Quantum-Chemical Calculations of Radial Functions for Rotational and Vibrational *g* Factors, Electric Dipolar Moment and Adiabatic Corrections to the Potential Energy for Analysis of Spectra of HeH^+

Stephan P. A. Sauer,[1] Hans Jørgen Aa. Jensen[2] and John F. Ogilvie[3]

[1]*Department of Chemistry, University of Copenhagen, Universitetsparken 5,*
DK-2100 København Ø, Denmark
[2]*Department of Chemistry, University of Southern Denmark, Campusvej 55,*
DK-5230 Odense M, Denmark
[3]*Escuela de Quimica, Universidad de Costa Rica, San Pedro de Montes de Oca,*
San Jose 2060, Costa Rica

Abstract

Computational spectrometry, which implies an interaction between quantum chemistry and analysis of molecular spectra to derive accurate information about molecular properties, is needed for the analysis of the pure rotational and vibration–rotational spectra of HeH^+ in four isotopic variants to obtain precise values of equilibrium internuclear distance and force coefficient. For this purpose, we have calculated the electronic energy, rotational and vibrational *g* factors, the electric dipolar moment, and adiabatic corrections for both He and H atomic centres for internuclear distances over a large range 10^{-10}m [0.3, 10]. Based on these results we have generated radial functions for atomic contributions for g_r, g_v, and adiabatic corrections, involving the coefficients s_j^{He}, s_j^{H}, t_j^{He}, t_j^{H}, u_j^{He}, and u_j^{H} of z^j for $^4He^1H^+$ for further spectral analysis.

Contents

ADVANCES IN QUANTUM CHEMISTRY, VOLUME 48
ISSN: 0065-3276 DOI: 10.1016/S0065-3276(05)48017-X

1. INTRODUCTION

Computational spectrometry [1] implies an interaction between quantum chemistry, in a practice of calculations of molecular electronic structure, and analysis of spectra of small free molecules so as to derive, from the latter, information of maximal physical and statistical significance. The best relative accuracy of measurement of spectral frequencies is about two parts in 10^{10} [2]; to obtain a comparable accuracy in differences of quantum-mechanical energies still exceeds the capabilities of algorithms and computer hardware, but the calculation of other pertinent quantities can play a valuable role in the analysis of spectra. For instance, an accurate knowledge of the dynamic electric dipolar polarisability [3–7] of a particular molecular species facilitates the observation of that compound through Raman scattering; likewise accurate data for the molecular rotational g_r factor [8–14] and electric dipolar moment [15] enable extraction of information about the vibrational g_v factor and adiabatic effects from frequency data for pure rotational and vibration–rotational transitions [16–18] as well as an accurate function for the internuclear potential energy, within a conventional treatment involving separation of electronic and nuclear motions. Our work on LiH [17] was undertaken before a comprehensive theoretical treatment relating the vibrational g_v factor and spectral parameters became available [19]. Afterward we developed and implemented an algorithm for the calculation of the vibrational g_v factor [18]. With a new implementation of the coding of adiabatic corrections in an established suite of Fortran routines for quantum-chemical calculations in Dalton [23], we are able to calculate to satisfactory accuracy the principal auxiliary terms in an effective Hamiltonian for vibrational and rotational motion of atomic centres in a diatomic molecule. Because these auxiliary terms have only a small, but significant, effect on energies of molecular vibration–rotational states, there is no necessity to attain an accuracy comparable with that of electronic energy.

Here we apply this quantum-chemical capability to provide quantitative knowledge about these auxiliary quantities to assist the extraction of information about equilibrium properties of helium hydride diatomic molecular cation, HeH^+. By its ionic nature, this compound is highly reactive under laboratory conditions and hence only a transient species in experiments in the gaseous phase, but measurements of spectra have yielded moderately precise frequencies of pure rotational and vibration–rotational transitions throughout energies in a range from the ground state up to the dissociation limit – even beyond that limit for further states quasi-bound within the centrifugal barrier – for both $^4He^1H^+$ and $^4He^2H^+$, as well as less abundant data for two analogous species containing ^3He. Because the curve for the internuclear potential energy of this molecule in the ground electronic state possesses both a broad and a shallow minimum, a radial function to represent that potential energy encompasses internuclear distances over a large range. To cover satisfactorily a corresponding range of energies and ancillary molecular properties would require radial functions involving as parameters some 70 or 80 coefficients of a distance variable to various powers, which would require fitting from known frequencies of only some 200 measured transitions within the electronic ground state. In contrast, wave numbers of about 5500 transitions of GeO are satisfactorily reproduced with only six fitted parameters [24], but these many transitions sample energy for only a small fraction of states below the dissociation limit. Moreover, the small masses of both nuclei in HeH$^+$ cause intervals of energy between adjacent states in vibrational manifolds to be relatively large, and likewise for rotational manifolds, such that below the dissociation limit this curve for the potential energy supports only a few vibrational states, with their associated rotational manifolds. For these reasons the simultaneous reduction of all these spectral data of HeH$^+$ is challenging to an extent far beyond that associated with other and less elusive diatomic molecular species existing in the gaseous phase. In contrast, the calculation of molecular electronic structure and properties is greatly facilitated by the facts that there are only two electrons associated with two atomic nuclei and that the symmetry class of the electronic ground state of HeH$^+$ is $^1\Sigma^+$, implying that no important magnetic effects need be included in the computation of those properties. In summary, one can readily appreciate that this molecular species is an excellent candidate for the application of the practice of computational spectrometry, so that analysis of molecular spectra thus assisted can yield information about equilibrium and other properties to serve both for characterization of this molecular species and as reference for future calculations.

