RESEARCH PAPER

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The vibrational g-factor of dihydrogen from theoretical calculation and analysis of vibration-rotational spectra

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Received 20th January 2005, Accepted 9th March 2005
First published as an Advance Article on the web 23rd March 2005

We present the first results from quantum-chemical calculation of a vibrational g-factor; the calculations were performed at the level of full configuration interaction using a basis set of aug-cc-pVQZ quality. The theoretical results are consistent with experimental results from analysis of pure rotational and vibration-rotational spectra of dihydrogen in six isotopic variants, in which calculated results for either the rotational g-factor or adiabatic corrections are employed to constrain fits of coefficients of radial functions from wave numbers of transitions. When fits are constrained with data for the rotational g-factor, we reproduce also the radial dependence of adiabatic corrections relative to their value at equilibrium internuclear separation.

Introduction

According to a theoretical description, coupling between electronic and nuclear motions in molecules produces terms of two types, called adiabatic if they involve expectation values of electronic operators on nuclear wave functions within a particular electronic state, or nonadiabatic if they involve matrix elements of the same operators between separate electronic states.[1–6] When van Vleck derived these terms,[1] he distinguished between nonadiabatic vibrational terms, which connect states with symmetries of the same class, and nonadiabatic rotational terms, which connect electronic states with symmetries of distinct classes, but he made no association between these nonadiabatic rotational terms and the rotational g-factor of which experimental measurements had been first made a few years earlier.[7] When Herman and Asgharian[2] rederived an effective molecular Hamiltonian for nuclear motion, they described a relation between nonadiabatic rotational terms and the rotational g-factor, which they interpreted in terms of electrons ‘slipping’ as nuclei rotate about the molecular centre of mass; the nonadiabatic vibrational term has an analogous physical interpretation. These authors noted[2] that there is no magnetic effect of low order that can yield experimental manifestation of this nonadiabatic vibrational term, comparable to a Zeeman effect, for instance, connected to the rotational g-factor that produces splitting of spectral lines for rotational transitions.[8,9] Despite the consequently lacking association with a ‘proper’ vibrational g-factor, *i.e.* a dimensionless magnetogyric ratio between a magnetic dipolar moment and an angular momentum, the nonadiabatic vibrational term is called the vibrational g-factor,[6] a convention that we accept here. Whereas the rotational g-factor, g_r, is a quantity well understood from both experiment and theoretical calculation,[10–13] especially for a diatomic molecular species in electronic state $^1\Sigma$,[14] apart from those formal theoretical derivations[1,2,4–6] little was known about the vibrational g-factor, g_v, before the present work. In an earlier calculation[15] of the vibrational g-factor for the degenerate bending mode of HCN, this quantity was obtained from the rotational g-factor evaluated at a distorted geometry and therefore not from the original expressions of Herman and Asgharian.[2]

From a theoretical point of view, we define pertinent quantities through a Hamiltonian. For two atoms interacting as point masses or lacking internal structure, a conventional Hamiltonian to describe their motion, relative to axes fixed in space with the origin at the centre of molecular mass, is expressed as

$$\hat{H}(R) = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \hbar^2\frac{J(J+1)}{2\mu R^2} + V(R) \qquad (1)$$

in which the first term on the right side of the equality denotes kinetic energy of two atoms with linear momentum,

$$\hat{P} = -\mathrm{i}\hbar\frac{\partial}{\partial R} \qquad (2)$$

along an axis connecting their centres a distance R apart, with Dirac’s constant $\hbar = h/2\pi$; a second term denotes kinetic energy of atoms moving perpendicularly to that axis or energy of rotation about the centre of molecular mass in a state with quantum number J for angular momentum, and a third term denotes interatomic potential energy $V(R)$, generally referred to a minimum at equilibrium internuclear distance R_e. The former two terms contain atomic reduced mass,

$$\mu = \frac{M_a M_b}{M_a + M_b} \qquad (3)$$

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DOI: 10.1039/b500992h

of a system comprising two atoms of masses M_a and M_b, whereas the other term is formally independent of mass. To take into account that a real diatomic molecule contains no explicit atom, merely two atomic nuclei and their associated electrons, and that electrons follow imperfectly the motion of one or other nucleus, we include a correction to each term in the preceding primitive Hamiltonian to achieve an effective molecular Hamiltonian[1–6,16] neglecting magnetic effects, for relative motion of two atomic nuclei in a field of their associated electrons:

$$\hat{H}_{\mathrm{eff}}(R) = -\frac{\hbar^2}{2\mu}\frac{\partial}{\partial R}\left(1+\frac{m_e}{m_p}g_v(R)\right)\frac{\partial}{\partial R} + \frac{\hbar^2}{2\mu}\left(1+\frac{m_e}{m_p}g_r(R)\right)\frac{J(J+1)}{R^2} + V(R) + V'(R) \tag{4}$$

Radial functions $g_v(R)$ for the vibrational g-factor and $g_r(R)$ for the rotational g-factor each have as coefficient a ratio of electronic m_e and protonic m_p rest masses, according to convention, and are associated with nonadiabatic corrections to the vibrational and rotational reduced mass,[2,4–6] respectively, as explained below. A further radial function $V'(R)$ takes into account a small dependence of internuclear potential energy on separate nuclear masses, known as an adiabatic correction $V_{\mathrm{ad}}(R)$, whereby total internuclear potential energy depends not only on static coulombic interactions but also, through reactions of nuclear motions, on electronic motions in an attempt to conserve linear momentum.[6] Further nonadiabatic corrections[4] $V_{\mathrm{non\text{-}ad}}(R)$ to potential energy that involve a ratio of electronic mass to nuclear mass to a power greater than for any term in the latter equation are neglected.[6] Although one can move the radial function for the vibrational g-factor from between the momentum operators,[6] such a shift produces a further contribution to $V'(R)$; as we can work with that function for the vibrational g-factor equally well between the momentum operators,[17] we avoid generation of such further terms.

Experiments to determine the rotational g-factor of particular molecular species have been performed since 1933,[7–9,14] for instance to evaluate an expectation value $\langle v,J|g_r,R)|v,J\rangle$ in a particular vibration-rotational state, typically only for $v = 0$ and $J = 1$, through a Zeeman effect on molecular beams or in microwave spectra.

When van Vleck made the first derivation of a nonadiabatic vibrational term,[1] he also extended Dunham's expressions[18] for eigenvalues of an effective Hamiltonian to include these corrections to a primitive Hamiltonian equivalent to that in eqn. (1). For a diatomic molecular species in which each atomic nucleus has the same atomic number, such as dihydrogen with $Z = 1$ in any isotopic variant, a convenient formula for these eigenvalues, or spectral terms, has the following form:[16]

$$E_{vJ} = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}(Y_{kl}+Z_{kl})\left(v+\frac{1}{2}\right)^k (J(J+1))^l \tag{5}$$

Here term coefficients Y_{kl} incorporate mechanical effects[18] reflecting terms in only the primitive Hamiltonian, eqn. (1), corresponding to classical oscillation and rotation; further term coefficients Z_{kl} reflect extra-mechanical effects,[16] arising from nonadiabatic vibrational, nonadiabatic rotational and adiabatic effects according to corrections within an extended effective Hamiltonian, eqn. (4). Term coefficients Z_{kl} can be formally partitioned into Z^v_{kl} for vibration-rotational contributions that arise from adiabatic and nonadiabatic vibrational contributions to the effective Hamiltonian, specifically $V'(R)$ and $g_v(R)$, respectively; coefficients Z^r_{kl} reflect further rotational contributions that arise from both nonadiabatic rotational and nonadiabatic vibrational contributions, thus $g_r(R)$ and $g_v(R)$.[16] From analysis of experimental data comprising wave numbers of pure rotational and vibration-rotational spectra of a single isotopic species, one might in suitable circumstances evaluate not only parameters contained in expressions for Y_{kl} but also some parameters, or their combinations, in Z^r_{kl}, whereas with spectra also of isotopic variants one might evaluate also parameters in Z^v_{kl}. From such experimental data measured for samples without externally applied electric or magnetic field, parameters related to only two of three kinds of extra-mechanical effects might in general be evaluated; to evaluate separately parameters for adiabatic, nonadiabatic vibrational and nonadiabatic rotational effects, either further experimental data for the only directly measurable quantity, the rotational g-factor, must be included during reduction of frequency data to parameters in radial functions $V(R)$, $V'(R)$, $g_v(R)$ and $g_r(R)$, or results of quantum-chemical calculations must be employed. The latter course of action was followed in the first such evaluation of separate effects,[19] involving calculation of the rotational g-factor to simulate prospective experimental data for LiH.

Although we are confident that such an approach is sound, a rigorous test has been generally impracticable because adiabatic effects corresponding to $V'(R)$ have generally not been calculated over a range of R, and because no explicit independent calculation of a vibrational g-factor is known before our present work. For our analysis of spectral data of dihydrogen here according to Dunham's approach[18] with extensions following van Vleck,[1] we not only compare our results with well established calculations of adiabatic effects[20,21] but also present for the first time explicit calculations of the vibrational g-factor employing the method of configuration interaction with all configurations included (full CI) and a basis set of valence quadruple zeta quality augmented with polarization and diffuse functions, aug-cc-pVQZ.[22] There exist few accurate experimental values of the rotational g-factor of H_2[23] to complement and to confirm our own extensive and accurate calculations of this quantity; extensive published data on adiabatic effects[20,21] combined with our newly calculated values of the vibrational g-factor make dihydrogen well characterised for these extra-mechanical effects, and thus an excellent test case in relation to spectral reduction. Our results provide not only fundamental data about the vibrational g-factor of dihydrogen from both calculation and spectral data but also an unequivocal justification of our method of spectral analysis, based ultimately on Dunham's formalism. This analysis is naturally limited by both the quality and quantity of available spectral data.

