

On the relation between the non-adiabatic vibrational reduced mass and the electric dipole moment gradient of a diatomic molecule

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Abstract The relation between the non-adiabatic vibrational correction to the reduced mass, i.e. the vibrational g -factor, and the electric dipole moment gradient of a diatomic molecule is investigated. An explicit expression for the “irreducible” non-adiabatic contribution in terms of excited electronic states is derived. The importance of this expression for the analysis of vibration-rotational spectra of diatomic molecules is discussed and explicit expressions are presented for the first two fitting parameters in an expansion of the non-adiabatic vibrational term in an effective vibration-rotational Hamiltonian. Results of ab initio multiconfigurational self consistent field calculations of the non-adiabatic contribution to vibrational g -factor of hydrides and fluorides of Li, B, Al, Ga and monoxides of C, Si and Ge are presented and compared with the corresponding non-adiabatic contributions to the rotational g -factor.

Keywords Vibrational g -factor ·
Non-adiabatic vibrational correction ·
Electric dipole moment gradient

1 Introduction

The analysis of infrared spectra of diatomic molecules with internuclear distance R in an electronic state $|\Psi_0\rangle$ of symmetry $^1\Sigma^+$ is commonly based on an effective vibration-rotation Hamiltonian H_{eff} for nuclear motion [1–9]

$$\hat{H}_{\text{eff}} = -\frac{\hbar^2}{2\mu} \frac{\partial}{\partial R} \left[1 + \frac{m_e}{m_p} g_v(R) \right] \frac{\partial}{\partial R} + \frac{\hbar^2}{2\mu R^2} \left[1 + \frac{m_e}{m_p} g_r(R) \right] \times J(J+1) + E_0^{\text{BO}}(R) + V'(R) \quad (1)$$

in which $J(J+1)\hbar$ is the eigenvalue of $\hat{\mathbf{J}}^2$, the square of the total angular momentum operator about the molecular centre of mass, with rotational quantum number J . The atomic reduced mass is denoted $\mu = M_A M_B / (M_A + M_B)$ and $E_0^{\text{BO}}(R)$ is the potential energy for nuclear motion within the Born-Oppenheimer approximation. The terms $V'(R) = V^{\text{ad}}(R) + V^{\text{nad}}(R)$, $g_v(R)$ and $g_r(R)$ are corrections to the Born-Oppenheimer approximation and take into account that electrons fail to follow the nuclei perfectly [1–6, 9, 10]. Whereas V^{ad} consists of expectation values of various operators within the given electronic state $|\Psi_0\rangle$ [11–13] and is therefore called an adiabatic correction to the potential energy, the other three, nonadiabatic, terms include virtual excitation to other electronic states $|\Psi_0\rangle$. They represent therefore the effect of the breakdown of the Born-Oppenheimer approximation [1] and are thus called Born-Oppenheimer-breakdown (BOB) corrections. $\frac{m_e}{m_p} g_v(R)$ and $\frac{m_e}{m_p} g_r(R)$ are non-adiabatic contributions to the reduced masses of the vibrational and rotational motion of the nuclei, i.e. they are due to the inertia of the electrons with respect to the nuclear vibrational and rotational motion [2].

The expression for the non-adiabatic rotational reduced mass $\frac{m_e}{m_p} g_r(R)$ is at least similar to the one of the rotational g -factor [14–21] of molecular beam [22–25] or rotational Zeeman experiments [26–28], i.e. the dimensionless magnetogyric ratio between the rotational magnetic dipole moment and the angular momentum of molecular rotation, which was first pointed out by Herman and Asgharian [2]. Measured as well as calculated rotational g -factors can therefore be utilized in the analysis of vibrational-rotational

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spectra, where calculations have the advantage that radial functions can easily be generated [29–39].