2. THEORY

As a point of departure we assume, within a conventional separation of nuclear and electronic motions, an effective Hamiltonian for the motion of two atomic nuclei and their associated electrons both along and perpendicular to the internuclear vector, directly applicable to a molecule of symmetry class $^1\Sigma^+$ for which magnetic effects are absent or negligible [25]:

$$\begin{aligned}\hat{H}(R) = \frac{1}{2\mu}\ \hat{P}\left(1 + \frac{m_\mathrm{e}}{m_\mathrm{p}} g_v(R)\right)\hat{P} + \left(1 + \frac{m_\mathrm{e}}{m_\mathrm{p}} g_r(R)\right)\frac{\hbar^2 J(J+1)}{2\mu R^2} \\ + V(R) + V'(R) \qquad (1)\end{aligned}$$

here $\hat{P}$ is an operator for linear momentum conjugate to internuclear distance R; $\mu = M_\mathrm{a}M_\mathrm{b}/(M_\mathrm{a} + M_\mathrm{b})$ is the atomic reduced mass for atomic centres A and B and their respective masses M_a and M_b; $g_v(R)$ and $g_r(R)$ are, respectively, radial functions for the vibrational and rotational g factors; J is a quantum number for angular momentum of the molecule about the molecular centre of mass; $V(R)$ denotes internuclear potential energy independent of nuclear mass (including relativistic corrections); and $V'(R)$ denotes adiabatic corrections to take into account a small dependence on nuclear mass that $V(R)$ would otherwise exhibit. Both rotational and vibrational g factors have an electronic contribution, which is regarded to pertain to rotational and vibrational non-adiabatic effects, as discussed below. An additional contribution to both the g factors, which is normally called the nuclear contribution, arises on the transition from nuclear masses to atomic masses in the effective Hamiltonian [18,19]. Energy values of this effective

Hamiltonian are expressed in this form [25]

$$E_{v,J} = \sum_k \sum_l (Y_{k,l} + Z_{k,l}) \left(v + \frac{1}{2} \right)^k [J(J+1)]^l \tag{2}$$

in which Dunham coefficients $Y_{k,l}$ result from the principal terms in the effective Hamiltonian, equation (1), and $Z_{k,l}$ reflect the presence therein of auxiliary terms – the rotational and vibrational g factors and adiabatic corrections.

2.1. The g_r and g_v factors

The electronic contributions to the g factors arise in second-order perturbation theory from the perturbation of the electronic motion by the vibrational or rotational motion of the nuclei [19,26]. This non-adiabatic coupling of nuclear and electronic motion, which exemplifies a breakdown of the Born–Oppenheimer approximation, leads to a mixing of the electronic ground state with excited electronic states of appropriate symmetry. The electronic contribution to the vibrational g factor of a diatomic molecule is then given as a sum-over-excited-states expression

$$g_v^{\mathrm{el}}(R) = \frac{m_{\mathrm{p}}}{m_{\mathrm{e}}} \frac{2\hbar}{\mu} \sum_{n \neq 0} \frac{|\langle \Psi_0(\{\vec{r}_i\}, R)| \{ \frac{\partial}{\partial R} |\Psi_n(\{\vec{r}_i\}, R)\rangle \}|^2}{E_0^{\mathrm{BO}}(R) - E_n^{\mathrm{BO}}(R)} \tag{3}$$

whereas the electronic contribution to the rotational g factor of a diatomic molecule consists of two contributions

$$g_r^{\mathrm{el}}(R) = g_r^{\mathrm{para}}(R) + g_r^{\mathrm{dia}}(R) \tag{4}$$

The ‘paramagnetic’ contribution again involves excited states

$$\begin{aligned} g_r^{\mathrm{para}}(R) = & \frac{m_{\mathrm{p}}}{m_{\mathrm{e}}} \frac{1}{\mu R^2} \left\{ \sum_{n \neq 0} \left(\frac{\langle \Psi_0 | \sum_i l_{i,x}(\vec{R}_0) | \Psi_n \rangle \langle \Psi_n | \sum_i l_{i,x}(\vec{R}_{\mathrm{CM}}) | \Psi_0 \rangle}{E_0^{\mathrm{BO}}(R) - E_n^{\mathrm{BO}}(R)} \right. \right. \\ & \left. \left. + \frac{\langle \Psi_0 | \sum_i l_{i,y}(\vec{R}_{\mathrm{CM}}) | \Psi_n \rangle \langle \Psi_n | \sum_i l_{i,y}(\vec{R}_0) | \Psi_0 \rangle}{E_0^{\mathrm{BO}}(R) - E_n^{\mathrm{BO}}(R)} \right) \right\} \end{aligned} \tag{5}$$

in which for brevity $\Psi_{0|n}(\{\vec{r}_i\}, R)$ is abbreviated in this equation as $\Psi_{0|n}$, whereas the ‘diamagnetic’ contribution is a simple average value over the electronic ground state:

$$g_r^{\text{dia}}(R) = -\frac{m_\text{p}}{\mu R^2}\left\{\frac{1}{2}\left(\langle\Psi_0(\{\vec{r}_i\},R)|\sum_i(r_{i,x}-R_{\text{CM},x})(R_{\text{o},x}-R_{\text{CM},x})|\Psi_0(\{\vec{r}_i\},R)\rangle\right.\right.$$
$$\left.+\langle\Psi_0(\{\vec{r}_i\},R)|\sum_i(r_{i,y}-R_{\text{CM},y})(R_{\text{o},y}-R_{\text{CM},y})|\Psi_0(\{\vec{r}_i\},R)\rangle\right)$$
$$\left.+\langle\Psi_0(\{\vec{r}_i\},R)|\sum_i(r_{i,z}-R_{\text{CM},z})(R_{\text{o},z}-R_{\text{CM},z})|\Psi_0(\{\vec{r}_i\},R)\rangle\right\} \tag{6}$$

The nuclear contribution to the rotational or vibrational g factor becomes for a diatomic molecule AB containing nucleus A of protonic number Z_a along the z-axis at $z_\text{a} = |\vec{R}_\text{a} - \vec{R}_\text{CM}|$, and nucleus B with protonic number Z_b at $z_\text{b} = |\vec{R}_\text{b} - \vec{R}_\text{CM}|$

$$g^n = \frac{m_\text{p}}{I}(Z_\text{a}z_\text{a}^2 + Z_\text{b}z_\text{b}^2) = m_\text{p}\frac{Z_\text{a}M_\text{b}^2 + Z_\text{b}M_\text{a}^2}{M_\text{a}M_\text{b}(M_\text{a}+M_\text{b})} \tag{7}$$

in which the moment of inertia is

$$I = \mu R^2 = \frac{M_\text{a}M_\text{b}}{M_\text{a}+M_\text{b}}(\vec{R}_\text{a} - \vec{R}_\text{b})^2. \tag{8}$$

The second form of g_r^n shows that the nuclear contribution, being independent of internuclear distance, is constant for a particular molecular species in all its electronic states.

