6. Again, agreement between theory and experiment is very good. Excitation of one quantum of the bending vibration leads to a slight decrease in the rotational constant in all four cases. This is an unusual behaviour for most linear molecules, but appears to be a common feature for linear centrosymmetric molecules of type H-M-H, where M is a metal atom of group 12 (Zn, Cd, Hg) [4, 27, 28].

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Figure 2 predicts the absorption spectra of the ν_2 bands of $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ at 293 K. The band origins of the two bands are calculated to be 784.3 and 564.1 cm^{-1} , respectively. Neon matrix data [8] are ν_2 (HgH_2) = 781.7 cm^{-1} and ν_2 (HgD_2) = 561.9 cm^{-1} , both quite close to the present gas-phase predictions. The absolute IR intensities of the two ν_2 bands of $^{202}\text{HgH}_2$ and

$^{202}\text{HgD}_2$ are calculated to be 67.8 (64.4) and 33.8 (32.6) km mol^{-1} , respectively, where DH values are given in parentheses.

The band origin of the ν_2 band of $^{202}\text{HgHD}$ is calculated to be 684.1 cm^{-1} (PP/CCSD(T)+SO+corr). It may be compared with a value of 681.4 cm^{-1} as obtained in solid neon [8]. The absolute IR intensity of that band is predicted as 51.0 km mol^{-1} . The corresponding values [8] are 72 km mol^{-1} (MP2) and 50 km mol^{-1} (DFT/B3LYP). Spectroscopic constants for the singly excited bending vibrational state (0, 1¹, 0) are $B_{010} = 2.04907 \text{ cm}^{-1}$, $D_{010} = 1.390 \cdot 10^{-5} \text{ cm}^{-1}$, $q_{010} = 0.02269 \text{ cm}^{-1}$ and $q^J_{010} = 4.5 \cdot 10^{-7} \text{ cm}^{-1}$.

For the quantitative interpretation of intensities of emission spectra, the knowledge of Einstein coefficients of spontaneous emission is required (see, e.g., [29] for their definition). Results for those vibrational transitions which were observed for $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ [4] are listed in table 7. Throughout, the quoted Einstein coefficients should be accurate to 1-2 %.

From the empirically corrected PEF, the harmonic vibrational wavenumbers of $^{202}\text{HgH}_2$ (in cm^{-1}) were obtained to be $\omega_1 = 2106.0$ (2112), $\omega_2 = 816.5$ (770) and $\omega_3 = 1988.4$ (1994.4), where approximate experimental values [4] are given in parentheses. The values of the present work are expected to be accurate to 1 cm^{-1} for ω_1 and ω_3 since the stretching part of the PP/CCSD(T)+SO+corr potential was improved through the use of the experimental value for ν_3 . The error in ω_2 may be slightly larger. Shangesteh et al. [4] expect that their approximate values for ω_1 and ω_2 have uncertainties of more than 1 %, while they appear to consider their value for ω_3 , quoted as $1994.5880(4) \text{ cm}^{-1}$ in table 3 of ref. 4, to be very accurate. This has to be taken with caution, however. In the experimental work, ω_3 was obtained by means of the following equation:

$$\omega_3 \approx \nu_3 - 2X_{33} - X_{23} - X_{13}/2 \quad (8)$$

The anharmonicity constant X_{33} was calculated according to

$$X_{33} \approx [(2\nu_3) - 2 \cdot \nu_3]/2 = -15.1200(1) \text{ cm}^{-1} \quad (9)$$

Since the first overtone of the antisymmetric stretching vibration ($2\nu_3$) undergoes Darling-Dennison resonance with the first overtone of the symmetric stretching vibration ($2\nu_1$), which shifts down the lower-lying former vibrational state, the X_{33} value calculated via equation (9) is too small (in a mathematical sense; note that X_{33} is negative). Consequently, a too high value results for ω_3 . Using the variational data from table 3 (PP/CCSD(T)+SO+corr) we may calculate X_{33} in the same way as the experimentalists and arrive at -14.5 cm^{-1} , very close to the value obtained from equation (9),

However, when the anharmonicity constant X_{33} is calculated by means of conventional 2nd order perturbation theory in normal coordinate space, (see, e.g. [30]), using a quartic force field as extracted from the empirically corrected PEF of this work, we obtain at $X_{33} = -12.0 \text{ cm}^{-1}$. The other two anharmonicity constants which may be compared with experiment are $X_{13} = -71.9$ (-70.8) and $X_{23} = -16.1$ (-16.1) cm^{-1} , both almost identical to the corresponding experimental values (in parentheses).

