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Evaluation of adiabatic and nonadiabatic effects from vibration–rotational spectra of LiH X $^{1}\Sigma^{+}$

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Abstract

We combined radial functions for the rotational g-factor and electric dipole moment, from molecular electronic computations but tested with experimental data, with spectral data of 557 pure rotational and vibration-rotational transitions of LiH in four isotopic variants; on this basis we evaluated separate radial functions related to particular terms in the effective Hamiltonian for adiabatic, nonadiabatic rotational and nonadiabatic vibrational effects of the separate nuclei, in addition to the internuclear potential energy that predominantly determines the wavenumbers of these transitions. The contributions of the former (extramechanical) effects to term coefficients defining the energies of vibration-rotational states have comparable magnitudes.

1. Introduction

Van Vleck delineated adiabatic and nonadiabatic effects [1] in intramolecular dynamics of a diatomic molecule of electronic symmetry Σ^+ nearly sixty years ago. In a sense these nominal effects lack physical significance because they are mathematical artifacts: they arise from the endeavour to treat separately electronic and nuclear motions, according to the procedure originally devised by Born and Oppenheimer [2], and developed later by many other scientists [3], whereby one imposes the classical idea of molecular structure on a quantum-mechanical system [4]. According to a qualitative and quasi-physical explanation, the adiabatic effects are attributed to the dependence of the internuclear potential energy not only on internuclear distance but also on relative nuclear momenta, hence on the masses of the individual nuclei. Nonadiabatic rotational effects are associated with inertia of the electrons with respect to rotation of the nuclei about the centre of mass, and analogously the nonadiabatic vibrational effects to inertia of the electrons with respect to nuclear oscillations along the internuclear axis. Adiabatic effects involve formally only the electronic state of interest, commonly the ground state ${}^{1}\Sigma^{+}$ for vibration-rotational spectra, whereas nonadiabatic effects can be calculated theoretically in terms of matrix elements connecting that electronic state to electronically excited states, correspondingly of species ${}^{1}\Pi$ for rotational effects and ${}^{1}\Sigma^{+}$ for vibrational effects [1].

2. The effective Hamiltonian

As the basis of a quantitative treatment we adopt an effective Hamiltonian for nuclear motion of the form [5]

$$\mathcal{H}_{\text{eff}} = \hat{P}[1 + \beta(R)]\hat{P}/2\mu + V(R) + V'(R) + hcB_{\text{e}}[1 + \alpha(R)]J(J + 1)R_{\text{e}}^2/R^2.$$
(1)

Here R is the internuclear separation and R_e its value at the minimum of potential energy, μ is the reduced mass, $B_e = h/(8\pi^2 c \mu R_e^2)$ is the equilibrium rotational parameter, and \hat{P} is the operator for linear momentum of the nuclei; $\beta(R)$, V'(R) and $\alpha(R)$ represent nonadiabatic vibrational, adiabatic, and nonadiabatic rotational effects respectively [5]. To apply this Hamiltonian we transform to the reduced displacement variable

$$z \equiv 2(R - R_e)/(R + R_e) \tag{2}$$

that possesses the property of remaining finite throughout the range of molecular existence: as $0 \le R < \infty$, $-2 \le z < 2$ [6,7]. With units of wavenumber henceforth assumed for appropriate quantities and with SI units for all quantities as recommended by IUPAP [8], the potential energy V(R) formally independent of nuclear mass we represent in the form [6]

$$V(z) = c_0 z^2 \left(1 + \sum_{j=1}^{n} c_j z^j \right).$$
(3)

For an assumed diatomic molecule AB having nuclei with protons of unequal number, the further functions dependent on individual nuclear masses M_a and M_b we represent by means of separate expansions for the nucleus of each type A and B; we have for the nonadiabatic vibrational effects [9],

$$\beta(R) = \beta^{a}(R) + \beta^{b}(R)$$
$$= m_{e} \left(\sum_{j=0} s_{j}^{a} z^{j} / M_{a} + \sum_{j=0} s_{j}^{b} z^{j} / M_{b} \right)$$
(4)

for the nonadiabatic rotational effects,

$$\alpha(R) = \alpha^{a}(R) + \alpha^{b}(R)$$
$$= m_{e} \left(\sum_{j=0} t_{j}^{a} z^{j} / M_{a} + \sum_{j=0} t_{j}^{b} z^{j} / M_{b} \right)$$
(5)

and for the contribution to the internuclear potential energy dependent on nuclear mass, i.e. the adiabatic effects,

$$V'(R) = V^{a}(R) + V^{b}(R)$$

= $m_{e} \left(\sum_{j=1}^{a} u_{j}^{a} z^{j} / M_{a} + \sum_{j=1}^{a} u_{j}^{b} z^{j} / M_{b} \right).$ (6)