The same authors noted also that no equivalent similarity exists between the non-adiabatic vibrational reduced mass $\frac{m_e}{m_p}g_v(R)$ and a low order magnetic effect. Nevertheless Herman and Ogilvie [9] coined the phrase vibrational g -factor for $g_v(R)$, which for a diatomic molecule AB as a function of the internuclear distance R is given as [1, 2, 5, 6, 9, 36]

$$g_v(R) = \frac{m_p}{\mu R^2} Z_A (R_{A,z} - R_{CM,z})^2 + \frac{m_p}{\mu R^2} Z_B (R_{B,z} - R_{CM,z})^2 + \frac{2m_p}{m_e \mu} \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{P}_R | \Psi_n \rangle \langle \Psi_n | \hat{P}_R | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} \quad (2)$$

where $\mathbf{R}_{A/B}$ are the position vectors of the nuclei with atomic numbers $Z_{A/B}$ and atomic masses $M_{A/B}$, placed along the z -axis pointing from atom A to B , \mathbf{R}_{CM} is the position vector of the atomic center of mass and $\{\mathbf{r}_i\}$ stands for the set of position vectors of all electrons in the molecule and $\hat{P}_R = -i\hbar \frac{\partial}{\partial R}$ is the linear momentum operator of the relative nuclear motion. $|\Psi_0\rangle$ and $E_0^{\text{BO}}(R)$ are the wavefunction and energy of the electronic state of interest, whereas $|\Psi_n\rangle$ and $E_n^{\text{BO}}(R)$ refer to other electronic states of the same total spin, all for the given internuclear distance R .

Quantum chemical calculations [36, 37, 39] are thus the only alternative source for the vibrational g -factor to fitting spectral data using the effective Hamiltonian in Eq. 1 [31, 32, 35, 40–64]. In order to fit spectra of several isotopomers, the radial functions $g_r(R)$ and $g_v(R)$ need to be partitioned into two isotopically invariant contributions [4, 6, 9, 42] associated with each nucleus and expanded in a power series of e.g. the Ogilvie-Tipping z -variable, $z = 2(R - R_e)/(R + R_e)$ [65, 66],

$$g_r(R) = m_p \left(\frac{1}{M_A} \sum_{j=0} t_j^A z^j + \frac{1}{M_B} \sum_{j=0} t_j^B z^j \right) \quad (3)$$

and

$$g_v(R) = m_p \left(\frac{1}{M_A} \sum_{j=0} s_j^A z^j + \frac{1}{M_B} \sum_{j=0} s_j^B z^j \right) \quad (4)$$

One should note that $t_0^{A/B}$ is often called $(\mu g_J)_{a/b}$ [4, 28] without giving explicit expressions for it, whereas Watson [6] has presented explicit expressions for $t_0^{A/B}$ and $s_0^{A/B}$, which he called $R_{a/b}^n$ and $Q_{a/b}^n$, respectively, in terms of excited electronic states.

For the case of neutral but polar diatomic molecules it was shown [9] that the rotational and vibrational g -factors have in addition to “irreducible” non-adiabatic contributions, g_r^{nad} and g_v^{nad} , also a contribution from the molecular

electric dipole moment \mathbf{d} or the gradient $\frac{\partial}{\partial R} \mathbf{d}$ of the molecular electric dipole moment¹

$$g_J(R) = g^{\text{nad}}(R) - \frac{m_p}{eR} d_z(R) \left(\frac{1}{M_A} - \frac{1}{M_B} \right) \quad (5)$$

$$g_v(R) = g_v^{\text{nad}}(R) - \frac{m_p}{e} \frac{\partial}{\partial R} d_z(R) \left(\frac{1}{M_A} - \frac{1}{M_B} \right) \quad (6)$$

The interpretation of the “irreducible” non-adiabatic contributions, g_r^{nad} and g_v^{nad} , however, was stated [9] to be unclear and no direct derivation had been presented.

In a previous Letter [67], in the following called paper I, the nature and derivation of the “irreducible” non-adiabatic rotational contribution was investigated. The purpose of this work is now to present explicit expressions for g_v^{nad} in terms of excited electronic states, to derive Eq. 6 also for charged molecules and to illustrate the importance of g_v^{nad} with ab initio results for hydrides and fluorides of Li, B, Al, Ga and monoxides of C, Si and Ge.

2 Theory

Watson [4, 6] showed that the desired partitioning of the vibrational g -factor into isotopically invariant contributions can be achieved with the following isotopically invariant operators

$$\hat{P}_{zA} = \hat{P}_R + \frac{(R_{B,z} - R_{CM,z})}{R} \sum_i \hat{p}_{i,z} \quad (7)$$

$$\hat{P}_{zB} = \hat{P}_R + \frac{(R_{A,z} - R_{CM,z})}{R} \sum_i \hat{p}_{i,z} \quad (8)$$

where $\hat{p}_{i,z} = -i\hbar \frac{\partial}{\partial r_{i,z}}$ is the canonical momentum operator of electron i and the molecule is placed along the z -axis.