In an attempt to determine a very accurate value for the equilibrium bond length r_e of HgH_2 , Shayesteh et al. [4] proceeded as follows. Vibration-rotation coupling constants α_i ($i = 1-3$) were calculated as differences of rotational constants between the vibrational ground-state and the three excited states with single-quantum excitation of only one vibrational mode. The equilibrium rotational constants B_e of those symmetric isotopomers, which contain $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ atoms, were then calculated according to the formula:

$$B_e \approx B_{000} + \sum_{i=1}^3 \alpha_i \cdot d_i / 2 \quad (10)$$

In equation (10), d_i is a degeneracy factor (1 for the two stretching vibrations, 2 for the bending vibration). From the B_e value for each isotopomer, the corresponding r_e value was then computed through

$$r_e = \left(\frac{h}{16\pi^2 c_0 M B_e} \right)^{\frac{1}{2}} \quad (11)$$

In equation (11), M denotes the nuclidic mass of the hydrogen isotope under consideration (H or D). The fundamental physical constants h and c_0 have their usual meaning. Due to the centrosymmetric equilibrium structure of HgH_2 , B_e should not depend on the mass of the central mercury atom. The experimentally determined B_e values given in table 3 of ref. [4] fulfil this requirement within 10^{-5} cm^{-1} . The r_e values determined therefrom for the isotopomers $^{202}\text{HgH}_2$, $^{200}\text{HgH}_2$, $^{202}\text{HgD}_2$ and $^{200}\text{HgD}_2$ are 1.63324(1) Å, 1.63324(1) Å, 1.63315(1) Å and 1.63315(1) Å, respectively, the standard deviation in terms of the least significant digit being given in parentheses. As expected, the r_e values for $^{202}\text{HgH}_2$ and $^{200}\text{HgH}_2$ are equal within experimental precision and the same holds for the corresponding deuterated species. However, between H and D isotopomers a small, but significant r_e difference of 0.00009 Å was obtained. It was attributed to the breakdown of the Born-Oppenheimer approximation without further, more physical explanation.

To our opinion, a more detailed discussion might be desirable. Firstly, we would like to emphasize that equation (10), as used by the experimentalists, is only a (linear) approximation. Preferably, one would like to calculate the difference

$$\Delta B_0 = B_e - B_{000} \quad (12)$$

directly, i.e., without the necessity to make use of data for excited vibrational states which may always be subject to some sort of perturbation. Within variational calculations we can easily test the goodness of the indirect procedure, which spectroscopists have to take, versus the direct one. For the corrected PEF, which reproduces the experimental B_{000} ($^{202}\text{HgH}_2$), one obtains ΔB_0 (direct) = 0.04982 cm^{-1} and ΔB_0 (indirect) = 0.05025 cm^{-1} , a noticeable difference of 0.00043 cm^{-1} . This is an indication that the indirect experimental value of 0.05047 cm^{-1} (cf. table 3 of ref. 4) is about too high by the noted difference and consequently the B_e value of $3.135325(24) \text{ cm}^{-1}$ is too high by the same amount as well.

At this point of the discussion, it may be noteworthy to mention the great success of accurate equilibrium structure determinations which were achieved through the deliberate combination of experimental and theoretical data (see, e.g., ref. [31]). These typically combine precise experimental ground-state rotational constants with directly calculated ΔB_0 values (either from variational calculations or obtained by 2nd order perturbation theory in normal coordinate space [30]). Since the joint use of variational and perturbation theory in this context is still rather scarce in the literature, we consider HgH_2 to be a good testing ground for the application of different procedures. Within the present work, both variational and perturbative calculations of ΔB_0 values may be easily performed on the basis of the three analytical potential energy functions described in table 1.

Calculated differences ΔB_0 for the four different symmetric isotopomers mentioned above are listed in table 8. These are combined with the corresponding experimental ground-state rotational constants B_{000} (cf. table 3 of ref.[4]) to produce B_e values, the latter being quoted in table 9. Finally, r_e values are calculated individually for each isotopomer and procedure through the application of equation (11). The results are given in table 10. Looking at a single column, corresponding to an individual isotopomer, the differences in the r_e values are quite small, the maximum differences amounting to $1.14 \cdot 10^{-4} \text{ \AA}$ for H isotopomers and to only $6.2 \cdot 10^{-5} \text{ \AA}$ for deuterated species. Between symmetric H and D species, however, the difference may be as large as $1.96 \cdot 10^{-4} \text{ \AA}$ (for the variational calculations employing the corrected PEF of the present work, for which one might expect the best values).