Theory of vibrational and rotational *g*-factors

Expressions for the nonadiabatic corrections to the rotational and vibrational reduced masses have been derived several times.[2,4–6] In this section we briefly review a derivation given by Bunker and Moss[4] before we discuss a relation to rotational and vibrational g-factors in detail. In the following section we show how the vibrational g-factor is obtained by quantum-chemical calculations.

We assume that spectral data of interest pertain primarily to the electronic ground state of a particular diatomic molecular species that might have multiple isotopic variants. After separation of the translation of the whole diatomic molecule, the isomorphic Hamiltonian for a molecule in an electronic state classified as $^1\Sigma$ becomes written in centre-of-nuclear-mass coordinates as[24]

$$\hat{H}(\{\vec{r}_i\}, R) = \hat{H}_0(\{\vec{r}_i\}; R) + \hat{H}'(\{\vec{r}_i\}, R) \tag{6}$$

in which $\{\vec{r}_i\}$ denotes the set of electronic coordinates. The zeroth-order electronic Hamiltonian,

$$\hat{H}_0(\{\vec{r}_i\}; R) = -\frac{\hbar^2}{2}\frac{1}{m_e}\sum_i \hat{\nabla}_i^2 + V(\{\vec{r}_i\}, R) \tag{7}$$

is the electronic Hamiltonian in the Born–Oppenheimer approximation of which eigenvalues $E_n^{\mathrm{BO}}(R)$, *i.e.* the solutions of the electronic Schrödinger equation,

$$\hat{H}_0(\{\vec{r}_i\};R)\Psi_n(\{\vec{r}_i\},R) = E_n^{\mathrm{BO}}(R)\Psi_n(\{\vec{r}_i\},R) \tag{8}$$

are the energies of electronic states in the Born–Oppenheimer approximation. The potential $V(\{\vec{r}_i\},R)$ includes the electron–electron, electron–nuclear and nuclear–nuclear potential energy and $\hat{\vec{\nabla}}_i$ is the gradient operator with respect to the coordinates of electron i. The remaining three terms in the Hamiltonian,

$$\hat{H}'(\{\vec{r}_i\},R) = -\frac{\hbar^2}{2\mu_{\mathrm{nuc}}}\frac{\partial^2}{\partial R^2} + \frac{1}{2\mu_{\mathrm{nuc}}R^2} \times \left(\hat{\vec{J}} - \hat{\vec{L}}\left(\vec{R}_{\mathrm{NCM}}\right)\right)^2 - \frac{\hbar^2}{2}\frac{1}{m_{\mathrm{a}}+m_{\mathrm{b}}}\sum_{i,j}\hat{\vec{\nabla}}_i\cdot\hat{\vec{\nabla}}_j \tag{9}$$

are first the kinetic-energy operator along the internuclear axis of two nuclei of masses m_{a} and m_{b}, second the energy of rotation of the nuclei about the centre of nuclear mass and third a mass polarization term, in which

$$\mu_{\mathrm{nuc}} = \frac{m_{\mathrm{a}}m_{\mathrm{b}}}{m_{\mathrm{a}}+m_{\mathrm{b}}} \tag{10}$$

is the nuclear reduced mass. The angular momentum operator for rotation of the whole molecule about the molecular centre of mass is denoted $\hat{\vec{J}}$, and

$$\hat{\vec{L}}\left(\vec{R}_{\mathrm{NCM}}\right) = \sum_i \hat{\vec{l}}_i = \sum_i\left\{\left(\vec{r}_i - \vec{R}_{\mathrm{NCM}}\right)\times\hat{\vec{p}}_i\right\} \tag{11}$$

is the operator for total angular momentum of the electrons about the nuclear center of mass.

An effective Hamiltonian for vibration-rotational motion of the nuclei, as given in eqn. (4), is obtained on projecting the molecular Hamiltonian, eqn. (6), onto the corresponding electronic state $\Psi_0(\{\vec{r}_i\},R)$. As the Born–Oppenheimer energies depend on the internuclear distance R, Bunker and Moss[4] employed therefore a contact transformation, according to which the transformed Hamiltonian is given as

$$\hat{\tilde{H}} = \mathrm{e}^{-\mathrm{i}\hat{S}}\hat{H}\mathrm{e}^{\mathrm{i}\hat{S}} = \hat{\tilde{H}}_0 + \hat{\tilde{H}}_1 + \hat{\tilde{H}}_2 + \cdots \tag{12}$$

and in which $\hat{S}$ is chosen such that the transformed Hamiltonian $\hat{\tilde{H}}$ couples no separate electronic states through first order, *i.e.*

$$\left\langle\Psi_0(\{\vec{r}_i\};R)\middle|\hat{\tilde{H}}_1\middle|\Psi_n(\{\vec{r}_i\};R)\right\rangle = 0 \tag{13}$$

The effective vibration-rotational Hamiltonian is then obtained as an expectation value of the transformed Hamiltonian in eqn. (12) over the electronic ground-state wavefunction

$$\hat{H}_{\mathrm{eff}} = \left\langle\Psi_0(\{\vec{r}_i\};R)\middle|\hat{\tilde{H}}\middle|\Psi_0(\{\vec{r}_i\};R)\right\rangle \tag{14}$$

which after manipulation[4] yields the following expression for an effective vibration-rotational Hamiltonian:

$$\hat{H}_{\mathrm{eff}} = -\frac{\hbar^2}{2\mu_{\mathrm{nuc}}}\frac{\partial}{\partial R}\{1+\beta(R)\}\frac{\partial}{\partial R} + \frac{1}{2\mu_{\mathrm{nuc}}R^2} \times \{1+\alpha(R)\}\hat{\vec{J}}^2 + E_0^{\mathrm{BO}}(R) + V_{\mathrm{ad}}(R) + V_{\text{non-ad}}(R) \tag{15}$$

The non-adiabatic corrections to the vibrational and rotational reduced masses are then given as

$$\beta(R) = -\frac{2}{\mu_{\mathrm{nuc}}}\sum_{n\neq 0}\frac{\left(\langle\Psi_0(\{\vec{r}_i\},R)|\left(-\mathrm{i}\hbar\frac{\partial}{\partial R}|\Psi_n(\{\vec{r}_i\},R)\rangle\right)\right)^2}{E_0^{\mathrm{BO}}(R)-E_n^{\mathrm{BO}}(R)} \tag{16}$$

$$\alpha(R) = \frac{1}{\mu_{\mathrm{nuc}}R^2}\sum_{n\neq 0}\frac{\left|\left\langle\Psi_0(\{\vec{r}_i\},R)\middle|\hat{L}_x\left(\vec{R}_{\mathrm{NCM}}\right)\middle|\Psi_n(\{\vec{r}_i\},R)\right\rangle\right|^2}{E_0^{\mathrm{BO}}(R)-E_n^{\mathrm{BO}}(R)} + \frac{1}{\mu_{\mathrm{nuc}}R^2}\sum_{n\neq 0}\frac{\left|\langle\Psi_0(\{\vec{r}_i\},R)|\left|\hat{L}_y\left(\vec{R}_{\mathrm{NCM}}\right)\right||\Psi_n(\{\vec{r}_i\},R)\rangle\right|^2}{E_0^{\mathrm{BO}}(R)-E_n^{\mathrm{BO}}(R)} \tag{17}$$

whereas the adiabatic correction to the nuclear potential energy is

$$V_{\mathrm{ad}}(R) = -\frac{\hbar^2}{2}\frac{1}{m_{\mathrm{a}}+m_{\mathrm{b}}}\left\langle\Psi_0(\{\vec{r}_i\},R)\middle|\sum\nolimits_{i,j}\hat{\vec{\nabla}}_i\cdot\hat{\vec{\nabla}}_j\middle|\Psi_0(\{\vec{r}_i\},R)\right\rangle + \frac{1}{2\mu_{\mathrm{nuc}}R^2}\left\langle\Psi_0(\{\vec{r}_i\},R)\middle|\hat{L}^2\middle|\Psi_0(\{\vec{r}_i\},R)\right\rangle - \frac{\hbar^2}{2\mu_{\mathrm{nuc}}}\langle\Psi_0(\{\vec{r}_i\},R)|\left(\frac{\partial^2}{\partial R^2}|\Psi_0(\{\vec{r}_i\},R)\rangle\right) \tag{18}$$

The non-adiabatic corrections to the nuclear potential energy are complicated and are neglected in the following.