Isotopically invariant contributions to the vibrational g -factor can thus be defined as [6]

$$g_v^A(R) = \frac{m_p}{\mu} Z_B + \frac{2m_p}{m_e \mu} \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{P}_{zB} | \Psi_n \rangle \langle \Psi_n | \hat{P}_{zB} | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} \quad (9)$$

$$g_v^B(R) = \frac{m_p}{\mu} Z_A + \frac{2m_p}{m_e \mu} \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{P}_{zA} | \Psi_n \rangle \langle \Psi_n | \hat{P}_{zA} | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} \quad (10)$$

Primarily these two contributions are just a way of separating the mass dependence of the vibrational g -factor. However, from the expressions for the vibrational g -factor of an isotopic variant of molecule AB [9] it can be deduced that $g_v^A(R)$ is actually the vibrational g -factor of an hypothetical isotopic variant where the atom B has zero mass

¹ The molecule is placed along the z -axis pointing from A to B.

and therefore only atom A vibrates and correspondingly for $g_v^B(R)$.

Similar to the derivation of the “irreducible” non-adiabatic contribution g_r^{nad} of the rotational g -factor in paper I [67], we can derive the desired expression for the “irreducible” non-adiabatic contribution g_v^{nad} by relating Eqs. 9 and 10 to Eq. 2 following the derivation of the relation between the g -factors of two isotopomers [9]. Starting from $g_v^A(R)$ we insert the expression for the isotopically invariant operator \hat{P}_{zB} , Eq. 8, expand the electronic matrix elements $\langle \Psi_0 | \hat{P}_{zB} | \Psi_n \rangle$ and replace $\frac{(R_{A,z} - R_{\text{CM},z})}{R}$ with $-\frac{M_B}{M_A + M_B} = -\frac{\mu}{M_A}$ valid if the z axis points from atom A to B

$$g_v^A(R) = \frac{m_p Z_B}{\mu} + \frac{2m_p}{m_e \mu} \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{P}_R | \Psi_n \rangle \langle \Psi_n | \hat{P}_R | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} - \frac{2m_p \mu}{m_e \mu M_A} \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{P}_R | \Psi_n \rangle \langle \Psi_n | \sum_i \hat{p}_{i,z} | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} - \frac{2m_p \mu}{m_e \mu M_A} \sum_{n \neq 0} \frac{\langle \Psi_0 | \sum_i \hat{p}_{i,z} | \Psi_n \rangle \langle \Psi_n | \hat{P}_R | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} + \frac{2m_p \mu^2}{m_e \mu M_A^2} \sum_{n \neq 0} \frac{\langle \Psi_0 | \sum_i \hat{p}_{i,z} | \Psi_n \rangle \langle \Psi_n | \sum_i \hat{p}_{i,z} | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} \quad (11)$$

The second term is the electronic contribution to the vibrational g -factor, whereas the last three terms can be rewritten on making use of a hypervirial relation

$$\left\langle \Psi_n \left| \sum_i \hat{p}_i \right| \Psi_0 \right\rangle = \frac{m_e}{i\hbar} [E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)] \left\langle \Psi_n \left| \sum_i \hat{r}_i \right| \Psi_0 \right\rangle \quad (12)$$

the orthogonality of the eigenstates [9], which implies that

$$\frac{\partial}{\partial R} \langle \Psi_0 | \Psi_n \rangle = \left\langle \frac{\partial}{\partial R} \Psi_0 \right| \Psi_n \rangle + \left\langle \Psi_0 \left| \frac{\partial}{\partial R} \Psi_n \right\rangle = 0 \quad (13)$$

and thus

$$\left\langle \Psi_0 \left| \frac{\partial}{\partial R} \right| \Psi_n \right\rangle = - \left\langle \frac{\partial}{\partial R} \Psi_0 \right| \Psi_n \rangle \quad (14)$$