On the basis of these results, we are convinced that part of the “failure” to obtain mass-independent r_e values with an accuracy of better than 10^{-4} \AA through the applied procedures lies in

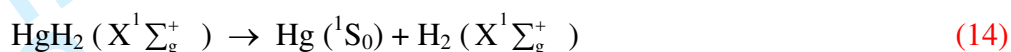
1
2 the usage of nuclidic masses for the bare hydrogen and deuterium atom in equation (11). As was
3 already noted above in the short discussion of the high value of the absolute IR intensity of the
4 antisymmetric stretching vibration of $^{202}\text{HgH}_2$, the Hg-H bond must be considered to exhibit a
5 significant degree of polarity according to $\text{Hg}^{\delta+} - \text{H}^{\delta-}$, corresponding to some hydride character of
6 the terminal hydrogen atoms in HgH_2 . In an attempt to solve the problem of determining a mass-
7 independent r_e value, this means that (larger) M values, as appropriate to the molecular situation,
8 would have to be applied. These might be written
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$$M^* = M + \delta m \quad (13)$$

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20 where δm may be considered to be some fraction of the electron rest mass, corresponding to some
21 electron transfer from the mercury atom to the two hydrogen atoms. A quantitative measure of the
22 size of the charge transfer from Hg to the H atoms is hard to obtain; a crude Mulliken population
23 analysis at the PP/Hartree-Fock level yields a value of ca. $\frac{1}{4}$ electron charge per H atom. The
24 corresponding mass change δm will already significantly reduce the differences in r_e values
25 between symmetric H and D species. Using the B_e values for $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ from the second-
26 last line of table 9 in conjunction with $\delta m = m_e/4$ we arrive at $r_e(^{202}\text{HgH}_2) = 1.633294 \text{ \AA}$ and r_e
27 ($^{202}\text{HgD}_2$) = 1.633153 \AA , the difference being reduced by 0.000055 \AA . On the whole it appears safe
28 to make the following statement: about 10^{-4} \AA is probably a realistic margin to which quotation of
29 metal-hydrogen equilibrium bond lengths makes sense, even for very small molecules. We would
30 thus like to recommend a mass-independent $r_e = 1.6332(1) \text{ \AA}$.
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4. Conclusions

Making use of a recent small-core pseudopotential for the mercury atom [10] and large basis sets within CCSD(T) and SO-CI calculations, the near-equilibrium potential energy and electric dipole moment functions of linear HgH₂ have been studied. As is well known (see, e.g., ref. 9), HgH₂ in its X¹Σ_g⁺ electronic ground state lies higher in energy compared to the asymptote Hg (¹S₀) + H₂, but the barrier height to dissociation is very high. The decomposition reaction



is thus exothermic. Without zero-point energy, the (equilibrium) reaction energy is calculated to be 89.17 kJ mol⁻¹ at the PP/CCSD(T) level and 89.67 kJ mol⁻¹ when spin-orbit interaction is explicitly taken into account. Inclusion of zero-point energy reduces both values by 7.28 kJ mol⁻¹. The PP/CCSD(T)+SO value of 82.39 kJ mol⁻¹ is expected to be accurate to about 1%. It may be compared with the earlier value of 86.8 kJ mol⁻¹ by Li et al. [9].

The analytical potential energy function obtained by least-squares fit to PP/CCSD(T)+SO energy points yields wavenumbers for the anti-symmetric stretching vibrations of HgH₂ and HgD₂ which are accurate to ca. 0.1 %. This means that about an order of magnitude improvement has been achieved compared to the best previous work [9]. Further improvement is attained by making use of two pieces of experimental information, the ground-state rotational constant and the wavenumber of the antisymmetric stretching vibration for the most abundant isotopomer ²⁰²HgH₂. All rotational constants which may be compared with experimental data [6] are then in error by no more than 0.0036 cm⁻¹ or 0.1 % (for B₀₀₃ of ²⁰²HgH₂ and ²⁰⁰HgH₂), but mostly much less. **The problem of determining a unique Hg-H equilibrium distance, independent of the molecular isotopomer under consideration, has been discussed in considerable detail with the conclusion that no value with an accuracy of better than 10⁻⁴ Å appears to be determinable from the union of experimental and theoretical data available at present.**

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Table 1. Non-redundant parameters of analytical potential energy functions for HgH_2^a