As $-\mathrm{i}\hbar\partial/\partial R$ is an Hermitian operator and therefore

$$\begin{aligned}\langle\Psi_0(\{\vec{r}_i\},R)|\left(-\mathrm{i}\hbar\frac{\partial}{\partial R}|\Psi_n(\{\vec{r}_i\},R)\rangle\right) &= \left(\langle\Psi_n(\{\vec{r}_i\},R)|\left(-\mathrm{i}\hbar\frac{\partial}{\partial R}|\Psi_0(\{\vec{r}_i\},R)\rangle\right)\right)^* \\ &= -\langle\Psi_n(\{\vec{r}_i\},R)|\left(-\mathrm{i}\hbar\frac{\partial}{\partial R}|\Psi_0(\{\vec{r}_i\},R)\rangle\right)\end{aligned} \tag{19}$$

we rewrite the nonadiabatic vibrational correction alternatively as

$$\beta(R) = \frac{2\hbar^2}{\mu_{\mathrm{nuc}}}\sum_{n\neq 0}\frac{\left|\langle\Psi_0(\{\vec{r}_i\},R)|\left(\frac{\partial}{\partial R}|\Psi_n(\{\vec{r}_i\},R)\rangle\right)\right|^2}{E_0^{\mathrm{BO}}(R)-E_n^{\mathrm{BO}}(R)} \tag{20}$$

or

$$\beta(R) = -\frac{2\hbar^2}{\mu_{\mathrm{nuc}}} \times \sum_{n\neq 0}\frac{\langle\Psi_0(\{\vec{r}_i\},R)|\left(\frac{\partial}{\partial R}|\Psi_n(\{\vec{r}_i\},R)\rangle\right)\langle\Psi_n(\{\vec{r}_i\},R)|\left(\frac{\partial}{\partial R}|\Psi_0(\{\vec{r}_i\},R)\rangle\right)}{E_0^{\mathrm{BO}}(R)-E_n^{\mathrm{BO}}(R)} \tag{21}$$

The relation between $\beta(R)$ and the corresponding properties δ_d and $g_2^e(R)$ discussed by van Vleck[1] and Herman and Asgharian,[2] respectively, are

$$\beta(R) = 2\delta_d = \frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}g_2^{\mathrm{e}}(R) \tag{22}$$

Herman and Asgharian[2] as well as Bunker and Moss[4] recognized that the nonadiabatic rotational correction $\alpha(R)$ is proportional to the electronic contribution to the rotational g-factor[15] $g_{r,\mathrm{nuc}}^{\mathrm{el}}(R)$

$$\alpha(R) = \frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}g_{r,\mathrm{nuc}}^{\mathrm{el}}(R) \tag{23}$$

Even though a corresponding magnetic property for the non-adiabatic vibrational correction $\beta(R)$ is lacking, Herman and co-workers[2,4] defined a corresponding vibrational g-factor $g^{\mathrm{el}}_{v,\mathrm{nuc}}(R)$ as

$$\beta(R) = \frac{m_\mathrm{e}}{m_\mathrm{p}} g^{\mathrm{el}}_{v,\mathrm{nuc}}(R) \tag{24}$$

The effective Hamiltonian for vibration-rotational motion of nuclei, eqn. (15), thus contains a term $(1/\mu_\mathrm{nuc})\{1 + g^{\mathrm{el}}_{\mathrm{nuc}} m_\mathrm{e}/m_\mathrm{p}\}$, in which $g^{\mathrm{el}}_{\mathrm{nuc}}$ is either a rotational or vibrational g-factor; the subscript "nuc" indicates that each quantity is calculated with the nuclear reduced mass μ_nuc. However, as atomic masses $M_{a,b}$ are measured accurately, with minimum relative uncertainty $\sim 10^{-11}$, whereas nuclear masses are calculated from atomic masses with much less accurate corrections, for all practical purposes involving precise spectral data of type frequency, for which relative uncertainty might approach 2×10^{-10}, usage of atomic masses is essential. Herman and Ogilvie[6] showed how the above expression involving nuclear masses can be converted to depend on atomic masses M_a and M_b. The inverse of the atomic reduced mass μ, in eqn. (3), is expressed in terms of nuclear masses and atomic numbers $Z_{a,b}$ as

$$\begin{aligned}\frac{1}{\mu} &= \frac{(m_\mathrm{a} + Z_\mathrm{a} m_\mathrm{e}) + (m_\mathrm{b} + Z_\mathrm{b} m_\mathrm{e})}{(m_\mathrm{a} + Z_\mathrm{a} m_\mathrm{e})(m_\mathrm{b} + Z_\mathrm{b} m_\mathrm{e})} \\ &= \frac{(m_\mathrm{a} + Z_\mathrm{a} m_\mathrm{e}) + (m_\mathrm{b} + Z_\mathrm{b} m_\mathrm{e})}{m_\mathrm{a} m_\mathrm{b}\left[1 + m_\mathrm{e}\left(\frac{Z_\mathrm{a}}{m_\mathrm{a}} + \frac{Z_\mathrm{b}}{m_\mathrm{b}}\right)\right] + m_\mathrm{e}^2 Z_\mathrm{a} Z_\mathrm{b}}\end{aligned} \tag{25}$$

Neglecting the term proportional to m_e^2 and expanding the remaining denominator as

$$\left[1 + m_\mathrm{e}\left(\frac{Z_\mathrm{a}}{m_\mathrm{a}} + \frac{Z_\mathrm{b}}{m_\mathrm{b}}\right)\right]^{-1} \approx 1 - m_\mathrm{e}\left(\frac{Z_\mathrm{a}}{m_\mathrm{a}} + \frac{Z_\mathrm{b}}{m_\mathrm{b}}\right) \tag{26}$$

leads to

$$\begin{aligned}\frac{1}{\mu} &\approx \frac{m_\mathrm{a} + m_\mathrm{b}}{m_\mathrm{a} m_\mathrm{b}}\left[1 - m_e \frac{Z_\mathrm{a} m_\mathrm{b}^2 + Z_\mathrm{b} m_\mathrm{a}^2}{(m_\mathrm{a} + m_\mathrm{b}) m_\mathrm{a} m_\mathrm{b}}\right] \\ &\quad - m_e^2 \frac{Z_\mathrm{a} + Z_\mathrm{b}}{m_\mathrm{a} m_\mathrm{b}}\left(\frac{Z_\mathrm{a}}{m_\mathrm{a}} + \frac{Z_\mathrm{b}}{m_\mathrm{b}}\right)\end{aligned} \tag{27}$$

Neglecting once more the term proportional to m_e^2 Herman and Ogilvie obtained the following approximate relation between the atomic and nuclear reduced masses

$$\frac{1}{\mu} \approx \frac{1}{\mu_\mathrm{nuc}}\left[1 - m_\mathrm{e}\frac{Z_\mathrm{a} m_\mathrm{b}^2 + Z_\mathrm{b} m_\mathrm{a}^2}{(m_\mathrm{a} + m_\mathrm{b}) m_\mathrm{a} m_\mathrm{b}}\right] \tag{28}$$

Tests of the corresponding error for H_2 or HeH^+ in various isotopic species indicate a maximum difference of order 10^{-7} u or smaller, and even smaller for molecules with more massive atomic centres, hence negligible. Recalling the definition of the nuclear contribution to the rotational g-factor[2,6,11] of a diatomic molecule expressed in terms of nuclear masses,

$$g^{\mathrm{nu}}_{\mathrm{nuc}} = m_\mathrm{p}\frac{Z_\mathrm{a} m_\mathrm{b}^2 + Z_\mathrm{b} m_\mathrm{a}^2}{(m_\mathrm{a} + m_\mathrm{b}) m_\mathrm{a} m_\mathrm{b}} \tag{29}$$

which is independent of internuclear distance and invariably a positive quantity, we rewrite eqn. (28) as

$$\frac{1}{\mu_\mathrm{nuc}} \approx \frac{1}{\mu}\left[1 + \frac{m_\mathrm{e}}{m_\mathrm{p}} g^{\mathrm{nu}}_{\mathrm{nuc}}\right] \tag{30}$$

Table 1 Ratio of atomic and nuclear reduced masses and nuclear g-factors defined with atomic and nuclear masses for isotopic variants of dihydrogen

Variant	μ/μ_nuc	$g^{\mathrm{nu}}_{\mathrm{nuc}}/g^{\mathrm{nu}}$	$(\mu/\mu_\mathrm{nuc})^2$
$^1H^1H$	1.000 54	1.000 54	1.001 09
$^1H^2H$	1.000 45	1.000 53	1.000 91
$^1H^3H$	1.000 45	1.000 56	1.000 91
$^2H^2H$	1.000 27	1.000 27	1.000 54
$^2H^3H$	1.000 24	1.000 25	1.000 47
$^3H^3H$	1.000 18	1.000 18	1.000 36

The terms for the vibrational and rotational reduced masses in eqn. (15) thereby become approximated as

$$\frac{1}{\mu_\mathrm{nuc}}\left\{1 + \frac{m_\mathrm{e}}{m_\mathrm{p}} g^{\mathrm{el}}_{\mathrm{nuc}}\right\} \approx \frac{1}{\mu} + \frac{1}{\mu_\mathrm{nuc}}\frac{m_\mathrm{e}}{m_\mathrm{p}} g_\mathrm{nuc} \tag{31}$$

in which g_nuc is the total vibrational or rotational g-factor defined with nuclear masses

$$g_\mathrm{nuc} = g^{\mathrm{el}}_{\mathrm{nuc}} + g^{\mathrm{nu}}_{\mathrm{nuc}} \tag{32}$$

The change from nuclear to atomic masses thus introduces a term that is equal to the nuclear contribution to the rotational g-factor of diatomic molecules. Herman and Ogilvie[6] defined analogously the total vibrational g-factor to include the same nuclear contribution, as given in eqn. (29). The non-adiabatic corrections to the vibrational and rotational reduced masses in eqn. (31) still depend on the nuclear masses. From eqn. (16) and (17) we discern that the electronic contributions to the g-factors include a second factor $1/\mu_\mathrm{nuc}$. Furthermore, the electronic contribution to the rotational g-factor, eqn. (17), depends also on the masses, because the angular momentum operator $\hat{\vec{L}}\left(\vec{R}_\mathrm{NCM}\right)$ is defined with respect to the centre of nuclear mass. We ignore this dependence here, although this dependence on masses allows the determination of the electric dipolar moment from the rotational g-factors of isotopic variants.[25,26] The mass dependence of the nuclear g-factor, eqn. (29), is more complicated.