Calculation of rotational and vibrational g factors by linear response methods using multiconfigurational self-consistent-field wave functions is described in detail elsewhere [18,27].

According to convention we suppose that the g factors of a neutral diatomic molecule can be partitioned into a term depending on the electric dipolar moment $\vec{d}$ or its derivative $\text{d}d_z/\text{d}R$ and an 'irreducible' non-adiabatic contribution $g_{r/v}^{\text{irr}}$ [19,28]

$$g_r(R) = g_r^{\text{irr}}(R) - \frac{m_\text{p}}{eR}d_z(\vec{R}_\text{CM},R)\left(\frac{1}{M_\text{a}} - \frac{1}{M_\text{b}}\right) \tag{9}$$

$$g_r(R) = g_v^{\text{irr}}(R) - \frac{m_\text{p}}{e}\frac{\text{d}d_z(\vec{R}_\text{CM},R)}{\partial R}\left(\frac{1}{M_\text{a}} - \frac{1}{M_\text{b}}\right) \tag{10}$$

in which the sign of the dipolar moment is chosen to be $d_z < 0$ for a molecule of polarity $+\text{AB}-$ and with the z-axis pointing from A to B. A detailed expression for this irreducible non-adiabatic contribution to the rotational g factor has been derived [29]

$$g_r^{\text{irr}}(R) = \frac{1}{2}\left(g_r^\text{A}(R) + g_r^\text{B}(R)\right) \tag{11}$$

in which

$$g_r^{\mathrm{A|B}}(R) = \frac{m_\mathrm{p}}{\mu} Z_{\mathrm{b|a}} + \frac{m_\mathrm{p}}{m_\mathrm{e}} \frac{1}{\mu R^2} \left\{ \sum_{n \neq 0} \left(\frac{|\langle \Psi_0(\{\vec{r}_i\}, R)| \sum_i l_{i,x}(\vec{R}_{\mathrm{a|b}}) | \Psi_n(\{\vec{r}_i\}, R)\rangle|^2}{E_0^{\mathrm{BO}}(R) - E_n^{\mathrm{BO}}(R)} \right. \right.$$
$$\left. \left. + \frac{|\langle \Psi_0(\{\vec{r}_i\}, R)| \sum_i l_{i,y}(\vec{R}_{\mathrm{a|b}}) | \Psi_n(\{\vec{r}_i\}, R)\rangle|^2}{E_0^{\mathrm{BO}}(R) - E_n^{\mathrm{BO}}(R)} \right) \right\} \tag{12}$$

A related function called $R_{\mathrm{b|a}}^{(n)} = (\mu/m_\mathrm{p}) g_r^{\mathrm{A|B}}$ was previously introduced [30].

For a molecular ion with charge number Q a transformation between isotopic variants becomes complicated in that the g factors are related directly to the electric dipolar moment and irreducible quantities for only one particular isotopic variant taken as standard; for this species these factors become partitioned into contributions for atomic centres A and B separately. For another isotopic variant the same parameters independent of mass are still applicable, but an extra term must be taken into account to obtain the g factor and electric dipolar moment of that variant [19]. The effective atomic mass of each isotopic variant other than that taken as standard includes another term [19]. In this way the relations between rotational and vibrational g factors and d_z and its derivative, equations (9) and (10), are maintained as for neutral molecules. Apart from the qualification mentioned below, each of these formulae applies individually to each particular isotopic variant, but, because the electric dipolar moment, referred to the centre of molecular mass of each variant, varies from one cationic variant to another because the dipolar moment depends upon the origin of coordinates, the coefficients in the radial function apply rigorously to only the standard isotopic species; for any isotopic variant the extra term is required to yield the correct value of either g factor from the value for that standard species [19].

Although the relation between the vibrational g factor and the derivative of electric dipolar moment, equation (10), is formally equivalent to the relation between the rotational g factor and this dipolar moment, equation (9), there arises an important distinction. The derivative of the electrical dipolar moment involves the linear response of the ground-state wave function and thus a non-adiabatic expression for a sum over excited states similar to electronic contributions to the g factors. The vibrational g factor can hence not be partitioned in the same as was the rotational g factor into a contribution that depends only on the ground-state wave function and 'irreducible non-adiabatic' contribution. Nevertheless $g_v^{\mathrm{irr}}(R)$ is treated as such. A detailed expression for $g_v^{\mathrm{irr}}(R)$ in terms of quantum-mechanical operators and a sum over excited states, similar to equations (11) and (12), is not yet reported.

2.2. The adiabatic correction

The adiabatic correction to the Born–Oppenheimer potential energy for a diatomic molecule A–B is simply given by the sum of the expectation values of the nuclear kinetic energy operators [20,21]:

$$V'(R) = \frac{1}{M_\mathrm{A}}\Delta U^\mathrm{A}(R) + \frac{1}{M_\mathrm{B}}\Delta U^\mathrm{B}(R) \tag{13}$$

in which ($K=A$ or $K=B$)

$$\frac{1}{M_K}\Delta U^K(R) = \langle \Psi_0(\{\vec{r}_i\}, R)| - \frac{1}{2M_K}\Delta_K |\Psi_0(\{\vec{r}_i\}, R)\rangle. \tag{14}$$

By calculating $\Delta U^\mathrm{A}(R)$ and $\Delta U^\mathrm{B}(R)$ separately, we can straightforwardly calculate the total adiabatic correction $V'(R)$ for any isotopes of A and B. The adiabatic corrections are calculated by numerical differentiation of the multi-configurational self-consistent field (MCSCF) wave functions calculated with Dalton [23]. The numerical differentiation was performed with the Westa program developed 1986 by Ågren, Flores-Riveros and Jensen [22].