PEF term			PP/CCSD(T) ^b	PP/CCSD(T)+SO ^c	PP/CCSD(T)+SO+corr ^d
i	j	k			
2	0	0	0.7525261	0.7572922	0.7585439
3	0	0	-0.8293839	-0.8317045	-0.8321240
4	0	0	0.5214234	0.5262532	0.5271633
5	0	0	-0.3594378	-0.3581124	-0.3566265
6	0	0	-0.1066616	-0.1085722	-0.1083338
0	0	2	0.0595367	0.0598235	0.0599674
0	0	4	-0.0129835	-0.0131381	-0.0131833
0	0	6	0.0026699	0.0027722	0.0027808
0	0	8	-0.0001471	-0.0001818	-0.0001818
0	0	10	-0.0000311	-0.0000311	-0.0000311
1	1	0	0.0938135	0.0936407	0.0945669
2	1	0	-0.2188693	-0.2151642	-0.2151008
3	1	0	-0.0196751	-0.0187335	-0.0177071
2	2	0	-0.0001480	-0.0027895	-0.0014460
4	1	0	-0.1336816	-0.1343863	-0.1343862
3	2	0	-0.2072690	-0.2080222	-0.2080222
1	0	2	-0.0671012	-0.0668978	-0.0668336
1	1	2	0.0588180	0.0577594	0.0572919
2	0	2	-0.0584167	-0.0584352	-0.0587222
2	1	2	0.1074363	0.1083442	0.1088229
3	0	2	0.0520476	0.0524896	0.0528657
2	2	2	-0.0325512	-0.0320726	-0.0319124
3	1	2	-0.1276744	-0.1271083	-0.1267475
4	0	2	-0.0556763	-0.0556575	-0.0555806
4	1	2	-0.0707280	-0.0714053	-0.0714053
3	2	2	-0.0242001	-0.0248102	-0.0248102
1	0	4	0.0209749	0.0210034	0.0210157
1	1	4	-0.0237151	-0.0235816	-0.0234696
2	0	4	0.0059288	0.0060408	0.0061047
2	1	4	-0.0259260	-0.0260035	-0.0260035
3	0	4	-0.0111657	-0.0111308	-0.0111308
1	0	6	-0.0039909	-0.0039930	-0.0039930

^a Throughout, the non-linear parameter β has a value of 1.36. The mathematical forms of the PEFs are described in equations (1) and (2). At the end of the iterative processes (see the text), r_e and \tilde{r}_e are numerically identical.

^b $r_e = 1.636948 \text{ \AA}$.

^c $r_e = 1.634481 \text{ \AA}$.

^d $r_e = 1.633405 \text{ \AA}$.

Table 2. PP/CCSD(T) electric dipole moment function (EDMF) for $^{202}\text{HgH}_2$ ^a

i	j	k	D_{ijk}^{\parallel}	i	j	k	D_{ijk}^{\perp}
0	1	0	0.63049	0	0	1	-0.39535
0	3	0	0.00543	0	0	3	-0.14125
0	5	0	0.00205	0	0	5	0.04957
0	7	0	-0.00026	0	0	7	-0.00472
1	1	0	0.09082	1	0	1	-0.14330
1	3	0	-0.03636	1	0	3	0.04729
1	5	0	0.01613	1	0	5	-0.01218
1	7	0	0.00708	2	0	1	0.02936
2	1	0	-0.11662	2	0	3	0.01585
2	3	0	-0.00608	2	0	5	0.00471
2	5	0	-0.01299	0	2	1	0.00727
2	7	0	-0.00143	0	4	1	0.00018
0	1	2	-0.06225	0	2	3	0.01188
0	1	4	0.02033	0	4	3	-0.00067
0	1	6	0.00492	0	2	5	-0.00442
0	1	8	-0.00178	0	4	5	-0.00104
0	3	2	-0.00845	1	2	1	0.01966
0	3	4	0.00369	2	2	1	0.02234
0	3	6	-0.00042	1	2	3	0.03896
0	5	2	0.00167				
1	1	2	0.13423				
2	1	2	-0.14829				
1	1	4	-0.01800				
2	1	4	-0.00432				
1	3	2	0.00962				

^a The EDMF is expanded around $r_e = 1.633405 \text{ \AA}$ (minimum of PEF “PP/CCSD(T)+SO+corr”).

All EDMF terms (for definition see equation (3)) are given in atomic units.

Table 3. Term energies for lowest 19 excited vibrational states (in cm^{-1}) of $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ ^a