Table 1 shows that for dihydrogen in all isotopic variants the ratio $g^{\mathrm{nu}}_{\mathrm{nuc}}/g^{\mathrm{nu}}$ is almost equal to μ/μ_nuc; we hence approximate the non-adiabatic corrections to vibrational and rotational reduced masses as

$$\frac{1}{\mu_\mathrm{nuc}}\frac{m_\mathrm{e}}{m_\mathrm{p}} g_\mathrm{nuc} \approx \frac{1}{\mu}\left(\frac{\mu}{\mu_\mathrm{nuc}}\right)^2 \frac{m_\mathrm{e}}{m_\mathrm{p}} g \tag{33}$$

Neglecting also the ratio $(\mu/\mu_\mathrm{nuc})^2$, which introduces an error at most 0.1%, we achieve an ultimate expression for non-adiabatic corrections to the vibrational and rotational reduced masses. The effective vibration-rotational Hamiltonian in eqn. (15) therefore becomes written approximately as

$$\begin{aligned}\hat{H}_\mathrm{eff} = &-\frac{\hbar^2}{2\mu}\frac{\partial}{\partial R}\left\{1 + \frac{m_\mathrm{e}}{m_\mathrm{p}} g_v(R)\right\}\frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left\{1 + \frac{m_\mathrm{e}}{m_\mathrm{p}} g_r(R)\right\} \\ &\times \hat{\vec{J}} + E_0^{\mathrm{BO}}(R) + V_\mathrm{ad}(R) + V_{\text{non-ad}}(R)\end{aligned} \tag{34}$$

The rotational and vibrational g-factors defined with respect to atomic masses $M_{a,b}$ are then given in the following expressions:

$$g_{v,r} = g^{\mathrm{el}}_{v,r} + g^{\mathrm{nu}}_{v,r} \tag{35}$$

$$g^{\mathrm{nu}}_{v,r} = m_\mathrm{p}\frac{Z_\mathrm{a} M_\mathrm{b}^2 + Z_\mathrm{b} M_\mathrm{a}^2}{(M_\mathrm{a} + M_\mathrm{b}) M_\mathrm{a} M_\mathrm{b}} \tag{36}$$

$$g_v^{\mathrm{el}}(R) = -\frac{m_{\mathrm{p}}}{m_{\mathrm{e}}}\frac{2\hbar^2}{\mu}\sum_{n\neq 0} \frac{\langle \Psi_0(\{\vec{r}_i\},R)|\left(\frac{\partial}{\partial R}|\Psi_n(\{\vec{r}_i\},R)\rangle\right)\langle \Psi_n(\{\vec{r}_i\},R)|\left(\frac{\partial}{\partial R}|\Psi_0(\{\vec{r}_i\},R)\rangle\right)}{E_0^{\mathrm{BO}}(R) - E_n^{\mathrm{BO}}(R)} \tag{37}$$

$$\begin{aligned} g_r^{\mathrm{el}}(R) = & \frac{m_{\mathrm{p}}}{m_{\mathrm{e}}}\frac{1}{\mu R^2}\sum_{n\neq 0}\frac{\left|\left\langle \Psi_0(\{\vec{r}_i\},R)\middle|\hat{L}_x\left(\vec{R}_{\mathrm{CM}}\right)\middle|\Psi_n(\{\vec{r}_i\},R)\right\rangle\right|^2}{E_0^{\mathrm{BO}}(R) - E_n^{\mathrm{BO}}(R)} \\ & + \frac{m_{\mathrm{p}}}{m_{\mathrm{e}}}\frac{1}{\mu R^2}\sum_{n\neq 0}\frac{\left|\left\langle \Psi_0(\{\vec{r}_i\},R)\middle|\hat{L}_y\left(\vec{R}_{\mathrm{CM}}\right)\middle|\Psi_n(\{\vec{r}_i\},R)\right\rangle\right|^2}{E_0^{\mathrm{BO}}(R) - E_n^{\mathrm{BO}}(R)} \end{aligned} \tag{38}$$

Because previous treatment of the vibrational g-factor is lacking, we consider the sign of its electronic component. According to eqn. (20) the sum contains only real positive numbers in the numerator and a denominator that is negative: the electronic contribution g_v^{el} is therefore invariably negative. Whether the net value $g_v = g_v^{\mathrm{el}} + g_v^{\mathrm{nu}}$ is positive or negative at a particular value of internuclear distance R depends thus on relative magnitudes of these contributions. An analogous argument applies to the total electronic contribution to g_r, and thus to its net value at a particular R.

Computation of the vibrational *g*-factor

We employed a local development version of the general-purpose quantum-chemistry program Dalton[27] to calculate the electronic contributions to the vibrational and rotational g-factors, $g_v^{\mathrm{el}}(R)$ and $g_r^{\mathrm{el}}(R)$, as a function of internuclear distance. The implementation of the rotational g-factor, $g_r^{\mathrm{el}}(R)$, has been described,[28] whereas the electronic contribution to the vibrational g-factor $g_v^{\mathrm{el}}(R)$ is newly implemented for multi-configurational self-consistent-field (MCSCF) wave functions[29] in our local development version of Dalton. Both Hartree–Fock and full-configuration-interaction wave functions are special cases of the general MCSCF wave function. For this reason our implementation covers also these two models, although it might not be considered efficient for these special cases.

Recalling the definition of the polarization propagator[30,31] or linear response function[32] for two operators A and B,

$$\langle\langle A;B\rangle\rangle_\omega = \sum_{n\neq 0}\left(\frac{\langle \Psi_0(R)|A|\Psi_n(R)\rangle\langle \Psi_n(R)|B|\Psi_0(R)\rangle}{\hbar\omega + E_0^{\mathrm{BO}}(R) - E_n^{\mathrm{BO}}(R)} + \frac{\langle \Psi_0(R)|B|\Psi_n(R)\rangle\langle \Psi_n(R)|A|\Psi_0(R)\rangle}{-\hbar\omega + E_0^{\mathrm{BO}}(R) - E_n^{\mathrm{BO}}(R)}\right) \tag{39}$$

we identify the electronic contribution to the vibrational g-factor, eqn. (37), as the following polarization propagator

$$g_v^{\mathrm{el}}(R) = -\frac{m_{\mathrm{p}}}{m_{\mathrm{e}}}\frac{\hbar^2}{\mu}\left\langle\left\langle\frac{\partial}{\partial R};\frac{\partial}{\partial R}\right\rangle\right\rangle_{\omega=0} \tag{40}$$

For the sake of brevity we do not specify explicitly the dependence of the wavefunctions $|\Psi(\vec{r}_i,R)\rangle$ on the electronic coordinates $\{\vec{r}_i\}$ in this section.

To outline how this propagator is evaluated in our implementation, we rewrite it as

$$\left\langle\left\langle\frac{\partial}{\partial R};\frac{\partial}{\partial R}\right\rangle\right\rangle_{\omega=0} = \langle \Psi_0(R)|\frac{\partial}{\partial R}\left(E_0^{\mathrm{BO}}\mathbf{1} - \boldsymbol{H}\right)^{-1}\frac{\partial}{\partial R}|\Psi_0(R)\rangle \tag{41}$$

in which symbols **1** and ***H***, in bold, define matrices for the super-operator identity and the super-operator Hamiltonian, respectively.[33,34]

On introduction of a complete set of orthonormal wave functions $\{|\Psi_\beta(R)\rangle\}$, the propagator becomes

$$\begin{aligned} \left\langle\left\langle\frac{\partial}{\partial R};\frac{\partial}{\partial R}\right\rangle\right\rangle_{\omega=0} = & \sum_{\alpha\beta}\left\langle \Psi_0(R)\middle|\frac{\partial}{\partial R}\middle|\Psi_\alpha(R)\right\rangle \times \langle \Psi_\alpha(R)| \\ & \times \left(E_0^{\mathrm{BO}}\mathbf{1} - \boldsymbol{H}\right)^{-1}|\Psi_\beta(R)\rangle \\ & \times \left\langle \Psi_\beta(R)\middle|\frac{\partial}{\partial R}\middle|\Psi_0(R)\right\rangle \end{aligned} \tag{42}$$

Defining a vector V_α as

$$V_\alpha = \sum_\beta \langle \Psi_\alpha(R)|\left(E_0^{\mathrm{BO}}\mathbf{1} - \boldsymbol{H}\right)^{-1}|\Psi_\beta(R)\rangle\langle \Psi_\beta(R)|\frac{\partial}{\partial R}|\Psi_0(R)\rangle \tag{43}$$

the propagator in eqn. (41), and thus the electronic contribution to the vibrational g-factor, is calculated as

$$\left\langle\left\langle\frac{\partial}{\partial R};\frac{\partial}{\partial R}\right\rangle\right\rangle_{\omega=0} = \sum_\alpha \left\langle \Psi_0(R)\middle|\frac{\partial}{\partial R}\middle|\Psi_\alpha(R)\right\rangle V_\alpha \tag{44}$$

The components of V_α are obtained from the following set of linear equations

$$\sum_\alpha \langle \Psi_\beta(R)|\left(E_0^{\mathrm{BO}}\mathbf{1} - \boldsymbol{H}\right)|\Psi_\alpha(R)\rangle V_\alpha = \left\langle \Psi_\beta(R)\middle|\frac{\partial}{\partial R}\middle|\Psi_0(R)\right\rangle \tag{45}$$

In the approximate MCSCF model, wave functions at an internuclear distance R are given as[35]

$$\begin{aligned} |\Psi(R)\rangle = & \exp\left[\sum_{i>j}\kappa_{ij}(R)\left(q_{ij}^\dagger(R) - q_{ij}(R)\right)\right] \\ & \times \exp\left[\sum_{m\neq 0}P_m(R)\left(T_m^\dagger(R) - T_m(R)\right)\right] \\ & \times \sum_g C_{g0}(R_0)|\Phi(R)\rangle \end{aligned} \tag{46}$$

in which the configuration state functions $|\Phi(R)\rangle$ are fixed linear combinations of Slater determinants,

$$|\Phi^{\mathrm{SD}}(R)\rangle = a_i^\dagger(R)\cdots a_i^\dagger(R)\cdots a_N^\dagger(R)|\mathrm{vacuum}\rangle \tag{47}$$

in which the creation operator $a_i^\dagger(R)$ creates an electron in the MCSCF spin orbital $\varphi_i(R)$, which itself is expanded in a finite set of basis functions. The state-transfer $T_m^\dagger(R)$ and orbital rotation operators $q_{ij}^\dagger(R)$ are then defined as

$$\begin{aligned} T_m^\dagger(R) &= |\Psi_m(R)\rangle\langle \Psi_0(R)| \\ q_{ij}^\dagger(R) &= a_i^\dagger(R)a_j(R) \end{aligned} \tag{48}$$

in which $T_m(R)$, $q_{ij}(R)$ and $a_i(R)$ are the Hermitian conjugate operators of $T_m^\dagger(R)$, $q_{ij}^\dagger(R)$ and $a_i^\dagger(R)$.