3. COMPUTATIONAL DETAILS

Both the electronic energy and the electronic contributions to the rotational and vibrational g factors, dipolar moment and derivative of the dipolar moment were calculated with full CI wave functions using the aug-cc-pVTZ basis set of Dunning and co-workers [31,32]. In the calculation of the rotational g factor we used rotational London orbitals [27,33]. In the calculation of the adiabatic correction to the potential energy surface we used an MCSCF wavefunction [34] of the complete-active-space type (CASSCF) [35] with two electrons in nine orbitals (5σ and 2π orbitals) included in the active space and using the aug-cc-pVQZ basis set. This model was verified for the iso-electronic H_2 molecule, for which we found that the differences to the reference values by Kołos and Wolniewicz [36] were up to the order of 0.5 cm^{-1}. It was also verified that the reported digits do not include any errors because of the numerical differentiation. All calculations were performed with local development versions of Dalton [23] and Westa [22]. In Table 1 and Figs 1 and 2 we present calculated values of the 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 He and H atoms far apart. Each g factor comprises two contributions, one from nuclei, equation (7), that depends on only atomic numbers and masses and that has hence for ^{4}He^{1}H$^+$ the same value 0.8997 at all internuclear distances, and another from electrons that is related formally to non-adiabatic effects of either type. For g_v the total value at a particular R is just the sum of an electronic contribution, equation (3), that is invariably negative, and the positive nuclear contribution; the net result is either positive or negative depending on the relative magnitudes. For g_r, equation (4), the same positive nuclear contribution sums with a diamagnetic term, equation (6), that is invariably positive, and a paramagnetic term, equation (5), that is

Table 1. Calculated properties of $^{4}\mathrm{He}^{1}\mathrm{H}^{+}$ in its electronic ground state $X\,^{1}\Sigma^{+}$ 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/hartree	g_v	g_r^{dia}	g_r^{para}	g_r
0.3	−2.2315269416	0.6255	0.0023	−0.0328	0.8692
0.4	−2.6867512113	0.6489	0.0001	−0.0321	0.8676
0.5	−2.8713081448	0.6687	0.0002	−0.0336	0.8663
0.6	−2.9456497493	0.6814	0.0005	−0.0371	0.8630
0.7	−2.9713464311	0.6869	0.0008	−0.0416	0.8588
0.77438	−2.9753915000	0.6867	0.0010	−0.0451	0.8556
0.8	−2.9750955024	0.6858	0.0011	−0.0462	0.8545
0.9	−2.9692499440	0.6792	0.0011	−0.0506	0.8501
1.0	−2.9597610664	0.6683	0.0010	−0.0549	0.8458
1.1	−2.9495466617	0.6552	0.0009	−0.0590	0.8415
1.2	−2.9399959858	0.6431	0.0008	−0.0630	0.8375
1.3	−2.9316980164	0.6357	0.0009	−0.0669	0.8336
1.4	−2.9248160702	0.6354	0.0009	−0.0707	0.8298
1.5	−2.9192916304	0.6429	0.0009	−0.0743	0.8263
1.6	−2.9149610967	0.6568	0.0009	−0.0777	0.8229
1.7	−2.9116242596	0.6746	0.0009	−0.0807	0.8198
1.8	−2.9090833625	0.6938	0.0008	−0.0835	0.8170
1.9	−2.9071628083	0.7123	0.0007	−0.0859	0.8144
2.0	−2.9057163342	0.7288	0.0006	−0.0880	0.8123
2.25	−2.9034704823	0.7590	0.0004	−0.0919	0.8081
2.5	−2.9023290253	0.7758	0.0003	−0.0945	0.8054
3.0	−2.9013546908	0.7894	0.0002	−0.0975	0.8024
4.0	−2.9008220843	0.7958	0.0002	−0.0998	0.8001
5.0	−2.9006867790	0.7976	0.0002	−0.1006	0.7993
10.0	−2.9006033488	0.7991	0.0001	−0.1013	0.7985

invariably negative. For $^{4}\mathrm{He}^{1}\mathrm{H}^{+}$ net values of g_r are invariably positive, but another molecular species might have a negative or positive value.

Equations (9) and (11) indicate how the auxiliary radial function for the rotational factor g_r becomes separable into contributions from atomic centres of types A and B. An analogous separation is practicable for both the vibrational g factor and the total adiabatic corrections; for the latter quantity this separation is effected in the original quantum-chemical calculations. Accordingly we express these calculated values of rotational and vibrational g factors, presented in Table 1, and adiabatic corrections, presented in Table 3, of $^{4}\mathrm{He}^{1}\mathrm{H}^{+}$ to generate coefficients of radial functions for atomic centres of either type, He or H. The most useful variable for these functions is z, defined in terms of instantaneous R and equilibrium R_e internuclear distances as

$$z = 2\frac{R - R_e}{R + R_e} \tag{15}$$

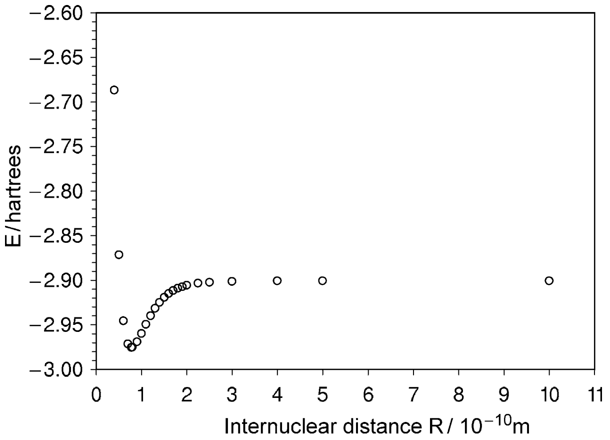

Fig. 1. Energy of ^{4}He^{1}H$^+$ as a function of internuclear distance R; circles denote points from quantum-chemical calculations.