(v_1, v_2, v_3)	$^{202}\text{HgH}_2$				$^{202}\text{HgD}_2$			
	PP/MRCI+Q [9]	PP/CCSD(T)	PP/CCSD(T)+SO	PP/CCSD(T)+SO+corr	PP/MRCI+Q [9]	PP/CCSD(T)	PP/CCSD(T)+SO	PP/CCSD(T)+SO+corr
(0, 2, 0)	1548.7	1542.3	1548.6	1551.7	1117.6	1112.9	1117.4	1119.5
(0, 0, 1)	1885.7	1900.4	1910.3	1912.8 (1912.8)	1355.3	1366.5	1373.5	1375.3 (1375.8)
(1, 0, 0)	1982.5	1998.8	2008.6	2012.3	1421.0	1433.4	1440.2	1442.8
(0, 4, 0)	3048.9	3037.2	3049.7	3055.7	2210.0	2201.3	2210.2	2214.5
(0, 2, 1)	3403.6	3410.5	3426.9	3432.4	2457.3	2463.0	2474.6	2478.5
(1, 2, 0)	3499.3	3509.0	3525.4	3532.1	2522.7	2530.2	2541.6	2546.3
(0, 0, 2)	3744.1	3771.9	3791.7	3796.7 (3795.4)	2697.5	2719.0	2733.0	2736.6 (2736.9)
(1, 0, 1)	3800.8	3829.2	3849.2	3855.4	2742.6	2764.7	2778.6	2783.0
(2, 0, 0)	3927.9	3958.9	3978.9	3986.3	2823.3	2847.0	2860.8	2866.0
(0, 6, 0)	4502.8	4486.4	4505.1	4514.0	3278.2	3265.9	3279.2	3285.6
(0, 4, 1)	4873.3	4873.4	4896.2	4904.8	3534.3	3535.1	3551.3	3557.3
(1, 4, 0)	4968.2	4972.3	4995.1	5004.8	3599.4	3602.7	3618.6	3625.5
(0, 2, 2)	5230.6	5249.6	5276.0	5284.1	3783.6	3790.1	3817.7	3823.5
(1, 2, 1)	5286.8	5306.9	5333.7	5343.0	3828.7	3845.0	3863.6	3870.2
(2, 2, 0)	5412.3	5436.9	5463.6	5474.2	3908.7	3927.6	3946.1	3953.5
(0, 0, 3)	5566.7	5605.1	5634.8	5642.8 (5637.4)	4024.3	4055.0	4075.9	4081.4 (4080.5)
(1, 0, 2)	5587.6	5626.1	5656.2	5665.0	4049.1	4079.9	4101.0	4107.2
(2, 0, 1)	5694.7	5736.7	5767.0	5776.7	4115.9	4148.6	4169.7	4176.6
(3, 0, 0)	5832.6	5876.3	5906.8	5918.1	4205.9	4239.5	4260.5	4268.4
ZPE ^b	2788.4	2803.1	2816.0	2820.5	1987.0	1997.9	2007.0	2010.3

^a Experimental values [4] in parentheses. ^b Zero-point vibrational energy.

Table 4. Comparison of calculated vibrational term energies

(l = 0) for $^{202}\text{HgHD}$ (in cm^{-1})

(v_1, v_2, v_3)	PP/MRCI+Q [9]	PP/CCSD(T)+SO+corr
(0, 2, 0)	1351.0	1353.9
(0, 0, 1)	1385.4	1405.8
(1, 0, 0)	1938.3	1966.9
(0, 4, 0)	2664.2	2670.6
(0, 2, 1)	2717.8	2741.7
(0, 0, 2)	2742.4	2780.5
(1, 2, 0)	3259.9	3290.6
(1, 0, 1)	3318.6	3367.9
(2, 0, 0)	3813.2	3867.7
(0, 6, 0)	3941.6	3951.7
(0, 4, 1)	4013.2	4040.1
(0, 2, 2)	4050.9	4096.8
(0, 0, 3)	4074.2	4125.8
(1, 4, 0)	4544.1	4577.7
(1, 2, 1)	4622.8	4674.2
(1, 0, 2)	4669.0	4737.1
(2, 2, 0)	5104.6	5160.8
(0, 8, 0)	5184.4	5198.8
(2, 0, 1)	5188.5	5263.7
(0, 6, 1)	5272.9	5303.2
(0, 4, 2)	5327.8	5376.4
(0, 2, 3)	5351.0	5417.0
(0, 0, 4)	5384.0	5445.7
(3, 0, 0)	5624.8	5702.9
ZPE ^a	2397.5	2425.3

^a Zero-point vibrational energy.

Table 5. Comparison of theoretical and experimental spectroscopic constants (in cm^{-1}) for vibrational states with $l = 0$ ^a