A requirement for both setting up the linear equations, eqn. (45), and evaluating the propagator in eqn. (44) is that the matrix elements $\langle \Psi_0(R)|(\partial/\partial R)|\Psi_\alpha\rangle$ be available. For MCSCF wave functions eqn. (46), we find from preceding work[35] that these matrix elements are expressible as

$$\begin{aligned}\left\langle \Psi_0(R)\left|\frac{\partial}{\partial R}\right|\Psi_\alpha(R)\right\rangle = \sum_{i>j}\frac{\partial\kappa_{ij}(R)}{\partial R}\langle\Psi_0(R)| \\ \times\left(q_{ij}^{\dagger}(R)-q_{ij}(R)\right)|\Psi_\alpha(R)\rangle \\ +\sum_{m\neq0}\frac{\partial P_m(R)}{\partial R}\langle\Psi_0(R)| \\ \times\left(T_m^{\dagger}(R)-T_m(R)\right)|\Psi_\alpha(R)\rangle \\ +\sum_{i,j}\left\langle\varphi_j(R)\left|\frac{\partial\varphi_i(R)}{\partial R}\right.\right\rangle \\ \times\langle\Psi_0(R)|q_{ij}(R)|\Psi_\alpha(R)\rangle\end{aligned} \tag{49}$$

When the natural connection of orthonormal molecular orbitals is used, the last term in eqn. (49) vanishes,[36] yielding the result

$$\begin{aligned}\left\langle \Psi_0(R)\left|\frac{\partial}{\partial R}\right|\Psi_\alpha(R)\right\rangle = \sum_{i>j}\frac{\partial\kappa_{ij}(R)}{\partial R}\langle\Psi_0(R)|\times\left(q_{ij}^{\dagger}(R)-q_{ij}(R)\right) \\ \times|\Psi_\alpha(R)\rangle+\sum_{m\neq0}\frac{\partial P_m(R)}{\partial R}\langle\Psi_0(R)| \\ \times\left(T_m^{\dagger}(R)-T_m(R)\right)|\Psi_\alpha(R)\rangle\end{aligned} \tag{50}$$

The geometrical derivatives of the coefficients $\partial\kappa_{ij}(R)/\partial R$ for orbital rotations and of the configurational amplitudes $\partial P_m(R)/\partial R$ are obtained from standard equations for the geometrical response, which are also solved when the molecular Hessian is calculated.[32]

In summary, the flow of calculations that we have implemented in Dalton to evaluate the electronic contribution to the vibrational *g*-factor with multi-configuration self-consistent-field wave functions is first to calculate the wave function $|\Psi_0(R)\rangle$ for the electronic ground state, then to solve the equations for geometric response using the natural connection of orthonormal molecular orbitals to obtain the geometric derivatives of the coefficients $\partial_{k\gamma}(R)/\partial R$ for orbital rotations and of the configurational amplitudes $\partial P_m(R)/\partial R$, to form and solve the linear equations, eqn. (45), for vector V_α, and eventually to calculate the polarisation propagator from components of that vector through eqn. (44).

Table 2 Calculated properties of $^1H_2$ as a function of internuclear distance *R*: electronic energy, vibrational *g*-factor, diamagnetic and paramagnetic electronic contributions to rotational *g*-factor, and total molecular rotational *g*-factor

$R/10^{-10}$ m	Energy/E_h	g_v	g_r^{dia}	g_r^{para}	g_r
0.1	2.483 037 89	0.6939	0.0165	−0.0265	0.9895
0.2	0.007 031 88	0.4462	0.0035	−0.0160	0.9870
0.3	−0.700 132 72	0.3346	0.0015	−0.0243	0.9767
0.4	−0.980 874 17	0.2822	0.0004	−0.0377	0.9622
0.45	−1.054 557 97	0.2677	0.0003	−0.0458	0.9540
0.5	−1.103 420 22	0.2581	0.0003	−0.0548	0.9450
0.55	−1.135 317 18	0.2515	0.0005	−0.0646	0.9354
0.6	−1.155 363 06	0.2465	0.0006	−0.0751	0.9250
0.65	−1.166 996 54	0.2420	0.0007	−0.0865	0.9137
0.7	−1.172 592 14	0.2372	0.0008	−0.0987	0.9016
0.741 382	−1.173 867 20	0.2325	0.0008	−0.1095	0.8908
0.8	−1.171 904 08	0.2240	0.0008	−0.1258	0.8745
0.85	−1.167 708 96	0.2146	0.0008	−0.1407	0.8596
0.9	−1.161 894 89	0.2028	0.0009	−0.1566	0.8438
0.95	−1.154 952 51	0.1883	0.0010	−0.1735	0.8270
1.0	−1.147 253 16	0.1705	0.0010	−0.1915	0.8090
1.1	−1.130 649 98	0.1238	0.0013	−0.2308	0.7700
1.2	−1.113 652 13	0.0603	0.0015	−0.2748	0.7262
1.3	−1.097 195 54	−0.0215	0.0017	−0.3233	0.6779
1.4	−1.081 839 24	−0.1207	0.0019	−0.3763	0.6251
1.5	−1.067 904 89	−0.2330	0.0020	−0.4332	0.5683
1.6	−1.055 555 98	−0.3496	0.0022	−0.4930	0.5087
1.7	−1.044 844 27	−0.4583	0.0023	−0.5542	0.4476
1.75	−1.040 095 31	−0.5055	0.0024	−0.5848	0.4171
1.8	−1.035 738 73	−0.5457	0.0024	−0.6151	0.3868
1.85	−1.031 761 05	−0.5778	0.0025	−0.6449	0.3571
1.9	−1.028 146 04	−0.6009	0.0025	−0.6739	0.3281
1.95	−1.024 875 23	−0.6146	0.0026	−0.7019	0.3002
2.0	−1.021 928 47	−0.6189	0.0026	−0.7287	0.2734
2.05	−1.019 284 45	−0.6143	0.0026	−0.7542	0.2479
2.1	−1.016 921 21	−0.6016	0.0027	−0.7782	0.2240
2.15	−1.014 816 59	−0.5820	0.0027	−0.8007	0.2015
2.2	−1.012 948 64	−0.5567	0.0027	−0.8216	0.1806
2.25	−1.011 295 95	−0.5270	0.0027	−0.8408	0.1614
2.3	−1.009 837 96	−0.4943	0.0027	−0.8585	0.1437
2.4	−1.007 429 18	−0.4243	0.0028	−0.8893	0.1130
2.49	−1.005 581 10	−0.3545	0.0028	−0.9143	0.0880
3.0	−1.001 251 29	−0.1134	0.0029	−0.9795	0.0229
4.0	−0.999 98 758	−0.0060	0.0028	−1.0010	0.0013
5.0	−0.999 90 935	0.0023	0.0028	−1.0022	0.0001
7.5	−0.999 89 752	0.0029	0.0028	−1.0023	0.0000
10.0	−0.999 89 679	0.0029	0.0028	−1.0023	0.0000
15.0	−0.999 89 666	0.0029	0.0028	−1.0023	0.0000

Details of the calculation

The electronic energy as well as the electronic contributions to the rotational and vibrational *g*-factors were calculated with full CI wave functions using the aug-cc-pVQZ basis set of Dunning and co-workers.[22] In preceding calculations we tested the cc-pVXZ, aug-cc-pVXZ and daug-cc-pVXZ series of basis sets[22] at the equilibrium geometry and found that no further significant changes in the desired properties were observed beyond the employed aug-cc-pVQZ basis set. All calculations were performed with our local development version of Dalton.[27]

In Table 2 and Figs. 1 and 2 we present calculated values of total electronic energy E_0^{BO} and of rotational and vibrational *g*-factors as a function of internuclear distance *R* from nearly a putative united atom to barely interacting H atoms far apart. Each *g*-factor comprises two contributions, one from nuclei, eqn. (36), that depends on only atomic numbers and masses and that has hence for $^1H_2$ the same value 0.9995 at all internuclear distances, and another from electrons that is related formally to nonadiabatic effects of either type. For g_v the total value at a particular *R* is just the sum of an electronic contribution, eqn. (37), that is invariably negative, and that positive nuclear contribution; the net result is either positive or negative depending on the relative magnitudes. For g_r the same positive nuclear contribution sums with a diamagnetic term, which is invariably positive, and a paramagnetic term, which is invariably negative. For $^1H_2$ net values of g_r are invariably positive, but another molecular species might have a negative or positive value;[14] for $^1H_2$ the sign of g_v alters from positive at small *R* to negative at large *R*. For either g_v or g_r the magnitude must approach zero at large *R* because under such a condition electrons follow perfectly one or other atomic nucleus: there can exist no slippage. Our result for g_r at R_e is identical to the earlier full CI value reported by Ruud *et al.*[37,38] using the same basis set.