and a resolution of the identity

$$1 = \sum_n |\Psi_n\rangle \langle \Psi_n| \quad (15)$$

such that

$$g_v^A(R) = g_v(R) + \frac{m_p Z_B}{\mu} - \frac{m_p}{\mu R^2} \left[Z_A (R_{A,z} - R_{\text{CM},z})^2 + Z_B (R_{B,z} - R_{\text{CM},z})^2 \right] - \frac{2m_p}{M_A} \left\langle \left\langle \frac{\partial}{\partial R} \Psi_0 \right| \sum_i \hat{r}_{i,z} \right| \Psi_0 \right\rangle \left\langle \Psi_0 \left| \sum_i \hat{r}_{i,z} \right| \frac{\partial}{\partial R} \Psi_0 \right\rangle - \frac{m_p \mu}{i\hbar M_A^2} \left\langle \Psi_0 \left| \sum_i [\hat{r}_{i,z}, \hat{p}_{i,z}] \right| \Psi_0 \right\rangle \quad (16)$$

Evaluating the commutator

$$\left\langle \Psi_0 \left| \sum_i [\hat{r}_{i,x}, \hat{p}_{i,\beta}] \right| \Psi_0 \right\rangle = i\hbar N \delta_{x\beta} \quad (17)$$

where N is the total number of electrons, and inserting the expressions for $(R_{A,z} - R_{\text{CM},z})$ and $(R_{B,z} - R_{\text{CM},z})$ gives

$$g_v^A(R) = g_v(R) + \frac{m_p}{\mu} \left(Z_B - Z_A \frac{\mu^2}{M_A^2} - Z_B \frac{\mu^2}{M_B^2} \right) - m_p \frac{\mu}{M_A^2} N - \frac{2m_p}{M_A} \frac{\partial}{\partial R} \left\langle \Psi_0 \left| \sum_i \hat{r}_{i,z} \right| \Psi_0 \right\rangle \quad (18)$$

As the z -component of a radial function for the electric dipole moment, calculated with the origin of the coordinate system at the centre of mass, is given as

$$d_z(\mathbf{R}_{\text{CM}}, R) = e [Z_A (R_{A,z} - R_{\text{CM},z}) + Z_B (R_{B,z} - R_{\text{CM},z})] - e \left\langle \Psi_0 \left| \sum_i (\hat{r}_{i,z} - R_{\text{CM},z}) \right| \Psi_0 \right\rangle \quad (19)$$

one rewrites this expression as

$$g_v^A(R) = g_v(R) + \frac{2m_p}{eM_A} \frac{\partial}{\partial R} d_z(\mathbf{R}_{\text{CM}}, R) + \frac{m_p}{\mu} \left(Z_B - Z_A \frac{\mu^2}{M_A^2} - Z_B \frac{\mu^2}{M_B^2} \right) - m_p \frac{\mu}{M_A^2} N + 2m_p Z_A \frac{\mu}{M_A^2} - 2m_p Z_B \frac{\mu}{M_A M_B} \quad (20)$$

Finally using that the total charge of the molecule is $eQ = e(Z_A + Z_B - N)$, one obtains

$$g_v^A(R) = g_v(R) + \frac{2m_p}{eM_A} \frac{\partial}{\partial R} d_z(\mathbf{R}_{\text{CM}}, R) + m_p Q \frac{\mu}{M_A^2} \quad (21)$$

and correspondingly for nucleus B

$$g_v^B(R) = g_v(R) - \frac{2m_p}{eM_B} \frac{\partial}{\partial R} d_z(\mathbf{R}_{\text{CM}}, R) + m_p Q \frac{\mu}{M_B^2} \quad (22)$$

Adding these two equations yields the desired relation between the vibrational g -factor and electric dipole moment gradient

$$g_v(R) = \frac{1}{2} [g_v^A(R) + g_v^B(R)] - \frac{m_p}{e} \frac{\partial}{\partial R} d_z(\mathbf{R}_{\text{CM}}, R) \left(\frac{1}{M_A} - \frac{1}{M_B} \right) - \frac{m_p}{2} Q \mu \left(\frac{1}{M_A^2} + \frac{1}{M_B^2} \right) \quad (23)$$

which for a neutral molecule ($Q = 0$) reduces to Eq. 6, thereby identifying the “irreducible” non-adiabatic contribution g_v^{nad} as

$$g_v^{\text{nad}}(R) = \frac{1}{2} [g_v^A(R) + g_v^B(R)] = \frac{m_p}{\mu} \frac{Z_A + Z_B}{2} + \frac{m_p}{\mu m_e} \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{P}_{zA} | \Psi_n \rangle \langle \Psi_n | \hat{P}_{zA} | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} + \frac{m_p}{\mu m_e} \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{P}_{zB} | \Psi_n \rangle \langle \Psi_n | \hat{P}_{zB} | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} \quad (24)$$