As nuclear masses are known generally less accu-

rately than atomic masses and as the small differences between these masses have immaterial effects on the ultimate parameters and their interpretation, we henceforth employ atomic masses [10]. We express the discrete molecular energies within a particular electronic state, or vibration-rotational terms in the form [9]

$$E_{\omega J} = \sum_{k=0}^{N} \sum_{l=0}^{N} \left(Y_{kl} + Z_{kl}^{\text{r,a}} + Z_{kl}^{\text{r,b}} + Z_{kl}^{\text{v,a}} + Z_{kl}^{\text{v,b}} \right)$$
$$\times \left(v + \frac{1}{2} \right)^{k} (J^{2} + J)^{l}.$$
(7)

Here the term coefficients Y_{kl} depend, in a nonlinear manner, on only the equilibrium force coefficient k_{e} (through $U_{1,0}$, defined below), the equilibrium internuclear separation $R_{\rm e}$ (through $U_{0,1}, c_0 \equiv U_{1,0}^2/4U_{0,1}$), the reduced mass μ and the coefficients c_i in the radial function, Eq. (3), for potential energy. To take into account vibration-rotational ramifications of adiabatic and nonadiabatic effects, the term coefficients Z_{kl}^{v} of each nucleus a or b depend on the preceding parameters plus coefficients s_i^a , u_i^a and M_a or $s_i^{\rm b}$, $u_i^{\rm b}$ and $M_{\rm b}$ respectively, whereas for the additional rotational consequences of these effects the coefficients Z_{kl}^{r} of nucleus a or b depend on parameters in the first group plus s_i^a , t_i^a and M_a or s_i^b , t_i^b and $M_{\rm b}$. In Eq. (7) the explicit dependences of $E_{\nu J}$, Y_{kl} and various Z_{kl} on the isotopic variant are suppressed. To treat adiabatic and nonadiabatic effects, which imply the coupling of electronic and nuclear motions, by means of radial functions of R, which imply the separate treatment of these motions, may appear incongruous; for the electronic ground state and in particular for its vibration-rotational states far from the dissociation limit, the formal interactions with energetically distant, electronically excited states may be sufficiently weak that they can be considered to represent small and homogeneous perturbations [5].

Even though these adiabatic and nonadiabatic effects are mathematical artifacts, experimental information is associated specifically with the nonadiabatic rotational effects. The rotation of an otherwise non-magnetic diatomic molecule induces a small magnetic dipole moment [11]. The factor g_J is formally an expectation value $\langle vJ|\alpha(R)|vJ\rangle$ or $\langle vJ|g_J(R)|vJ\rangle$ of a particular state denoted by vibrational quantum number v and rotational quantum number J. For an electrically neutral diatomic molecule of polarity ${}^{+}AB^{-}$, there arise two contributions to the *g*-factor, g_{J}^{na} attributed to interaction between electronic and nuclear motions and the other from the rotating electric dipole moment μ_{e} [12],

$$g_J = g_J^{na} + m_p (M_a^{-1} - M_b^{-1}) \mu_e / eR_e , \qquad (8)$$

in which m_p is the mass of the proton and e its charge. The equations, adapted from Ref. [13], for partition of the g-factor to contributions of the separate atomic centres thus become

$$\alpha^{a}(R) = \mu[g_{J}(R)/m_{p} + 2\mu_{e}(R)/(eRM_{b})], \quad (9)$$

$$\alpha^{b}(R) = \mu[g_{J}(R)/m_{p} - 2\mu_{e}(R)/(eRM_{a})]. \quad (10)$$

As previously discussed [9], there are radial functions of three kinds beyond mechanical effects embodied in the potential energy V(z), namely functions for the adiabatic, nonadiabatic rotational and nonadiabatic vibrational effects of atomic centres of each type; in practice information of at most two kinds can be deduced from spectra recorded for samples without externally applied fields, namely the dependence on individual atomic (or nuclear) masses and the extra rotational effects. Measurement of the rotational g-factor in varied vibration-rotational states by means of the Zeeman effect provides further information that enables in principle separate evaluation of adiabatic and nonadiabatic effects [9]. For few molecules has the vibrational dependence of g_1 been measured, and for even fewer its rotational dependence. No experimental method to yield data that pertain specifically to either adiabatic or nonadiabatic vibrational effects in the effective Hamiltonian is known.