The most striking feature of the radial function, $g_v(R)$, for the vibrational *g*-factor is the minimum at an internuclear distance about 2×10^{-10} m. We learn about the origin of this minimum by the sum-over-excited-states expression for the electronic contribution to the vibrational *g*-factor in eqn. (37). For that purpose we need to calculate the excitation

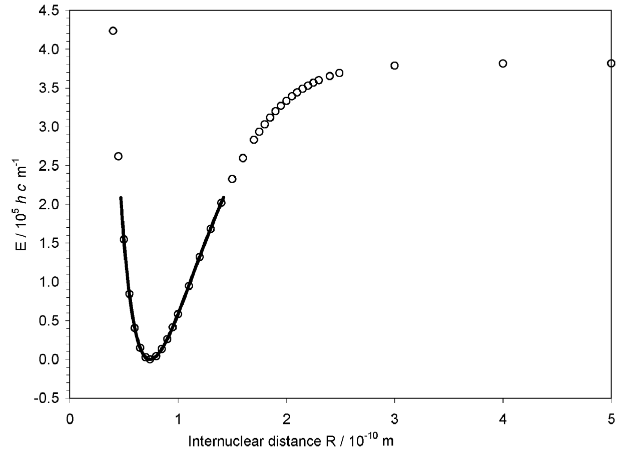

Fig. 1 Energy of H_2 as a function of internuclear distance R; circles denote points from quantum-chemical calculations; the curve denotes $V(R)$ deduced from spectral analysis within the range of its validity.

energies, $\Delta E^{\mathrm{BO}}_{0n}(R) = E^{\mathrm{BO}}_{n}(R) - E^{\mathrm{BO}}_{0}(R)$, of the lowest excited states of same symmetry as the ground state and the corresponding transition moments $\langle \Psi_n(\{\vec{r}_i\},R)|(\partial|\Psi_0(\{\vec{r}_i\},R)\rangle/\partial R)$. Excitation energies are easily obtained as poles of a polarization propagator,[30–32,34] whereas the transition moments are known as first-order nonadiabatic coupling matrix elements (NACME) of which the calculation is also implemented in the Dalton program.[34]

In Fig. 3 the energies and NACME for the first three excited states and in Fig. 4 the contributions of these excited states to the electronic contribution of the vibrational g-factor, eqn. (37), are shown. With empty symbols the terms with $n = 1,2,3$ in eqn. (37) are given, whereas the solid symbols and lines are the the result of the summation over n from 1 to 2, n from 1 to 3 and all n in eqn. (37). From Fig. 3 we see that the energy of the first three excited states exhibits no atypical behaviour, but that the NACME to the first excited state has a clear maximum at an internuclear distance 2.05×10^{-10} m. The NACME to the second and third excited state show quite disparate behviour: the first falls steeply whereas the latter increases. The maximum in the NACME to the first excited state produces a minimum in the contribution to the vibrational g-factor from this state (see Fig. 4). However, due to the variation of the excitation energy which enters the denominator in eqn. (37), the minimum is slightly shifted to an internuclear distance 2.10×10^{-10} m. The contribution from the second excited state exhibits no extremum in the given range of internuclear distance, but adding it to the $n = 1$ contribution diminishes the curvature and shifts the minimum to an internuclear distance 1.95×10^{-10} m. Finally the third excited state shifts the minimum to an internuclear distance 2.0×10^{-10} m and increases slightly the curvature again. With only the first three excited states we thus obtain about 75% of the total electronic contribution and reproduce the position of the minimum and the curvature around the minimum. It is therefore safe to state that the minimum in the vibrational g-factor is due to an extremum in the first-order nonadiabatic coupling matrix element to the first excited state and not in the energy of the excited state. The exact position of the minimum in the vibrational g-factor is, however, influenced by the excitation energy and by more highly excited states.

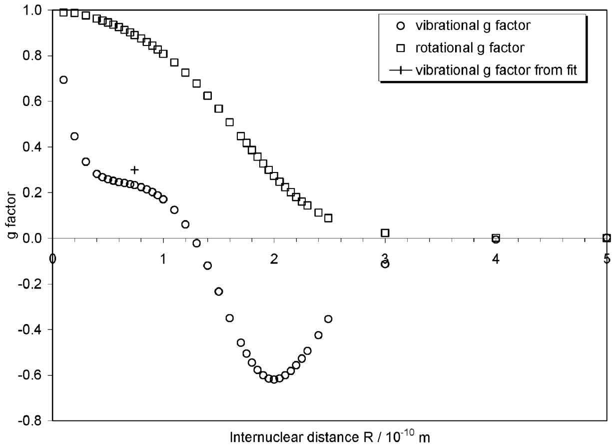

Fig. 2 Rotational and vibrational g-factors of $^1H_2$ as a function of internuclear distance R; points from quantum-chemical calculations (○ for g_v and □ for g_r) and a point marked + for g_v deduced from spectral data.

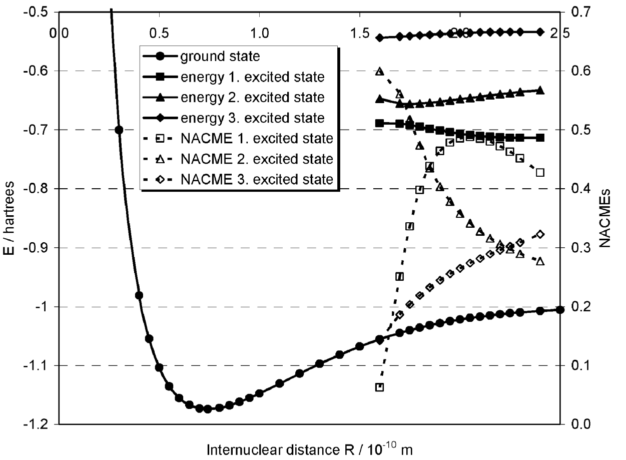

Fig. 3 Calculated energies and first-order nonadiabatic coupling matrix elements (NACME) of the first three excited states in $^1H_2$ as a function of internuclear distance R.

Analysis of spectral data

Spectral data of dihydrogen in pure rotational and vibration-rotational transitions exist for six isotopic species, but data are sparse for species containing ^{3}H. After extensive tests, data accepted for inclusion in a final set for reduction to parameters of radial functions originate in 32 papers from at least 16 laboratories, with widely varying optical resolution, yielding uncertainties of individual measurements of wave numbers/m^{-1} in the range [0.003,50], and varied conditions of gaseous samples, such as pressure with unknown effect of collisional

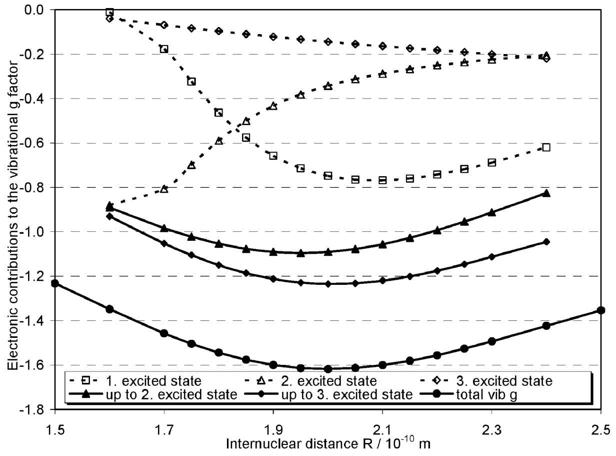

Fig. 4 Contributions from the lowest three excited states to the electronic contribution to the vibrational g-factor g_v eqn. (38) of $^1H_2$ as a function of internuclear distance R. Dashed lines and empty symbols are contributions from a particular excited state whereas solid lines and symbols are the sum of the contributions up to and including the given excited state.

broadening and shift of wave number of spectral lines. Analysis of 390 spectral lines yielded internally consistent results; we rejected 30 data of further prospective spectral lines, those for band 4–0 of $^1H^3H$ [39] that showed a systematic deviation -3.35 ± 0.22 m^{-1}, or about 17 times the nominal precision of their measurement, from back-calculated wave numbers, and bands 1–0 of $^1H_2$,[40] 1–0 of $^1H^2H$,[41] 0–0 of $^1H^3H$,[42] and 1–0 of $^1H^3H$, $^2H^3H$ [43] and $^3H_2$,[39] that show much larger systematic deviations, indicating problems of calibration of wave number scale. Data included in our analysis are specified in Table 3.

To achieve a global fit of those spectral data we applied procedure Radiatom,[69] in either its traditional Fortran version with precision 32 decimal digits for which expressions[70] were derived with Reduce through a JWKB treatment,[15,71] or a new version in Maple with precision 24 decimal digits in which all expressions are freshly evaluated symbolically according to hypervirial perturbation theory.[17,72] We verified that algebraic expressions of term coefficients Y_{kl} derived by either method are identical, but the latter method[17,72] is computationally more efficient. Numerical values of parameters derived through either version of Radiatom are not quite identical, because the algorithm for non-linear regression according to the approach of Levenberg and Marquardt has slightly different implementations, but differences in values are within specified uncertainties, as presented in Table 4 from the Fortran version. Initial estimates of all unconstrained parameters were set at zero except rough estimates of $U_{1,0}$ and $U_{0,1}$ and generic values of c_1 and c_2;[16] during progress towards convergence through ~ 16 iterations, weighted χ^2 decreased from $\sim 10^{13}$ to $\sim 10^3$. The duration of a given fit with Maple, for which code is partially interpreted, is 10–30 times larger than with the fully compiled Fortran procedure on comparable computers. All other fitting was performed with Maple procedures.