Other useful relations for analysis of vibration-rotational spectra can be obtained from Eqs. 9 and 10 for neutral molecules ($Q = 0$). Subtraction of Eqs. 9 and 10 (or (21) and (22)) gives the z -component of the radial function for the electric dipole moment gradient

$$\frac{\partial}{\partial R} d_z(\mathbf{R}_{\text{CM}}, R) = \frac{e\mu}{2m_p} [g_v^A(R) - g_v^B(R)] \quad (25)$$

whereas addition of Eqs. 9 and 10 (or (21) and (22)) weighted by the quotient of the reduced mass and the mass of the other nucleus yields the partitioning of the vibrational g -factor [9],

$$g_v(R) = \left[\frac{\mu g_v^A(R)}{M_B} + \frac{\mu g_v^B(R)}{M_A} \right] \quad (26)$$

Comparison of Eq. 26 and Eq. 4 shows that

$$g_v^A(R) = \frac{m_p}{\mu} \sum_{j=0} s_j^B z^j \quad (27)$$

$$g_v^B(R) = \frac{m_p}{\mu} \sum_{j=0} s_j^A z^j \quad (28)$$

The fitting parameters s_0^A and s_0^B of a neutral molecule ($Q = 0$) can thus be calculated directly from Eqs. 9 and 10

$$s_0^A = \frac{\mu}{m_p} g_v^B(R_e) = Z_A + \frac{2}{m_e} \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{P}_{zA} | \Psi_n \rangle \langle \Psi_n | \hat{P}_{zA} | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} \quad (29)$$

$$s_0^B = \frac{\mu}{m_p} g_v^A(R_e) = Z_B + \frac{2}{m_e} \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{P}_{zB} | \Psi_n \rangle \langle \Psi_n | \hat{P}_{zB} | \Psi_0 \rangle}{E_0^{\text{BO}}(R) - E_n^{\text{BO}}(R)} \quad (30)$$

which shows that s_0^A and s_0^B are independent of mass and thus of the isotopomers. Higher fitting parameters $s_j^{B/A}$ with $j > 0$, which describe the dependence of the non-adiabatic vibrational term on the internuclear distance, can be obtained from numerical derivatives of $g_v^{A/B}(R)$ in Eqs. 9 and 10, with respect to the internuclear distance R .

3 Applications

In order to investigate the importance of and trends in the “irreducible” non-adiabatic contribution to the vibrational g -factor, g_v^{nad} , we have carried out ab initio calculations of g_v^A , g_v^B , g_v^{nad} and g_v for the hydrides and fluorides of Li, B, Al, Ga and the monoxides of C, Si and Ge, i.e. the same set of molecules as in paper I [67]. Calculations were made using self-consistent field (SCF) and multiconfigurational self-consistent field (MCSCF) linear response functions [68]. In the limit of a complete one-electron basis set Eq. 26 is fulfilled exactly for the SCF and MCSCF linear response functions, whereas this would not be the case for response functions based on perturbation theory through finite order, such as the second order polarization propagator approximation (SOPPA) [69–71] or the second order polarization propagator approximation with coupled cluster singles and doubles amplitudes—SOPPA(CCSD) [71, 72], or even Coupled Cluster response functions [73]. The disagreement between the SCF or MCSCF results for g_v calculated from Eq. 2 and Eq. 26 is therefore due to the incompleteness of the one-electron basis set. Large basis sets, especially optimized for calculation of rotational g -factors or magnetizabilities [32, 34, 67, 74], have been used for all molecules. Details of basis sets and internuclear distances for these calculations can be found in Table 1 of paper I [67]. All calculations were carried out with a development version of the DALTON program package [75, 36]. The MCSCF wavefunctions were of the complete active space (CAS) type [76] with the valence s - and p -orbitals included in the active space. Details of the active spaces are also shown in Table 1 of paper I [67]. The MCSCF calculations were started from the MP2 natural orbitals [77, 78] calculated with the inactive orbitals of the MCSCF calculation kept frozen.