3. Electronic calculations

In the absence of experimentally based information on the relative magnitudes of these extra-mechanical effects that cause departures from mass scaling in spectra of diatomic molecules [1], we sought to employ LiH as a test molecule for this purpose. Because of the relatively light masses of the nuclei and the availability of isotopic variants of both Li and H, this compound is expected to exhibit these extra-mechanical effects relatively readily, and previous spectral analyses already indicated their presence. Relatively consistent and precise spectra are reported, for pure rotational transitions in the millimetre-wave (10 lines with uncertainties 0.000167 m⁻¹ [14]) and farinfrared (151 lines at 0.06 m^{-1} [15] and 16 lines with variable uncertainties within the range/ m^{-1} 0.000167-0.0010 [16,17]) regions, and for vibration-rotational transitions in the mid-infrared region (377 lines at 0.08 m^{-1} [15] and an additional unduplicated three lines at 0.10 m⁻¹ [18]), of four isotopic variants ⁷Li¹H, ⁶Li¹H, ⁷Li²H and ⁶Li²H. The electric dipole moments of ⁷Li¹H. ⁶Li¹H and ⁶Li²H were accurately measured in the ground vibrational state [19]. The rotational g-factors of ⁷Li¹H and ⁷Li²H were accurately measured in the state v=0, J=1[20], and a rough estimate of the rotational dependence of g, for Li¹H in v=0 was made [21]; the latter information is inadequate to evaluate the nonadiabatic rotational effects. Because of its few electrons and light nuclei, LiH possesses the advantage that calculation of electronic structure with relatively great accuracy is practicable.

We chose to calculate the rotational g-factor and the electric dipole moment of LiH as a function of internuclear distance using a developed and tested computational method [22]. The vibration-rotationally averaged results were thus tested (vide infra) against the experimental data [19-21]. Combining these results with the spectral data enabled us to achieve our objective to distinguish these adiabatic and nonadiabatic effects.

The method [23] of polarization propagation enables direct calculation of second-order properties that depend on summation over the set of excited states. In this context 'direct' signifies that we calculate the property itself without actual evaluation of individual excitation energies and transition moments that enter the sum over states. Apart from trivial factors, the electronic part of the rotational g-factor is the same as the paramagnetic part of the magnetizability, thus a second-order property. The nuclear contribution to g_{J} is a simple function of the nuclear geometry; explicit expressions appear elsewhere [22]. As already demonstrated [22,24-26], methods of polarization propagation are appropriate to calculate this molecular property. We calculated g_J at the following levels of approximation of the polarization propagator - a random phase (RPA, a firstorder approximation for the polarization propagator), a second-order approximation (SOPPA), and two coupled-cluster approximations [27] based on reference states for either doubles (CCDPPA) or singles and doubles (CCSDPPA). For comparison with the experimental value -0.65842 ± 0.00017 of g, for ⁷Li¹H in the state with v=0 and J=1, the computed values were (RPA) -0.6898, (SOPPA) -0.6962, (CCDPPA) = 0.6717 and (CCSDPPA) = 0.6351. As these approximations produced only small variations and as CCSDPPA represents the theory at the highest level, all subsequent results refer to calculations at this approximation made with the Odense version of the program RPAC 9.0 [28], according to basis sets of Li and H [29] with minor modifications: f functions on Li were removed, d functions on Li and H were totally uncontracted, and p functions on Li with exponents 0.802261 and 0.362648 were also uncontracted. The resulting basis set, described as a set (13s8p6d) of Gaussian-type functions contracted to [8s6p6d] for Li and (12s7p5d] contracted to [8s5p5d] for H, consists of 104 functions. The sum rule of Thomas, Reiche and Kuhn states that the sum of all oscillator strengths equals the number of electrons; with this basis set at the RPA level the sums are 3.9909. 3.9912 and 3.9926 in the dipole-length. the mixed and the dipole-velocity approximations respectively. These results demonstrate that the basis set is complete and well balanced. Comparison of our SCF total energy $-3.4822704 \times 10^{-17}$ J and electric dipole moment 2.00231×10^{-29} C m with the numerical Hartree-Fock results [30] -3.4822721× 10^{-17} J and 2.00243×10⁻²⁹ C m respectively at the same internuclear distance 1.59530×10^{-10} m allows the same conclusion.