We have for adiabatic effects [26]

$$\frac{U_{\rm ad}(R)}{hc} \rightarrow \frac{V'(z)}{hc} = m_{\rm e}\left(\frac{1}{M_{\rm He}}\sum_{j=1} u_j^{\rm He} z^j + \frac{1}{M_{\rm H}}\sum_{j=1} u_j^{\rm H} z^j\right) \tag{16}$$

for non-adiabatic rotational effects [26]

$$\frac{m_{\rm e}}{m_{\rm p}} g_r(R) \rightarrow \frac{m_{\rm e}}{m_{\rm p}} g_r(z) = m_{\rm e}\left(\frac{1}{M_{\rm He}}\sum_{j=0} t_j^{\rm He} z^j + \frac{1}{M_{\rm H}}\sum_{j=0} t_j^{\rm H} z^j\right) \tag{17}$$

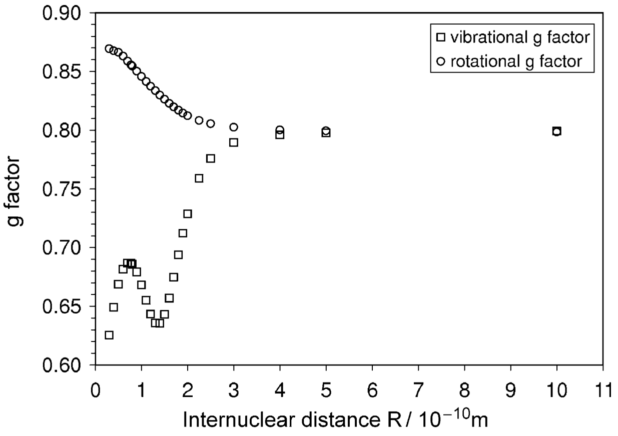

Fig. 2. Rotational and vibrational g factors of ^{4}He^{1}H$^+$ in electronic ground state $X\,^1\Sigma^+$ as a function of internuclear distance R; points from quantum-chemical calculations (○ for $g_r(R)$ and □ for $g_v(R)$).

Table 2. Calculated electric dipolar moment d_z and derivative of dipolar moment $\mathrm{d}d_z/\mathrm{d}R$, both in atomic units, of $^4\mathrm{He}^1\mathrm{H}^+$ in electronic ground state $X\,^1\Sigma^+$ as a function of internuclear distance R. The origin of the coordinate system is located at the centre of atomic mass.

R 10^{-10} m	d_z a.u.	$\mathrm{d}d_z/\mathrm{d}R$ a.u. 10^{10} m^{-1}
0.3	0.135301	0.722545
0.4	0.217406	0.918361
0.5	0.318590	1.102836
0.6	0.437390	1.269955
0.7	0.571942	1.418063
0.77438	0.681154	1.517001
0.8	0.720432	1.548979
0.9	0.881192	1.663442
1.0	1.052533	1.760218
1.1	1.232545	1.836251
1.2	1.418970	1.887935
1.3	1.609252	1.913332
1.4	1.800798	1.913702
1.5	1.991305	1.893508
1.6	2.179027	1.859144
1.7	2.362884	1.817262
1.8	2.542417	1.773467
1.9	2.717648	1.731718
2.0	2.888907	1.694312
2.25	3.303014	1.624030
2.5	3.703300	1.582100
3.0	4.483148	1.543951
4.0	6.013826	1.522514
5.0	7.532529	1.515933
10.0	15.092297	1.510389

and for non-adiabatic vibrational effects [26]

$$\frac{m_\mathrm{e}}{m_\mathrm{p}} g_v(R) \rightarrow \frac{m_\mathrm{e}}{m_\mathrm{p}} g_v(z) = m_\mathrm{e}\left(\frac{1}{M_\mathrm{He}} \sum_{j=0} s_j^\mathrm{He} z^j + \frac{1}{M_\mathrm{H}} \sum_{j=0} s_j^\mathrm{H} z^j\right) \tag{18}$$

The coefficients of z^j, s_j^He and s_j^H for the vibrational factor g_v, t_j^He and t_j^H for the rotational factor g_r, and u_j^He and u_j^H for adiabatic corrections, are obtained from fitting corresponding data in Tables 1–3. The resulting values of coefficients are presented in Table 4, and they reproduce satisfactorily the computational results within the likely precision for internuclear distances over the entire specified range.

4. RESULTS AND DISCUSSION

4.1. Electronic structure calculations

The most striking features of the radial function for the vibrational g factor, $g_v(R)$, are a minimum at an internuclear distance of about 1.4×10^{-10} m and a maximum

Table 3. Calculated adiabatic corrections for He and H, and total adiabatic correction for ^{4}He^{1}H$^+$ according to equation (19)

R 10^{-10} m	ΔU^{He} 10^2 u m^{-1}	ΔU^{H} 10^2 u m^{-1}	$V'(R)$ 10^2 m^{-1}
0.3	357.53	58.81	147.68
0.4	345.30	43.68	129.61
0.5	338.95	32.73	117.16
0.6	336.66	24.88	108.80
0.7	337.04	19.17	103.23
0.77438	338.43	15.89	100.32
0.8	339.06	14.91	99.51
0.9	342.08	11.66	97.04
1.0	345.65	9.15	95.43
1.1	349.40	7.18	94.42
1.2	353.07	5.63	93.79
1.3	356.42	4.39	93.40
1.4	359.33	3.39	93.14
1.5	361.74	2.60	92.95
1.6	363.64	1.96	92.79
1.7	365.11	1.45	92.66
1.8	366.22	1.06	92.54
1.9	367.04	0.76	92.46
2.0	367.65	0.54	92.39
2.25	368.58	0.23	92.31
2.5	369.03	0.09	92.29
3.0	369.41	0.02	92.31
4.0	369.61	0.00	92.35
5.0	369.67	0.00	92.36
10.0	369.70	0.00	92.36

at an internuclear distance of about 0.7×10^{-10} m (Fig. 2). We note, furthermore, that the derivative of the electric dipolar moment, $\mathrm{d}d_z/\mathrm{d}R$, has a maximum at about the same internuclear distance as that minimum in the vibrational g factor (Fig. 3). From equation (10) we discern that this condition implies that the maximum in the vibrational g factor at about 0.7×10^{-10} m is due to g_v^{irr} whereas the minimum at about 1.4×10^{-10} m must have a common origin with a maximum in the dipolar gradient at the same internuclear distance.