We fit those data in terms of coefficients of reduced variable z [17] for displacement of instantaneous internuclear separation R from equilibrium internuclear distance R_e,

$$z = 2\frac{R - R_e}{R + R_e} \tag{52}$$

in four radial functions, with coefficients c_j for potential energy independent of mass,

$$V(R) = E_0^{\text{BO}}(R) \rightarrow V(z) = hcc_0 z^2\left(1 + \sum_{j=1} c_j z^j\right) \tag{53}$$

s_j for nonadiabatic vibrational effects in the vibrational g-factor,

$$g_v(R) \rightarrow \frac{m_p}{\mu}\sum_{j=0} s_j z^j \tag{54}$$

t_j for nonadiabatic rotational effects in the rotational g-factor,[26]

$$g_r(R) \rightarrow \frac{m_p}{\mu}\sum_{j=0} t_j z^j \tag{55}$$

and u_j for adiabatic effects.

$$V_{\text{ad}}(R) \rightarrow hc\frac{m_e}{\mu}\sum_{j=0} u_j z^j \tag{56}$$

Because for available data of H_2 we are able to fit significantly coefficients s_j and t_j, with $j \geq 0$, and u_j, with $j \geq 1$, for extra-mechanical effects of at most two of those three types, we employed first calculated values of the rotational g-factor to constrain coefficients t_j,[26] and fitted values of coefficients c_j, s_j and u_j, in addition to $U_{0,1}$ and $U_{1,0}$, so to produce results in Table 4 according to fit T. As an alternative approach we employed calculated values of adiabatic effects[20,21] to constrain coefficients u_j, and fitted values of coefficients c_j, s_j and t_j in addition to $U_{0,1}$ and $U_{1,0}$, to produce results in Table 4 according to fit U. For values within brackets, uncertainties

Table 3 Vibrational quantum numbers v' and v'', number of lines N and source of data for each isotopic variant included in our spectral analysis

Variant	v',v''	N	Ref.
$^1H_2$	0,0	1	44
	0,0	5	45
	0,0	6	46
	0,0	1	47
	0,0	4	48
	0,0	6	49
	0,0	2	50
	0,0	4	41
	0,0	1	51
	0,0	6	52
	1,0	8	53
	1,0	13	54
	1,0	7	55
	1,0	8	56
	1,0	6	46
	1,0	5	48
	1,0	4	57
	1,0	4	41
	1,0	17	52
	2,0	4	52
	2,0	8	53
	2,0	2	55
	4,0	2	58
	5,0	1	58
	2,1	8	56
	3,2	11	56
	4,3	7	56
	5,4	3	56
$^1H^2H$	0,0	3	59
	0,0	5	41
	1,0	4	60
	1,0	1	61
	1,0	4	62
	1,0	12	63
	1,0	5	52
	2,0	1	64
	2,0	1	61
	3,0	8	65
	4,0	8	65
	5,0	1	66
	5,0	6	65
	6,0	5	65
$^2H_2$	0,0	9	46
	0,0	7	48
	0,0	5	41
	0,0	9	52
	1,0	1	40
	1,0	14	54
	1,0	9	58
	1,0	5	57
	1,0	11	67
	1,0	5	41
	1,0	19	52
	2,0	5	52
$^1H^3H$	1,0	5	52
	1,0	7	39
	5,0	6	39
$^2H^3H$	0,0	4	42
	0,0	6	68
	1,0	7	52
	1,0	13	68
$^3H_2$	0,0	4	43
	0,0	12	52
	1,0	9	52

Table 4 Coefficients of radial functions and other molecular parameters of H_2 X $^1\Sigma_g^+$

	Fit T	Fit U
c_0/m^{-1}	7970 836.8 ± 79	7970 784.5 ± 77
c_1/m^{-1}	−0.604 167 ± 0.000 118	−0.603 753 ± 0.000 135
c_2/m^{-1}	0.210 30 ± 0.000 24	0.209 73 ± 0.000 33
c_3/m^{-1}	−0.144 41 ± 0.001 87	−0.148 89 ± 0.001 86
c_4/m^{-1}	0.012 76 ± 0.0025	0.021 64 ± 0.0026
c_5/m^{-1}	−0.1404 ± 0.0085	−0.1308 ± 0.0086
c_6/m^{-1}	0.1973 ± 0.0102	0.1737 ± 0.0100
c_7/m^{-1}	−0.0524 ± 0.0106	−0.0614 ± 0.0109
c_8/m^{-1}	−0.0737 ± 0.0178	−0.0459 ± 0.0173
c_9/m^{-1}	0.0880 ± 0.0092	0.0694 ± 0.0082
c_{10}/m^{-1}	−0.1074 ± 0.0172	−0.1055 ± 0.0169
s_0/m^{-1}	0.1569 ± 0.0023	0.1301 ± 0.0043
s_1/m^{-1}	[0]	−0.528 ± 0.026
s_2/m^{-1}	[0]	[0]
s_3/m^{-1}	6.69 ± 0.69	9.59 ± 0.83
t_0/m^{-1}	[0.445 62 ± 0.000 44]	0.4523 ± 0.0030
t_1/m^{-1}	[−0.098 58 ± 0.0025]	−0.0836 ± 0.0174
t_2/m^{-1}	[−0.095 58 ± 0.0066]	−0.603 ± 0.108
t_3/m^{-1}	[−0.092 19 ± 0.021]	...
t_4/m^{-1}	[−0.1354 ± 0.0140]	...
t_5/m^{-1}	[−0.0468 ± 0.043]	...
t_6/m^{-1}	[0.4275 ± 0.027]	...
$u_0/10^6$ m^{-1}	...	[10.524 72 ± 0.000 72]
$u_1/10^6$ m^{-1}	−4.025 ± 0.024	[−4.0384 ± 0.0049]
$u_2/10^6$ m^{-1}	2.007 ± 0.061	[2.1451 ± 0.0197]
$u_3/10^6$ m^{-1}	[0]	[1.728 ± 0.033]
$u_4/10^6$ m^{-1}	2.75 ± 0.23	[1.384 ± 0.086]
$u_5/10^6$ m^{-1}	...	[0.353 ± 0.053]
$u_6/10^6$ m^{-1}	...	[−0.727 ± 0.109]
$U_{0,1}$/m^{-1} u[a]	3066.7339 ± 0.0110	3066.7074 ± 0.0124
$U_{1,0}$/m^{-1} u^2[a]	312694.3 ± 2.1	312691.95 ± 2.15
$R_e/10^{-10}$ m	0.741 413 01 ± 0.000 001 33	0.741 416 20 ± 0.000 001 50
k_e/N m^{-1}	576.0898 ± 0.0078	576.0810 ± 0.0079
$\hat{\sigma}$	1.458	1.457

[a] In this table, apart from coefficients in radial functions defined through formulae above, appear $U_{1,0}$ and $U_{0,1}$, which correspond to $Y_{1,0}$ and $Y_{0,1}$, respectively, without dependence on mass, equilibrium force coefficient k_e and reduced standard deviation of the fit $\hat{\sigma}$.

specified for coefficients t_t in fit T and u_j in fit U are standard errors arising from fitting available data from quantum-chemical calculations, and play no role in fits of spectral data. Each other uncertainty in Table 4 denotes an estimated single standard error associated with a parameter, appearing generally in a non-linear manner in expressions for Y_{kl} and Z_{kl},[16] in the best fits of available spectral data described above. Other values in that table are either constrained to zero, as implied by notation "[0]", or are indeterminate from available spectral data, indicated with ellipsis, like any further coefficients in the various radial functions.

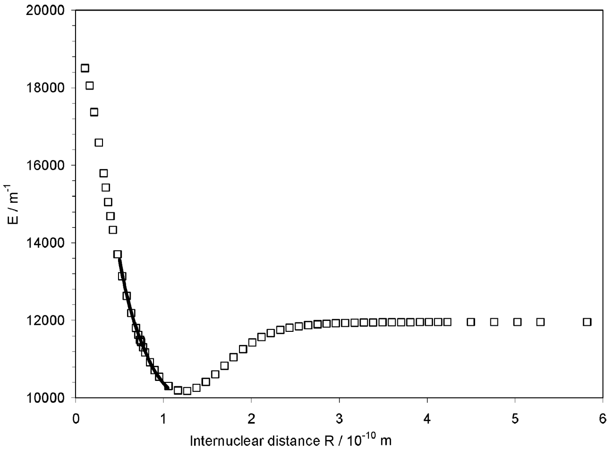

Fig. 5 Adiabatic correction for $^1H_2$ as a function of internuclear distance R; curve from spectral analysis (present work) and points from refs. 20 and 21.