We made calculations at all four levels of approximation for each of six isotopic variants, namely all binary combinations of ^{6,7}Li and ^{1,2,3}H; in each case we calculated g_J at twelve internuclear distances in the range 1.17196 $\leq R/10^{-10}$ m ≤ 2.1774 . Of these results we fitted [31] values of g_J of species ⁷Li¹H from the approach CCSDPPA to a polynomial in z to yield the result

$$g_{J} = (-0.6430283 \pm 0.0000019) + (1.344196 \pm 0.000026)z + (-1.983927 \pm 0.00031)z^{2} + (2.15743 \pm 0.00105)z^{3} + (-1.775174 \pm 0.0093)z^{4} + (2.053018 \pm 0.0087)z^{5} + (-1.329574 \pm 0.067)z^{6}, \qquad (11)$$

that reproduces the input data quantitatively within the specified range; the standard deviation of the fit is 3.5×10^{-6} . Calculated at the CCD level with the same basis set and at the same internuclear distances as for g_J , the function for the electric dipole moment is

$$\mu_{e}(R)/10^{-29} \text{ Cm} = (1.9534006 \pm 0.0000013) + (1.107589 \pm 0.000018)z + (0.930986 \pm 0.00021)z^{2} + (0.04591 \pm 0.00073)z^{3} + (-0.36581 \pm 0.0064)z^{4} + (-0.7603 \pm 0.0060)z^{5} + (-0.6268 \pm 0.046)z^{6}.$$
(12)

According to the polarity +LiH- [21] and Eqs. (9) and (10), we calculated $\alpha^{Li}(R)$ and $\alpha^{H}(R)$ at each internuclear distance and fitted each set of values to polynomials in z to yield values of coefficients t_i^{Li} , $0 \le j \le 6$, and t_i^{H} , $0 \le j \le 3$, listed in Table 1; the associated standard errors reflect error propagated during the fit of calculated data, but we constrained these values of $t_i^{\text{Li,H}}$ during the fit of spectral data. We derived the electric dipole moment from calculated results because the measured data [19] are insufficient to establish the radial dependence required in Eqs. (9) and (10). Partitioning the rotational g-factor between atomic centres according to the latter equations is valid because the function $\alpha(R)$ plays the same role in Eq. (1) as the conventional definition of the rotational g-factor in the same Hamiltonian [11], consistent with our previous usage for HCl [9].

j	C _j	t_j^{Li}	t _j H	
0	(6572492.8	0.7742804	-0.75264	
	± 8.6) m ⁻¹	± 0.0000020	± 0.00024	
1	-0.8971881	0.597210	1.2104	
	± 0.0000160	± 0.000028	±0.0024	
2	0.347705	-1.18823	-2.3488	
	±0.000095	± 0.00033	±0.0091	
3	-0.085814	1.32281	1.4478	
	± 0.00042	± 0.00112	± 0.051	
4	-0.045456	-1.5303		
	±0.00219	±0.0099		
5	-0.03125	1.4458	•••	
	±0.0064	±0.0093		
6	0.08284	-1.209	•••	
	±0.0104	±0.072		
$s_0^{\text{Li}} = 0.6686 \pm 0.042$		$u_1^{\rm Li}/10^6 {\rm m}^{-1} = -$	5.7153±0.0207	
		$u_{1}^{\text{Li}}/10^{6} \mathrm{m}^{-1} = 7.830 \pm 0.297$		
$s_0^{\rm H} = -0.3011 \pm 0.0079$		$u_1^{\rm H}/10^6 {\rm m}^{-1} = -5.2913 \pm 0.0026$		
$s_{1}^{H} = 0.508 \pm 0$).040	$u_2^{\rm H}/10^6 {\rm m}^{-1}=5.513\pm0.054$		
$s_{1}^{H} = 2.017 \pm 1$	9	$u_3^{\rm H}/10^6 {\rm m}^{-1} = -4.437 \pm 0.157$		
$U_{1.0}/m^{-1} u^{1/2}$	$^2 = 131994.713 \pm 0.106$	$U_{0,1}/m^{-1}u = 662.709146 \pm 0.000194$		
$k_{\rm e}/{\rm N}{\rm m}^{-1}=1$	02.651100±0.000176	$R_{\rm e}/10^{-10}$ m = 1.5949123 ± 0.00000136		