We learn about the origin of these extrema through an expression for the sum over excited states for the electronic contribution to the vibrational g factor in equation (3). For that purpose we calculate the excitation energies, $E_n^{\mathrm{BO}}(R) - E_0^{\mathrm{BO}}(R)$, of excited states of least energy but the same symmetry as the ground state and the corresponding transition moments

$$\langle\Psi_0(\{\vec{r}_i\},R)|\left\{\frac{\partial}{\partial R}|\Psi_n(\{\vec{r}_i\},R)\rangle\right\}.$$

Excitation energies are readily obtained as poles of a polarization propagator [37–40], whereas the transition moments are known as first-order non-adiabatic

Table 4. Fitted coefficients of z^j in the radial functions for vibrational (s_j) and rotational (t_j) g factors and adiabatic corrections (u_j) of $^4\mathrm{He}^1\mathrm{H}^+$ in its electronic ground state $X\,^1\Sigma^+$

j	s_j^{He}	s_r^{H}	t_j^{He}	t_j^{H}	$u_j^{\mathrm{He}}\ 10^6\mathrm{m}^{-1}$	$u_j^{\mathrm{H}}\ 10^6\mathrm{m}^{-1}$
0	0.10804	0.82887	−0.06000	0.87112	61.69249	2.89692
1	−1.00630	0.21951	−0.56414	0.10765	3.20200	−5.61943
2	−1.00294	0.23343	−0.14567	0.02173	7.72925	3.19362
3	−1.07478	0.26823	−0.04424	0.01772	1.29965	−0.24166
4	0.28861	−0.06439	−0.11731	−0.00518	−1.81693	−0.23783
5	1.79498	−0.42044	0.40975	−0.10477	−16.78919	−2.60926
6	−5.31950	1.23250	0.47226	−0.02612	4.92581	3.98440
7	−1.36709	0.32900	−0.61852	0.14400	19.19119	2.29043
8	12.15919	−2.82900	−0.21459	0.03022	−15.70526	−7.17792
9	−6.49368	1.52457	0.38251	−0.08647	3.49290	4.42733
10	−6.77346	1.58536	−0.10033	0.02491	0	−0.87705
11	7.42127	−1.75617	0	0	0	0
12	−1.94495	0.46452	0	0	0	0

coupling matrix elements (NACME) of which the calculation is also implemented in the Dalton program [41].

In Fig. 4 we present the energies and matrix elements for the first three excited states and in Fig. 5 we show the contributions of the five lowest excited states to the electronic contribution of the vibrational g factor, equation (3). The terms with $n = 1, 2, 3$ in equation (3) are displayed with hollow symbols, whereas the solid symbols and lines are the result of summation over n from 1 to 2, from 1 to 3, from 1 to 5 and all n in equation (3). According to Fig. 4 the energy of the first three excited states exhibits no atypical behaviour, but that the NACME to the first

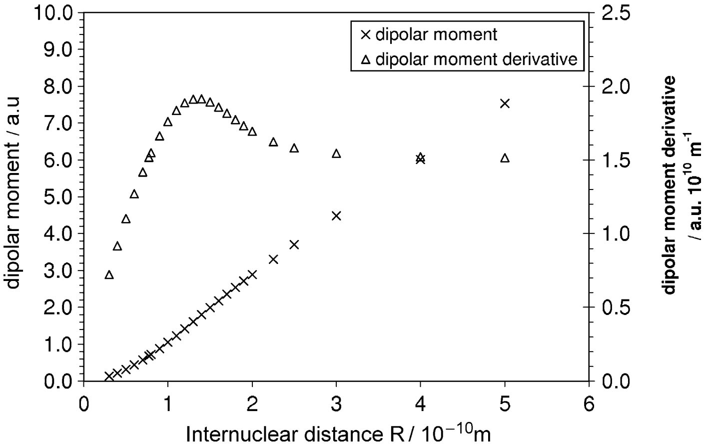

Fig. 3. Electric dipolar moment d_z and derivative of dipolar moment $\mathrm{d}d_z/\mathrm{d}R$ of $^4\mathrm{He}^1\mathrm{H}^+$ in electronic ground state $X\,^1\Sigma^+$ as a function of internuclear distance R; points from quantum-chemical calculations (× for d_z and △ for $\mathrm{d}d_z/\mathrm{d}R$). The origin of the coordinate system is located at the centre of atomic mass.

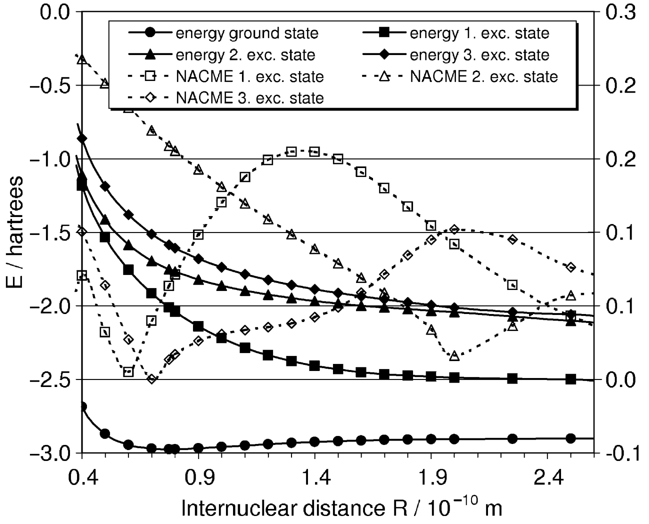

Fig. 4. Calculated energies (solid lines with filled symbols) and first-order non-adiabatic coupling matrix elements (NACME) (dotted lines with empty symbols) of the first three excited states in ^{4}He^{1}H$^+$ as a function of internuclear distance *R*.

excited state has a clear maximum at an internuclear distance of 1.4×10^{-10} m and a minimum at about 0.6×10^{-10} m. The NACME to the second and third excited states show disparate behaviour: the first falls steeply and goes through a minimum at about 2.0×10^{-10} m, whereas the latter has a minimum at about 0.7×10^{-10} m, increases to a maximum at 2.0×10^{-10} m and then decays slowly.