The SCF and MCSCF results for g_v in Table 1 calculated from the partitioned form, Eq. 26 and directly, Eq. 2, agree very well with each other. The differences are very small but increase slightly from B to Ga and from C to Ge. Only for AlH and AlF we observe slightly large deviations as was already found for the rotational g -factors in paper I [67] indicating that the aluminum basis set is of slightly lower quality than the other basis sets. Furthermore the deviations are virtually identical at the SCF and MCSCF

Table 1 Comparison of calculated values of the “irreducible” non-adiabatic contribution g_v^{nad} , its contributions g_v^A , g_v^B , the total vibrational g -factor g_v and the “irreducible” non-adiabatic contribution g_r^{nad} as well as total rotational g -factor g_r for selected diatomic molecules

AB	Method	g_v^A	g_v^B	g_v^{nad}	g_v		g_r^{nad}	g_r^a
		Eq. 9	Eq. 10	Eq. 24	Eq. 26	Eq. 2	[67]	[67]
$^7\text{Li}^1\text{H}$	SCF	-0.3090	0.8064	0.2487	-0.1689	-0.1697	-0.0224	-0.6962
	MCSCF	-0.2536	0.7149	0.2307	-0.1320	-0.1328	-0.0046	-0.6613
$^7\text{Li}^{19}\text{F}$	SCF	-0.1800	0.1889	0.0044	0.0894	0.0890	-0.0034	0.0729
	MCSCF	-0.1724	0.1834	0.0055	0.0875	0.0871	-0.0055	0.0691
$^{11}\text{B}^1\text{H}$	SCF	-0.5323	0.8503	0.1590	-0.4164	-0.4168	-8.5414	-8.2756
	MCSCF	-0.4054	0.8398	0.2172	-0.3010	-0.3015	-6.1391	-5.9365
$^{27}\text{Al}^1\text{H}$	SCF	-0.5358	1.4171	0.4406	-0.4655	-0.4689	-3.4294	-3.4654
	MCSCF	-0.3809	1.2877	0.4534	-0.3208	-0.3243	-3.0453	-3.0977
$^{69}\text{Ga}^1\text{H}$	SCF	-0.5825	1.6213	0.5194	-0.5507	-0.5531	-3.1811	-3.2452
	MCSCF	-0.4463	1.4842	0.5190	-0.4184	-0.4208	-2.8809	-2.9541
$^{11}\text{B}^{19}\text{F}$	SCF	-0.1902	0.1487	-0.0207	0.0244	0.0241	-0.2278	-0.2339
	MCSCF	-0.1701	0.1409	-0.0146	0.0268	0.0265	-0.2224	-0.2258
$^{27}\text{Al}^{19}\text{F}$	SCF	-0.0950	0.1405	0.0228	0.0023	0.0002	-0.0783	-0.0839
	MCSCF	-0.0851	0.1340	0.0244	0.0054	0.0033	-0.0772	-0.0823
$^{69}\text{Ga}^{19}\text{F}$	SCF	-0.0795	0.1344	0.0275	-0.0332	-0.0351	-0.0485	-0.0620
	MCSCF	-0.0722	0.1290	0.0284	-0.0287	-0.0305	-0.0484	-0.0605
$^{12}\text{C}^{16}\text{O}$	SCF	-0.1533	0.1489	-0.0022	0.0193	0.0191	-0.2805	-0.2800
	MCSCF	-0.0698	0.1145	0.0223	0.0355	0.0352	-0.2559	-0.2577
$^{28}\text{Si}^{16}\text{O}$	SCF	-0.0896	0.1364	0.0234	-0.0074	-0.0079	-0.1374	-0.1522
	MCSCF	-0.0452	0.0882	0.0215	0.0033	0.0027	-0.1298	-0.1413
$^{74}\text{Ge}^{16}\text{O}$	SCF	-0.0707	0.1394	0.0343	-0.0333	-0.0350	-0.1155	-0.1454
	MCSCF	-0.0301	0.1002	0.0351	-0.0069	-0.0085	-0.1046	-0.1272