Table 1 Coefficients of radial functions and other molecular properties, all independent of mass, of LiH X ${}^{1}\Sigma^{+*}$

^a Each uncertainty denotes a single estimated standard error. All parameters $t_j^{\text{Li},\text{H}}$ were constrained to the specified values during the fit of spectral data; their indicated standard errors result from the fit of theoretical data. The fit of 557 spectral transitions with 17 independently adjustable parameters R_e , c_j , $s_j^{\text{Li},\text{H}}$ and $u_j^{\text{Li},\text{H}}$ attained a normalized standard deviation 1.095; the F value was 5.0×10^{14} . The maximum range of validity of all functions is $1.25 \leq R/10^{-10} \text{ m} \leq 2.20$. The points ... signify that the pertinent quantities are indeterminate.

4. Radial functions

By means of the computer program Radiatom [9], we fitted 557 experimental differences $\tilde{\nu} = E_{\nu'J'} - E_{\nu J}$ between spectral terms to the parameters, pertinent coefficients of radial functions in Eqs. (3)-(6), based on analytic functions [9] of term coefficients Y_{kl} and various Z_{kl} in Eq. (7) in terms of these parameters according to the theoretical foundation [5]. Resulting values of the coefficients c_j , $s_j^{\text{Li,H}}$, $u_j^{\text{Li,H}}$ and other parameters in Table 1 constitute the best fit according to the unbiased test of the F statistic. The normalized standard deviation 1.095 is equivalent to that of a fit [12] of the same data according to an essentially empirical relation [32]

$$E_{\nu J} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} U_{kl} \mu^{-(\frac{1}{2}k+l)} (\nu + \frac{1}{2})^{k} (J^{2} + J)^{l} \times [1 + m_{e} (\Delta_{kl}^{a} / M_{a} + \Delta_{kl}^{b} / M_{b})].$$
(13)

Table 1 demonstrates that of seventeen indepen-

dently adjusted parameters the least significantly evaluated are c_5 and $s_3^{\rm H}$. Although $s_3^{\rm H}$ appears poorly evaluated, its presence was essential in the fit; without it the best normalized standard deviation was greatly increased (>1.7) whereas the F statistic was much smaller than the value presented in Table 1. Of 136 independent values of correlation coefficients from the matrix of variance and covariance, only three magnitudes exceed (slightly) 0.95; none involves $S_3^{\rm H}$. Values of coefficients c_i for potential energy and the related distance Re are statistically indistinguishable from those derived from fits of the same spectral data both through the coefficients U_{kl} according to Eq. (13) and separately by means of the program Radiatom without constrained values of $t_i^{\text{Li,H}}$, j > 0 [12]. Values of $u_i^{\text{Li,H}}$ that are insensitive to vibrational nonadiabatic effects [9] also reproduced those from the earlier fit of the same data [12]. Values of $\Delta_{kl}^{\text{Li,H}}$ that are incidentally produced by the program Radiatom reproduced the corresponding

values evaluated separately by means of Eq. (13) [12]. Hence application of this procedure to reduce spectral data of LiH yielded statistically meaningful results.