State (v_1, v_2, v_3)	²⁰² HgH ₂		²⁰⁰ HgH ₂		²⁰² HgD ₂		²⁰⁰ HgD ₂	
	B_v	$D_v/10^{-5}$	B_v	$D_v/10^{-5}$	B_v	$D_v/10^{-5}$	B_v	$D_v/10^{-5}$
(0, 0, 0)	3.08486 (3.08486)	2.819 (2.831)	3.08486 (3.08486)	2.819 (2.831)	1.55085 (1.55116)	0.703 (0.705)	1.55085 (1.55116)	0.703 (0.706)
(0, 0, 1)	3.05588 (3.05503)	2.845 (2.857)	3.05588 (3.05503)	2.845 (2.857)	1.54050 (1.54051)	0.707 (0.710)	1.54050 (1.54051)	0.707 (0.709)
(1, 0, 0)	3.03730 (3.03696)	2.822 (2.877)	3.03730 (3.03696)	2.822 (2.877)	1.53414 (1.53429)	0.703 (0.711)	1.53414 (1.53431)	0.703 (0.711)
(0, 0, 2)	3.02496 (3.02312)	2.891 (2.909)	3.02494 (3.02311)	2.891 (2.908)	1.52974 (1.52943)	0.713 (0.717)	1.52975 (1.52942)	0.713 (0.716)
(1, 0, 1)	3.00773 (3.00649)	2.855 (2.902)	3.00772 (3.00647)	2.855 (2.896)	1.52366 (1.51732)	0.708 (0.738)	1.52366 (1.52352)	0.708 (0.719)
(0, 0, 3)	2.98867 (2.98510)	3.043 (3.081)	2.98865 (2.98508)	3.045 (3.086)	1.51809 (1.51732)	0.728 (0.738)	1.51810 (1.51729)	0.728 (0.730)

^a From calculations with PEF “PP/CCSD(T)+SO+corr”; experimental values [4] are given in parentheses.

Table 6. Comparison of calculated and experimental spectroscopic constants (in cm^{-1}) for states with $l = 1^a$

Isotopomer	state (v_1, v_2^1, v_3)	B_v	$D_v/10^{-5}$	$q_v/10^{-2}$	$q_J/10^{-6}$
$^{202}\text{HgH}_2$	(0, 1 ¹ , 0)	3.07288 (3.07325)	2.851 (2.863)	4.339 (4.342)	-1.1 (-1.6)
	(0, 1 ¹ , 1)	3.04419 (3.04368)	2.878 (2.888)	4.235 (4.241)	-1.1 (-1.5)
$^{200}\text{HgH}_2$	(0, 1 ¹ , 0)	3.07288 (3.07326)	2.850 (2.863)	4.339 (4.341)	-1.1 (-1.5)
	(0, 1 ¹ , 1)	3.04419 (3.04369)	2.878 (2.892)	4.236 (4.240)	-1.1 (-1.4)
$^{202}\text{HgD}_2$	(0, 1 ¹ , 0)	1.54658 (1.54703)	0.708 (0.713)	1.530 (1.522)	-0.19
	(0, 1 ¹ , 1)	1.53630 (1.53646)	0.712 (0.719)	1.505 (1.498)	-0.19
$^{200}\text{HgD}_2$	(0, 1 ¹ , 0)	1.54658 (1.54704)	0.708 (0.713)	1.530 (1.522)	-0.19
	(0, 1 ¹ , 1)	1.53631 (1.53646)	0.712 (0.717)	1.505 (1.497)	-0.19

^a From calculations with PEF "PP/CCSD(T)+SO+corr"; experimental values [4] are given in parentheses.

Table 7. Einstein coefficients of spontaneous emission (in s^{-1}) for observed vibrational transitions of $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$

Transition	$^{202}\text{HgH}_2$	$^{202}\text{HgD}_2$
$(0, 0, 3) \rightarrow (0, 0, 2)$	430.1	125.1
$(0, 0, 2) \rightarrow (0, 0, 1)$	333.9	89.5
$(0, 0, 1) \rightarrow (0, 0, 0)$	177.4	46.4
$(1, 0, 1) \rightarrow (1, 0, 0)$	161.8	43.6
$(0, 1^1, 1) \rightarrow (0, 1^1, 0)$	175.3	46.0

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Table 8. Rotational constant differences ΔB_0 from variational (var.) and 2nd order perturbation theory (pert.)

Theoretical method		²⁰² HgH ₂	²⁰⁰ HgH ₂	²⁰² HgD ₂	²⁰⁰ HgD ₂
PP/CCSD(T)	var.	0.050028	0.050029	0.017767	0.017767
	pert.	0.050263	0.050264	0.017828	0.017829
PP/CCSD(T)+SO	var.	0.049860	0.049861	0.017709	0.017710
	pert.	0.050115	0.050116	0.017775	0.017776
PP/CCSD(T)+SO+corr	var.	0.049825	0.049826	0.017697	0.017698
	pert.	0.050085	0.050086	0.017765	0.017765

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Table 9. Equilibrium rotational constants B_e (in cm^{-1}) from different mixed experimental/theoretical procedures

Theoretical method		$^{202}\text{HgH}_2$	$^{200}\text{HgH}_2$	$^{202}\text{HgD}_2$	$^{200}\text{HgD}_2$
PP/CCSD(T)	var.	3.134887	3.134887	1.568923	1.568927
	pert.	3.135122	3.135122	1.568984	1.568989
PP/CCSD(T)+SO	var.	3.134719	3.134719	1.568865	1.568870
	pert.	3.134974	3.134974	1.568931	1.568936
PP/CCSD(T)+SO+corr	var.	3.134684	3.134684	1.568923	1.568858
	pert.	3.134944	3.134944	1.568921	1.568925