^a Experimental or experimentally derived values: $^7\text{Li}^1\text{H}$ $g_r = -(0.654 \pm 0.007)$ (molecular beam and magnetic resonance) [79], -0.65842 ± 0.00017 (molecular beam and electric resonance) [80]; $^7\text{Li}^{19}\text{F}$ $g_r = (0.0642 \pm 0.0004)$ (molecular beam and magnetic resonance) [81], (0.07367 ± 0.00050) (molecular beam and magnetic resonance) [82]; $^{27}\text{Al}^1\text{H}$ $g_r = -2.25 \pm 0.25$ (fitting of IR spectra) [40], -2.7 ± 0.5 (fitting of IR spectra) [31]; $^{27}\text{Al}^{19}\text{F}$ $g_r = -0.08051 \pm 0.0008$ (microwave rotational Zeeman effect) [83]; $^{69}\text{Ga}^{19}\text{F}$ $g_r = -0.06012 \pm 0.00012$ (microwave rotational Zeeman effect) [84]; $^{12}\text{C}^{16}\text{O}$ $g_r = (0.26910 \pm 0.0005)$ (microwave rotational Zeeman effect) [10], (0.267 ± 0.003) (microwaverotational Zeeman effect) [85], -0.26890 ± 0.00010 (molecular beam and magnetic resonance) [86], -0.26895 ± 0.00005 (molecular beam and electric resonance) [87], -0.262 ± 0.026 (magnetic vibrational circular dichroism) [88]; $^{28}\text{Si}^{16}\text{O}$ $g_r = -0.15359 \pm 0.00012$ (molecular beam and electric resonance) [89]; $^{74}\text{Ge}^{16}\text{O}$ $g_r = -0.141369 \pm 0.000151$ (microwave rotational Zeeman effect) [90], -0.14089 ± 0.00010 (molecular beam and electric resonance) [89]

level which supports the claim that the basis sets are close to completeness for the properties studied here.

The active spaces in the valence CAS MCSCF calculations presented in Table 1 are not large enough to allow a final statement about the effects of electron correlation on the vibrational g -factor. This is beyond the scope of this article. Nevertheless one should note that electron correlation increases the “irreducible” non-adiabatic contribution, g_v^{nad} , for the majority of molecules studied here apart from LiH, GaH and SiO, but becomes less important in absolute and percentage terms with increasing atomic number within one group of the periodic table. The total vibrational g -factor is also increased by inclusion of electron correlation with the sole exception of LiF, similar to the total rotational g -factor of the same molecules. However, no uniform trend can be observed with respect to

the importance of electron correlation for the total vibrational g -factor.

Comparing now g_v^{nad} and g_v for the various molecules at the MCSCF level reveals interesting trends. The vibrational g -factor as well as its “irreducible” non-adiabatic contribution g_v^{nad} is for all the atoms X studied here larger in the hydrides XH than in the fluorides XF as was previously also observed for the rotational g -factor [67]. However, g_v^{nad} increases within a group of the periodic table, which is not always the case for the total vibrational g -factor, whereas g_r^{nad} and g_r decrease within a group.

With the exception of LiH, the absolute value of the “irreducible” non-adiabatic contribution to the vibrational g -factor, g_v^{nad} , is smaller than the corresponding contribution to the rotational g -factor, g_r^{nad} . In the case of the group 13 hydrides, BH, AlH and GaH, this is not a surprise

because they exhibit unusually large non-adiabatic rotational contributions and thus rotational g -factors which is related to their known temperature independent paramagnetism or near paramagnetism (see e.g. [30, 31, 33, 34, 74, 91–98] and references therein). BH is actually paramagnetic and the perpendicular component of the magnetizability of AlH also shows paramagnetism.

Concerning the sign of the “irreducible” non-adiabatic contribution to the vibrational g -factor, g_v^{nad} , we observe that it is positive for the molecules studied here with the single exception of BF, whereas g_r^{nad} is negative for all our molecules. Furthermore and also contrary to g_r^{nad} , we observe that g_v^{nad} has for the majority of the studied systems the opposite sign of the total vibrational g -factor, whereas it has the same sign for LiF, AlF, CO and SiO.

In case of the rotational g -factor we could see that the non-adiabatic contribution was the dominant contribution for all of the studied molecules, but LiH and LiF, where the electric dipole moment contribution was the major contribution. In the case of the vibrational g -factor the situation is more complicated. For all our hydrides as well as BF and GaF, the contribution from the electric dipole moment gradient has the opposite sign of g_v^{nad} and is approximately twice as large. In the case of AlF, CO, SiO and GeO the dipole moment gradient and the “irreducible” non-adiabatic contributions have also opposite signs, but the latter is now larger. Finally for LiF both contributions are positive, but the electric dipole moment gradient contribution is at least 15 times larger.

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