The ratio of the estimated standard error to the magnitude of $u_1^{\rm H}$ is near the ratio of the electronic and nuclear masses; a value of $\delta u_1^{\rm H}/|u_1^{\rm H}|$ significantly less than the latter ratio would indicate treatment at a higher level to be required, as the adiabatic and nonadiabatic effects in the theory [5] were treated according to perturbation theory of first order in $m_e/M_{nuclear}$ relative to adjacent terms in Eq. (1). The absence of s_2^H but almost significant evaluation of $s_3^{\rm H}$ (Table 1) is worthy of note. During preliminary fits of spectral data in which s_2^H was allowed to vary, its magnitude was both relatively small and smaller than its estimated standard error; in further fits its value was constrained to zero. Term coefficients $Z_{k,0}^{r}$ of either atomic type are identically zero for all values of k, consistent with their origin in extra rotational contributions to the spectral terms. The absence from Table 1 of coefficients of z^{j} beyond s_{0}^{Li} and u_2^{Li} indicates that the values of coefficients $t_i^{\text{Li,H}}$ are meaningful; although it would be possible in principle for coefficients $s_i^{\text{Li},\text{H}}$ to assume values during fitting of spectral data so as to compensate for the effects of $t_j^{\text{Li,H}}$, in that way the imposed values of $t_j^{\text{Li,H}}$ and further values of $s_j^{\text{Li,H}}$, and even of $u_j^{\text{Li,H}}$, might generate meaninglessly small values of Z_{kl}^{r} and Z_{kl}^{v} for both Li and H that would have a negligible effect on spectral terms E_{uf} . That the latter cancellation failed to occur provides confirmation of the significance of all radial functions defined according to coefficients in Table 1.

5. Discussion

According to experimental data in relation to the Hamiltonian in Eq. (1), what are the relative magnitudes of adiabatic, nonadiabatic rotational and nonadiabatic vibrational contributions to the spectral terms? Underlying Van Vleck's work [1], this question is answered here within the framework of various term coefficients in Eq. (7). In Table 2 we compare various contributions to each term coefficient Z_{kl}^r of finite magnitude. We readily achieved this quantitative assessment by means of

analytic relations [9] that link the parameters, of which values appear in Table 1, with various term coefficients in Eq. (7).

Here follows a synopsis of notable qualitative features from Table 2. The magnitudes of ratios of auxiliary term coefficients Z_{kl}^{r} or Z_{kl}^{v} of Li or H in ⁷Li¹H to the dominant coefficients Y_{kl} are, if not zero, about 10^{-4} , i.e. comparable with $(2B_e/\omega_e)^2$ or m_e/μ (data not presented). The magnitudes of coefficients $Z_{kl}^{r,Li}$ or $Z_{kl}^{\mathbf{v},\mathrm{Li}}$ are smaller than those of corresponding coefficients of H generally in accordance with the ratio of masses of H and Li. Net contributions of nonadiabatic vibrational effects to the sum of term coefficients $Z_{0,l}^{r,H} + Z_{0,l}^{v,H}$ are lacking because the contribution of each term containing s_j in $Z_{0,l}^{r,H}$ is exactly balanced by a contribution of opposite sign within $Z_{0,l}^{v,H}$, and correspondingly for $Z_{0,l}^{r,Li}$ and $Z_{0,l}^{v,Li}$ [5]. Adiabatic and nonadiabatic rotational contributions have generally comparable magnitudes. The magnitudes of contributions of nonadiabatic vibrational effects to $Z_{kl}^{r,H}$ or $Z_{kl}^{r,Li}$ are smaller than those of corresponding nonadiabatic rotational effects, although to this trend an exception exists. In contrast, contributions of nonadiabatic vibrational effects to $Z_{kl}^{v,H}$ are smaller than those of adiabatic effects, but larger than contributions of the former to $Z_{kl}^{r,H}$ for those cases of k and l without exact cancellation. No particular trend of relative signs of contributions to $Z_{kl}^{v,H}$ to $Z_{kl}^{r,H}$ is discernible. In some cases the contributions thereto have comparable magnitudes but opposite signs, so tend to cancel one another. Although for rotational coefficients $(Z_{0,l}, l>0)$ the nonadiabatic vibrational effects make no net contribution because of exact cancellation between $Z_{0,l}^{v}$ and the corresponding $Z_{0,l}^{r}$, no such cancellation occurs for $Z_{k,l}$ with k>0. Our deductions apply specifically to ⁷Li¹H; whether they are applicable to other diatomic molecules or even to other hydrides remains to be ascertained. The nonadiabatic rotational contribution to $Z_{0,1}^{r}$ of atomic centre either C or O in CO [33] was much larger than the corresponding adiabatic contribution in $Z_{0,1}^{v}$, unlike the prevalence of comparable magnitudes in ⁷Li¹H here or ¹H³⁵Cl [9]. A general expectation, to which results for LiH, HCl and CO conform, is that adiabatic effects are larger, relative to nonadiabatic effects, for hydrides than for nonhydrides.