Discussion

Our approach in fit T is analogous to that practised in our original work on LiH.[19] Fit T has seven set parameters – t_j, $0 \le j \le 6$, related to the rotational g-factor – and 17 other adjustable parameters evaluated significantly; three other parameters that occur linearly had values that, when floated freely, hovered near zero with larger standard errors than magnitudes, and that were accordingly fixed to zero. In Fig. 1 we plot points calculated for electronic energy according to Table 2, but relative to that energy at R_e and converted to wave number unit, and a curve of $V(z)$ based on R_e and coefficients c_j, $0 \le j \le 10$, in Table 4 and fit T; according to spectral data the curve is defined over a range of internuclear distance R indicated in that figure. Fit U involves only six set parameters: u_j, $1 \le j \le 6$ – because u_0 plays no part in the fit, and 18 adjustable parameters, with one further linear parameter s_2 that in lieu of significant evaluation was set to zero. In Fig. 5 we plot a curve of function for $V'(R)$ from coefficients u_j, $1 \le j \le 4$, from fit T in Table 4 for comparison with points calculated by Kolos and Wolniewicz[20,21] for adiabatic effects; for a constant term for the curve, being a contribution to residual energy, which is undetectable from spectral observations, we employed for plotting purpose a value 11 458.5 m^{-1}.[20] The curve conforms closely to points calculated in a range of internuclear distance/10^{-10} m [0.45, 1.05] corresponding to classical turning points of $V(R)$ for $v \sim 2$ for $^1H_2$; although spectral data for isotopic species are available for greater energies, their quality precludes agreement over a great range. Coefficients of z for that polynomial fitted from quantum-chemical results [20,21] over their total range appear as values u_j in a column for fit U of Table 4; values of u_1 and u_2 in the two columns of that table agree satisfactorily within experimental error of values for fit T that reflect error propagated from measurement of experimental wave numbers. The value 0.8976 ± 0.0060 for g_r at R_e derived from spectral data according to fit U agrees satisfactorily with the calculated value 0.8908 in Table 2. Fig. 2 shows points of calculated values of $g_r(R)$ according to Table 2.

For that reason we employed values of coefficients u_j fitted from results of quantum-chemical calculations as constraints and made a second fit of spectral data with adjustable coefficients t_j. The values of t_0 and t_1 for fit U are comparable with those fitted from calculated values of g_r but values of t_2 differ by more than the larger standard error; the varied degrees of polynomials are likely responsible for this condition. Fits T and U have essentially the same reduced standard deviation $\hat{\sigma}$; that the values of this quantity significantly exceed unity reflects the diverse origins and quality of spectral data, which are beyond control in the present work. Our values of t_0, t_1 and t_2 obtained from fit U yield an expectation value 0.8852 ± 0.0060 of $g_r(R)$ in vibration-rotational state $|0,1\rangle$ for $^1H_2$ that is within experimental error of the measured value $0.882\,91 \pm 0.000\,07$.[23] For this reason our value $R_e/10^{-10}\ \mathrm{m} = 0.741\,4144 \pm 0.000\,0020$, as a weighted mean from fits T and U, represents the first truly direct and accurate experimental measurement of the equilibrium internuclear separation of dihydrogen independent of nuclear mass, as practically all extra-mechanical effects are taken explicitly into account in deriving this value. This value is, within three standard errors, equal to that, $0.741\,4196 \times 10^{-10}$ m with no estimate of uncertainty, obtained with 80-term functions by Kolos and Wolniewicz[20] who included relativistic corrections that are redundant to experimental results; for comparison, polynomial interpolation of electronic energies in Table 2 yields a minimum near $0.741\,94 \times 10^{-10}$ m, depending on the degree of polynomial. Likewise our value $k_e = (576.0855 \pm 0.0111)\ \mathrm{N\ m^{-1}}$ is the first accurate experimental measurement of the equilibrium force coefficient for dihydrogen independent of nuclear mass. For these calculations we employ contemporary values (CODATA 2003) of fundamental physical constants h, a_0 and N_A and include their known uncertainties in the estimated standard errors of our analysis of experimental results.

Values of coefficient s_0 from fits T and U are less consistent, likely because of the varying nature of other coefficients s_j between the two fits, than other common parameters; the mean indicates a value of the vibrational g-factor $g_v = s_0 m_p/\mu \sim 0.30 \pm 0.03$ for $^1H_2$ at R_e. Because all these reductions of spectral data were completed before quantum-chemical calculations of the vibrational g-factor were undertaken, this experimental value is a genuine prediction, which differs appreciably from the calculated value 0.2325 in Table 2. In Fig. 2 we denote by circles values of g_v according to calculations of molecular electronic structure and presented in Table 2, with a single point marked with a cross for g_v at R_e from our spectral analysis. A difference between values of g_v from experiment and calculation is evidently an artefact reflecting the moderate quality of spectral data, as further nonadiabatic effects, associated with $V'(R)$, are unlikely to be significant at this level; we thus attribute this difference to experimental error propagated from measurements of wave numbers of transitions. The magnitude of g_v at R_e differs much from that of g_r there, $\sim$0.9, in an apparently unpredictable manner; such a large difference shown by the results of our quantum-chemical calculations is qualitatively confirmed from our fit U of spectral data, even if not quantitatively accurate. These g-factors are supposed to indicate the extent to which electronic distributions slip[1] when following the respective nuclear motions, but there is no particular reason to expect that electrons might follow rapidly vibrating atomic nuclei much better than the same rotating nuclei.

In Table 4, all values of coefficients deduced from reduction of spectral data, apart from those fitted from quantum-chemical calculations, must be regarded as fitting parameters. For instance, according to Dunham's approach[18] to which we conform, term coefficients Y_{kl} in a finite set are optimally evaluated to reproduce wave numbers of available spectral transitions; because 60 values of Y_{kl} implied by fitting coefficients in $V(z)$ up to c_{10} for 390 spectral data are not all independent, a significant improvement in data reduction is achieved on directly fitting instead 12 parameters, namely $U_{0,1}$, $U_{1,0}$ and c_j with $1 \le j \le 10$, or equivalently R_e and c_j with $0 \le j \le 10$. The rotational g-factor, being a factor of proportionality in the splitting of spectral lines according to a Zeeman effect, can be regarded as a quantity observable from experiment; a measured value of g_r in a particular vibration-rotational state can be calculated as an expectation value $\langle v,J|(R)|v,J\rangle$ of radial function $g_r(R)$ that is not an observable. In contrast, potential energy $V(R)$ is merely a function that is an artefact of a theoretical approach, namely separate treatment of electronic and nuclear motions, and no expectation value of potential energy is directly observable. Likewise, adiabatic and nonadiabatic vibrational effects, represented with radial functions $V'(R)$ and $g_v(R)$, respectively, constitute merely corrections to that approach to take into account that electrons fail to follow perfectly atomic nuclei in their supposed vibrational and rotational motions. In fact, as well as reproducing wave numbers of 390 specified vibration-rotational transitions within a factor 1.46 times their uncertainties of measurement on average in conjunction with radial functions for extra-mechanical effects, $V(z)$, according to R_e and coefficients c_j in either column of Table 4, as a plot in Fig. 1 exhibits a typical curve expected for a function of potential energy, with no divergence within a range of internuclear distance defined by classical turning points of the state of greatest vibrational quantum number sampled by spectral observations included in our fits. Moreover, values of coefficients t_j derived in fit U and values of coefficients u_j in fit T to some extent conform to values derived from accurate calculation; likewise a value of s_0 implies a value of vibrational g-factor comparable with that derived from accurate calculation. In that sense our fitting parameters possess physical significance, within a limit set by the quality of a fit that reflects data from diverse sources.

Conclusion

Whereas calculations of molecular electronic structure of $^1H_2$ are readily and rapidly performed with almost arbitrary accuracy on common computers, the quality of spectral data for this molecular species in its several isotopic variants leaves much to be desired. In this work our emphasis in calculations of molecular electronic structure centred on the vibrational and rotational g-factors, which we have calculated over almost the entire range of internuclear distance relevant to molecular properties. Our calculation of the molecular vibrational g-factor of $^1H_2$ is the first such explicit theoretical evaluation of this quantity for any species. Combined with already published data for adiabatic corrections, we have an unprecedented collection of quantitative information about extra-mechanical effects of H_2.

Wolniewicz remarked[21] that for refinement of theoretical predictions of vibration-rotational spectra of dihydrogen in its isotopic variants "new [calculations of] nonadiabatic corrections are needed". In the present work we have practically achieved this objective, as our calculations of vibrational and rotational g-factors encompass the major part of these non-adiabatic corrections, leaving only a much smaller contribution to $V_{\text{non-ad}}(R)$ in eqn. (15). The quality of our calculation of g_r is proved by our agreement with accurate experimental data.[23] On the basis of calculations of electronic energy, as in Table 2, that serves as potential energy for nuclear vibrational motion, combined with separate calculations of the dependence of adiabatic corrections, rotational and vibrational g-factors on internuclear distance, one can accurately predict frequencies of spectral lines for vibration-rotational transitions of H_2 in its several isotopic variants over the entire range of energies up to the dissociation limit. An alternative approach,[73] in which the authors claim to make rigorous and fully variational calculations, involving all particles, of only the vibrational spectrum is computationally much more laborious, requiring protracted computations for each selected vibrational state, and has not been applied to states with angular momentum. The nature of those calculations[73] precludes assessment of any component or contribution, and fortuitous cancellation might hypothetically yield an apparently accurate result; in contrast our approach enables the testing of separate contributions relative to experimental data, within a framework of separate treatment of electronic and nuclear motions. We concur that much improved experimental measurements on vibration-rotational spectra of dihydrogen in its several isotopic variants are needed; available measurements are generally greatly inferior to what has been achieved for other and polar diatomic molecular species.

Acknowledgements

We thank Danish Natural Science Research Council, the Carlsberg Foundation and the Danish Center for Scientific Computing for support of this work. JFO thanks Dr M. L. Orlov for providing data on spectral transitions of dihydrogen.

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