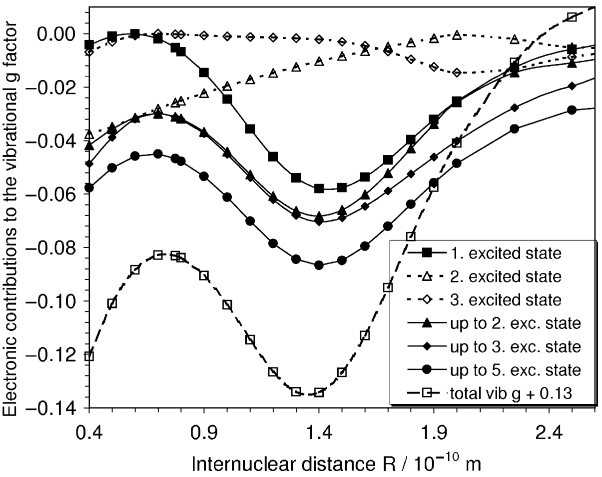

Fig. 5. Contributions from the lowest five excited states to the electronic contribution to the vibrational *g* factor, equation (3), of ^{4}He^{1}H$^+$ as a function of internuclear distance *R*. Dotted lines and empty symbols are contributions from a particular excited state whereas solid lines and symbols are the sum of the contributions up to and including the given excited state. The total electronic contribution (dashed line with □) is shifted by 1.3.

According to Fig. 5 the maximum and minimum in the NACME to the first excited state produce a minimum and maximum in the corresponding contribution to the electronic contribution to the vibrational g factor. The extrema are at the same internuclear distances and have positions near the extrema in the total electronic contribution to $g_v(R)$, but are not as steep. The contributions from the second, third, and up to the fifth excited states modify slightly the position and the form of the extrema but introduce no fundamental modification. We, therefore, conclude that the extrema in the vibrational g factor reflect extrema in the first-order NACME 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 more highly excited states.

Figure 2 shows directly that both rotational and vibrational g factors of $^4He^1H^+$ approach a common value of 0.8 as R becomes large. This behaviour is characteristic of $^4He^1H^+$, as for both neutral diatomic molecular species $^1H_2$ [18] or $^7Li^1H$ for which we have undertaken analogous calculations the asymptotic value of both g_r and g_v is zero. For $^3He^2H^+$ the corresponding value of g_r at $R = 10^{-9}$ m is 0.3.

The adiabatic corrections for the individual atomic centres He and H, listed as a function of R in Table 3, are combined in the final column of that table into a total correction according to this formula

$$\frac{V'(R)}{hc} = m_e \left(\frac{\Delta U^{\mathrm{He}}(R)}{M_{\mathrm{He}}} + \frac{\Delta U^{\mathrm{H}}(R)}{M_{\mathrm{H}}} \right) \tag{19}$$

in which m_e is the electronic rest mass. The total adiabatic correction for $^4He^1H^+$ approaches the value for the helium atom that reflects a difference in electronic energy calculated with the reduced mass of that atom in terms of nucleus and electrons and with the centre of coordinates at the position of the nucleus, because HeH^+ in its electronic ground state $X\,^1\Sigma^+$ dissociates into a neutral helium atom and an ionized hydrogen atom or bare proton.

4.2. Preliminary analysis of spectral data

As an application of this implementation of computational spectrometry, we present preliminary results of analysis of frequencies of pure rotational and vibration–rotational transitions, from the literature, of HeH^+ in four isotopic variants formed from ^4He, ^3He, ^1H and ^2H in appropriate combinations. With the values of $s_j^{\mathrm{He|H}}$, $t_j^{\mathrm{He|H}}$ and $u_j^{\mathrm{He|H}}$ in Table 4, we evaluated the auxiliary coefficients $Z_{k,l}$ in equation (2) and fitted available spectral data to obtain values of the Dunham coefficients $Y_{k,l}$. From $Y_{0,1}$ and $Y_{1,0}$, respectively, in equation (2) or equivalent quantities independent of nuclear mass, the equilibrium internuclear distance independent of nuclear mass has a value $R_e\ 10^{-10}\,\mathrm{m} = 0.7743424 \pm 0.0000020$, and the force coefficient has a value $k_e\ \mathrm{N\,m^{-1}} = 491.536 \pm 0.022$. For comparison, corresponding values for H_2 from spectral analysis [18] are 0.7414144 ± 0.0000020 and 576.0854 ± 0.0090, respectively. The equilibrium distances for these two molecular species in which the binding involves in each case only two electrons are hence almost identical, whereas the smaller force coefficient for HeH^+ likely reflects that its equilibrium binding energy is less than half that of H_2. From interpolation of the three, or five, points of least energy in Table 1 the corresponding value of R_e 10^{-10} m is 0.77843, or 0.77595, but these quantum-chemical computations are not intended for this purpose. Results from quantum-chemical calculations in Tables 1 and 2 will be applied in further analysis of spectra of HeH^+.

5. FINAL REMARKS AND CONCLUSIONS

Computational spectrometry can serve as a powerful adjunct in analysis of molecular spectra, especially in a challenging case such as HeH^+. Even for less esoteric diatomic molecules such as H_2 and LiH, the results of this approach are essential to allow an analyst to disentangle the effects of auxiliary terms in the effective Hamiltonian, equation (1), because of three auxiliary terms – rotational and vibrational g factors and adiabatic corrections – coefficients in only two such radial functions can, in general, be evaluated from data of only spectral frequencies of pure rotational and vibration–rotational transitions for samples without applied electric or magnetic field. In such circumstances these quantum-chemical calculations serve as a substitute for information from experiments involving applied fields, but they are able to generate satisfactorily accurate data for internuclear distance over a range much greater than has ever been derived from such experiments.