Although we utilized data from quantal computations of g_J and electric dipole moment rather than Table 2

k	1			Z _{kl}	
		nr	nv	ad	nv
0	1	0.04553	•••	-0.0511	
0	2	6.401×10 ⁻⁶	-4.498×10 ⁻⁶	11.84×10 ⁻⁶	4.498×10 ⁻⁶
1	0	•••	•••	-4.664	3.675
0	1	-0.3081		-0.3296	•••
0	2	1.272×10^{-4}	0.1410×10 ⁻⁴	0.6395×10 ⁻⁴	-0.1410×10^{-4}
0	3	-4.315×10^{-8}	-0.6451×10^{-8}	-1.425×10^{-8}	0.6451×10 ⁻⁸
0	4	1.281×10 ⁻¹¹	0.1975×10^{-11}	0.317×10 ⁻¹¹	-0.1975×10^{-11}
1	0	•••		-40.172	-11.52
1	1	0.418×10 ⁻³	-1.316×10^{-3}	5.749×10 ⁻³	5.314×10 ⁻³
1	2	1.96×10 ⁻⁶	0.334×10 ⁻⁶		-0.974×10^{-6}
2	0				0.624
2	1	***	0.203×10 ⁻⁴		•••

Partition of term coefficients/ $m^{-1} Z_{kl}^{t}$ and Z_{kl}^{v} (defined in Eq. (7)) of Li and H in ⁷Li¹H into adiabatic (ad), nonadiabatic rotational (nr) and nonadiabatic vibrational (nv) contributions ^a

^a The points ... indicate that the pertinent quantities are indeterminate.

from experiment as the origin of the radial functions $\alpha^{\text{Li,H}}(R)$, these data could in principle be derived experimentally if g_J and μ_e were measured in sufficiently many states of diverse v and J. Hence our computed results simulate prospective experimental results. The computed expectation values $\langle 0, 1|g_I|0,$ 1) of ⁷Li¹H or ⁷Li²H, -0.6351 and -0.6714 or -0.2653 and -0.2840 at levels CCSDPPA and CCDPPA respectively, bracket the experimental value -0.65842 ± 0.00017 or -0.27674 ± 0.00011 [19]. The small difference, less than 3.5 percent, between either computed value and the experimental value has an insignificant effect on the interpretation of our results; the relatively larger difference between the two computed values may signify that the perturbative calculation is not quite converged. The coefficient of the linear term in Eq. (11) is consistent with the rotational dependence of the rotational g-factor [21]. For molecules such as LiH all our computational methods at a level of approximation SOPPA or better are expected to yield reliable estimates of secondorder properties, such as g_{J} , within at least the range $0.4 \leq R/R_{\star} \leq 2$, which is larger than the range within which Eq. (11) applies. The computed value of μ_{e} (the constant term in Eq. (12)) at $R_{\rm e}$ deviates slightly from the experimental value $(1.94407 \pm 0.00022) \times$ 10^{-29} C m [19], but as the difference is less than one percent the effect on the interpretation of our results is insignificant. We are therefore confident that parameters in Table 1 constitute collectively the best representation of the specified spectral data of LiH in terms of radial functions related to the effective Hamiltonian in Eq. (1).

In summary, in order to reduce available data of wavenumbers of pure rotational and vibration-rotational transitions of LiH in its four isotopic variants. we constrained parameters pertaining to nonadiabatic rotational effects to values consistent with quantal results for radial dependence of the rotational g-factor and the electric dipole moment; we fitted spectra to evaluate other parameters of internuclear potential energy (independent of mass) and of adiabatic and nonadiabatic vibrational effects of each nucleus. Thereby we demonstrate for LiH that contributions to molecular terms associated with radial functions of adiabatic, nonadiabatic rotational and nonadiabatic vibrational effects in the effective Hamiltonian have roughly comparable magnitudes. The sums of adiabatic and nonadiabatic vibrational contributions to $Z_{1,0}^{v}$ for both Li and H in ⁷Li¹H associated with the dominant pure vibrational term coefficient $Y_{1,0}$ have negative signs; this result for LiH signifies that the potential energy independent of mass (i.e. that produced by a calculation in which electronic and nuclear motions are treated separately according to the procedure of Born and Oppenheimer

[2]) produces an upper limit of the true vibrational energy, at least within the range of small v to which the present results apply. These effects must be taken into account in quantitative treatments of molecular spectra and intramolecular dynamics according to conventionally applied quantum mechanics.

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