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Table 10. Equilibrium Hg-H distances (in Å) from mixed experimental/theoretical procedures

Theoretical method		$^{202}\text{HgH}_2$	$^{200}\text{HgH}_2$	$^{202}\text{HgD}_2$	$^{200}\text{HgD}_2$
PP/CCSD(T)	var.	1.633352	1.633352	1.633209	1.633207
	pert.	1.633291	1.633291	1.633177	1.633175
PP/CCSD(T)+SO	var.	1.633396	1.633396	1.633239	1.633237
	pert.	1.633329	1.633329	1.633206	1.633203
PP/CCSD(T)+SO+corr	var.	1.633405	1.633405	1.633209	1.633243
	pert.	1.633337	1.633337	1.633210	1.633208

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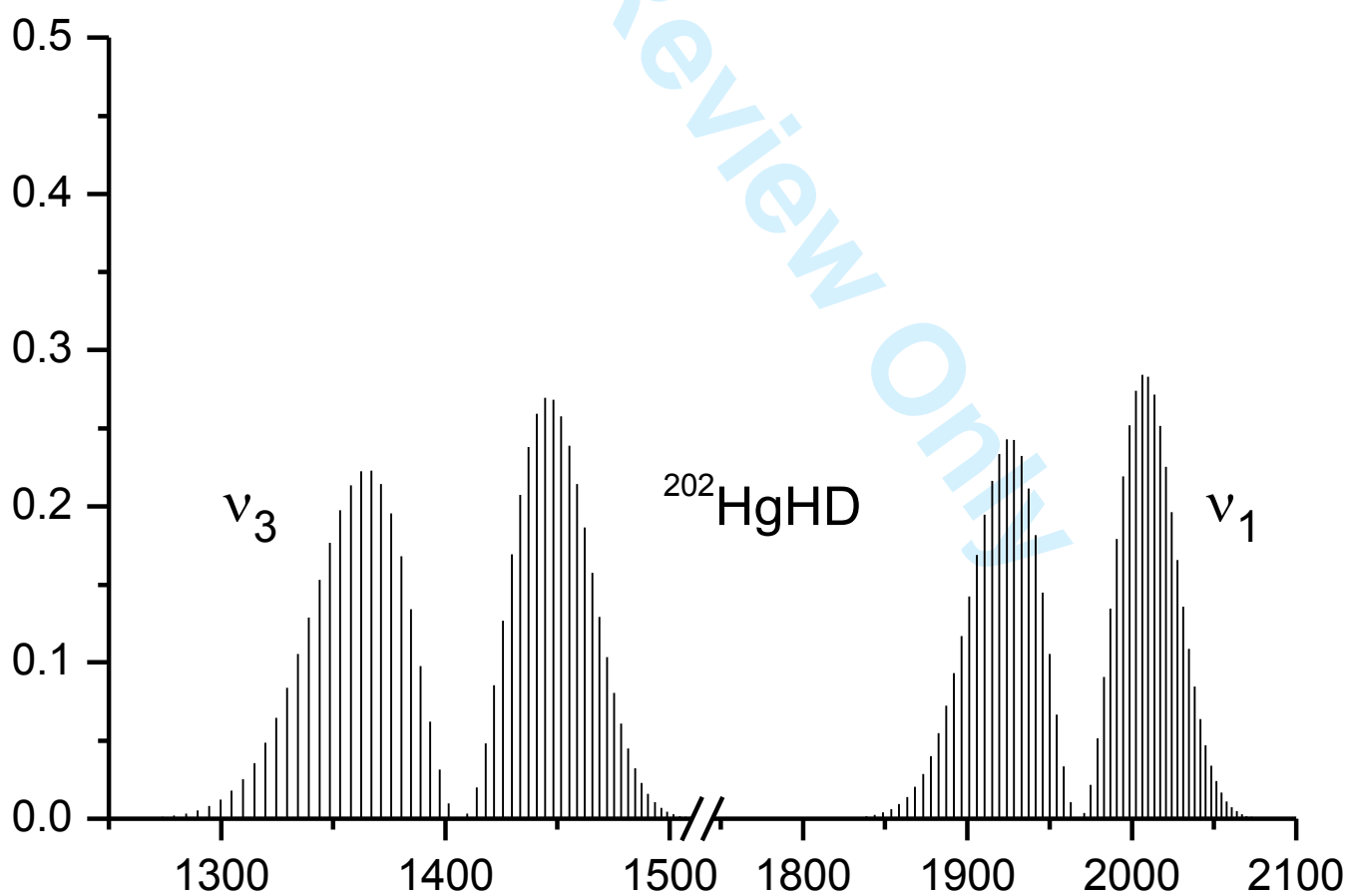
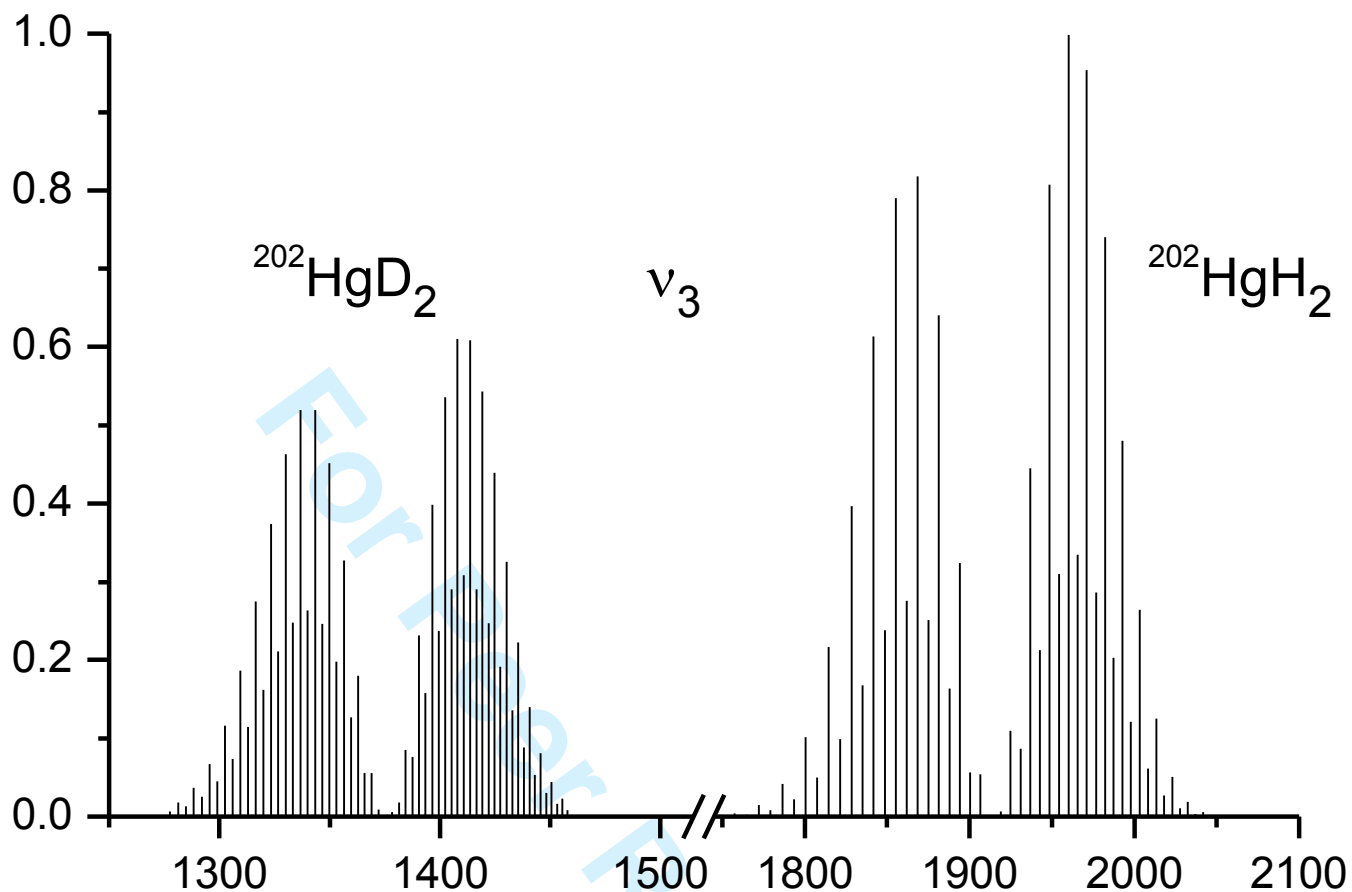
Figure captions**Figure 1.**

Predicted gas-phase IR absorption spectra for the stretching vibrations of $^{202}\text{HgH}_2$, $^{202}\text{HgD}_2$ and $^{202}\text{HgHD}$ at 293 K. The three spectra are normalized with respect to the strongest line in the R branch of $^{202}\text{HgH}_2$. Appropriate partition functions were considered enabling one to compare the three spectra directly.

Figure 2.

Calculated IR absorption spectra for the ν_2 bands of $^{202}\text{HgH}_2$ and $^{202}\text{HgD}_2$ at 293 K. The spectra are normalized independently with respect to the strongest line in the Q branches.

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