ACKNOWLEDGEMENTS

We are grateful to Professor Jens Oddershede for his inspiration and encouragement of this project. SPAS acknowledges support from the Carlsberg Foundation, and SPAS and HJAaJ acknowledge support from the Danish Natural Science Research Council, grant no. 21-02-0467, and the Danish Center for Scientific Computing.

REFERENCES

[1] J. F. Ogilvie and J. Oddershede, *Adv. Quantum Chem.*, 2005, **48**, 253.
[2] S. Saupe, B. Meyer, M. H. Wappelhorst, W. Urban and A. G. Maki, *J. Mol. Spectrosc.*, 1996, **179**, 13.
[3] J. Oddershede, P. Jørgensen and N. H. F. Beebe, *J. Chem. Phys.*, 1975, **63**, 2996.
[4] J. Oddershede and E. N. Svendsen, *Chem. Phys.*, 1982, **64**, 359.
[5] S. P. A. Sauer, G. H. F. Diercksen and J. Oddershede, *Int. J. Quantum Chem.*, 1991, **39**, 667.
[6] M. J. Packer, S. P. A. Sauer and J. Oddershede, *J. Chem. Phys.*, 1994, **100**, 8969.
[7] E. K. Dalskov and S. P. A. Sauer, *J. Phys. Chem. A.*, 1998, **102**, 5269.
[8] J. Oddershede and J. R. Sabin, *Chem. Phys.*, 1988, **122**, 291.
[9] S. P. A. Sauer, V. Špirko and J. Oddershede, *Chem. Phys.*, 1991, **153**, 189.
[10] S. P. A. Sauer, J. Oddershede and J. Geertsen, *Mol. Phys.*, 1992, **76**, 445.

[11] S. P. A. Sauer, V. Špirko, I. Paidarová and J. Oddershede, *Chem. Phys.*, 1994, **184**, 1.
[12] S. P. A. Sauer, *Chem. Phys. Lett.*, 1996, **260**, 271.
[13] T. Enevoldsen, T. Rasmussen and S. P. A. Sauer, *J. Chem. Phys.*, 2001, **114**, 84.
[14] S. P. A. Sauer, *Adv. Quantum Chem.*, 2005, **48**, 469.
[15] J. F. Ogilvie, S.-L. Cheah, Y.-P. Lee and S. P. A. Sauer, *Theor. Chem. Acc.*, 2002, **108**, 85.
[16] S. P. A. Sauer and J. F. Ogilvie, *J. Phys. Chem.*, 1994, **98**, 8617.
[17] J. F. Ogilvie, J. Oddershede and S. P. A. Sauer, *Chem. Phys. Lett.*, 1994, **228**, 183.
[18] K. L. Bak, S. P. A. Sauer, J. Oddershede and J. F. Ogilvie, *Phys. Chem. Chem. Phys.*, DOI.10.1039/B500992H.
[19] R. M. Herman and J. F. Ogilvie, *Adv. Chem. Phys.*, 1998, **103**, 187.
[20] N. C. Handy and A. M. Lee, *Chem. Phys. Lett.*, 1996, **252**, 425.
[21] W. Kutzelnigg, *Mol. Phys.*, 1997, **90**, 909.
[22] H. Ågren, A. Flores-Riveros and H. J. Aa. Jensen, *Phys. Rev. A*, 1986, **34**, 4606.
[23] T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, K. Ruud, H. Ågren, A. A. Auer, K. L. Bak, V. Bakken, O. Christiansen, S. Coriani, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, C. Hättig, A. Hald, K. Halkier, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T. B. Pedersen, T. A. Ruden, A. Sanchez, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. O. Sylvester-Hvid, P. R. Taylor and O. Vahtras. DALTON, an electronic structure program, Release 1.2. http://www.kjemi.uio.no/software/dalton/dalton.html, 2001.
[24] J. F. Ogilvie, H. Uehara and K. Horiai, *Canad. J. Anal. Sci. Spectrosc.*, 1999, **44**, 141.
[25] J. F. Ogilvie, *The Vibrational and Rotational Spectrometry of Diatomic Molecules*, Academic Press, London, 1998.
[26] J. F. Ogilvie, J. Oddershede and S. P. A. Sauer, *Adv. Chem. Phys.*, 2000, **111**, 475.
[27] J. Gauss, K. Ruud and T. Helgaker, *J. Chem. Phys.*, 1996, **105**, 2804.
[28] E. Tiemann and J. F. Ogilvie, *J. Mol. Spectrosc.*, 1994, **165**, 377.
[29] S. P. A. Sauer, *Chem. Phys. Lett.*, 1998, **297**, 475.
[30] J. K. G. Watson, *J. Mol. Spectrosc.*, 1980, **80**, 411.
[31] T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007.
[32] D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.*, 1993, **98**, 1358.
[33] T. Helgaker and P. Jørgensen, *J. Chem. Phys.*, 1991, **95**, 2595.
[34] T. Helgaker, P. Jørgensen and J. Olsen, *Molecular Electronic Structure Theory*, Wiley, Chichester, 2000.
[35] B. O. Roos, *Ab Initio* Methods in Quantum Chemistry – II, in *Advances in Chemical Physics* (ed. K. P. Lawley), Wiley, Chichester, 1987, pp. 399.
[36] W. Kołos and L. Wolniewicz, *J. Chem. Phys.*, 1964, **41**, 3663.
[37] J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry*, Academic Press, London, 1973.
[38] P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry*, Academic Press, New York, 1981.
[39] J. Olsen and P. Jørgensen, *J. Chem. Phys.*, 1985, **82**, 3235.
[40] J. Oddershede, P. Jørgensen and D. L. Yeager, *Comput. Phys. Rep.*, 1984, **2**, 33.
[41] K. L. Bak, P. Jørgensen, H. J. Aa. Jensen, J. Olsen and T. Helgaker, *J. Chem. Phys.*, 1992, **97**, 7573.