

Radial Functions for Potential Energy and Related Properties of Diatomic Molecules

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ABSTRACT

To illustrate the application of the theory described in the accompanying paper, we present results to define radial functions for the potential energy, adiabatic and nonadiabatic vibrational and rotational effects of the diatomic molecules LiH and SiS, including thus both a hydride (for which the effects of partial failure of the Born-Oppenheimer approximation are more readily detectable) and a non-hydride. The problem of current insufficiency of experimental data to permit the general separation of all effects is discussed. Alternative treatments to reduce spectral data, the frequencies and wavenumbers of rotational and vibration-rotational transitions and rovibronic data, to parameters of various types--spectral, isotopic and molecular, we discuss critically in order to assess the dependence of the derived molecular parameters on the nature of the model; such independence is a requisite of any physical interpretation of the results, and the uniqueness of such processes of spectral inversion is also relevant. Applications of results to analytical chemistry, specifically the monitoring of stable and unstable diatomic molecular species in terrestrial and other atmospheres, are outlined.

RESULTS AND DISCUSSION

The severity of the problem of reduction of spectral data increases with increasing spectral resolution and precision of measurements of the frequencies and wavenumbers of lines because of the necessity to take into account progressively smaller intramolecular effects and interactions. For diatomic molecules the relative simplicity consequent of the single degree of vibrational freedom is demonstrated in the accompanying paper¹ to yield a compact and meaningful representation of these data in terms of coefficients of radial functions, despite that these radial functions have no direct physical meaning; the reason is that the distinction of the internuclear distance from other distances between particles within the molecule relies on the Born-Oppenheimer separation of electronic and nuclear motions. The latter procedure, which results from the imposition of the classical notion of molecular structure onto a quantum-mechanical system, allows one to propose a radial function for potential energy that is so commonly invoked as to have assumed quasi-physical meaning despite its being entirely an artefact of the Born-Oppenheimer (or equivalent) approach and hence extraneous to a purely quantum-mechanical description of the internal and external motions of the constituent particles of molecules.² We restrict here our attention to a single electronic state that is sufficiently isolated from other electronic states that local spectral irregularities are lacking. A radial function for the nonadiabatic rotational effects (due to the imperfect following by the electrons of the nuclei rotating about the centre of molecular mass) arises analogously in relation to the rotational magnetogyric ratio that can be measured by means of experiments employing the Zeeman effect.³ For the adiabatic effects (the correction to the potential energy due to its slight dependence on relative nuclear momenta--hence nuclear mass--in addition to internuclear distance) and the nonadiabatic vibrational effects (arising because the electrons follow imperfectly one or other nuclei during their vibrational motion), there is no analogous specific experimental measurement that allows the distinction of these two contributions to the molecular energy,³ although the careful treatment of highly precise wavenumber data of spectral transitions of isotopic variants enables one to extract limited information about these effects.¹ A further complication to efforts to unravel these effects is that there has never been demonstrated a definitive proof that the process of spectral inversion, even with data from both vibrational and rotational transitions, can in principle yield a unique radial function (or set of radial functions).⁴ According to this important caveat, one should select the process of spectral inversion that leads to the most compact and computationally efficient representation of the spectral data so as to enable their

reproducibility within the accuracy of their measurement. In these circumstances one should describe the process of this spectral reduction to finite sets of radial coefficients not as determination of radial functions--which inherently lack direct physical meaning--but instead as their evaluation.

On this basis we have evaluated the parameters in radial functions of at most four types--potential energy (formally independent of nuclear mass), adiabatic effects and nonadiabatic rotational and vibrational effects, the latter three effects leading to separate functions for each nucleus if nuclei a and b have distinct atomic numbers. The function for potential energy with the argument $z=2(R-R_e)/(R+R_e)$ in terms of instantaneous R and equilibrium R_e internuclear distances is

$$V^{BO}(z) = c_0 z^2 (1 + \sum_{j=1} c_j z^j) \quad (1)$$

whereas the pairs of the other three functions are (in the same order)

$$V^{ad}(R) \rightarrow (m_e/M_a) \sum_{j=1} u_j^{aj} + (m_e/M_b) \sum_{j=1} u_j^{bj} \quad (2)$$

$$\alpha(R) \rightarrow (m_e/M_a) \sum_{j=0} t_j^{aj} + (m_e/M_b) \sum_{j=0} t_j^{bj} \quad (3)$$

$$\beta(R) \rightarrow (m_e/M_a) \sum_{j=0} s_j^{aj} + (m_e/M_b) \sum_{j=0} s_j^{bj} \quad (4)$$

By means of inversion of available spectral data we have evaluated the parameters in these functions for several diatomic molecules to the extent that the finite data allow. For those cases for which the rotational g value has been determined, we thereby estimate the parameters $t_0^{a,b}$ according to the reported relation;⁵ if the rotational and vibrational dependences of g_l were determined from experiment (or calculated) then the analogous relation would enable the evaluation of the parameters $t_1^{a,b}$ and $t_2^{a,b}$ by means of the appropriate vibration-rotational expectation values and matrix elements.⁶

The molecule LiH, for which particularly precise and consistent spectral data exist in the form of pure rotational transitions in the millimetre-wave and far infrared regions and of vibration-rotational transitions in the mid infrared regions for the isotopic variants ${}^6\text{Li}^1\text{H}$, ${}^6\text{Li}^2\text{H}$, ${}^7\text{Li}^1\text{H}$ and ${}^7\text{Li}^2\text{H}$,⁷ has been the subject of analyses in attempts to generate coefficients of radial functions,⁷⁻¹⁰ because one expects that the relatively small nuclear masses enable the significant evaluation of radial coefficients associated with the various effects. According to the most profound examination¹⁰ made in the light of preceding work, the leading coefficients in the functions for the nonadiabatic vibrational effects were estimated on the basis of the strongly electrically dipolar nature of this molecule, but those values were consistent (within the relatively large experimental uncertainty) with the rotational dependence of the rotational g factor that was measured in this exceptional instance.¹¹ Comparison of these results with earlier ones⁹ indicates that according to this representation in terms of the variable z only seventeen unconstrained parameters are evaluated during the fitting procedure, in common with the previous results⁹ in terms of z but at least nineteen parameters (of which two have poor statistical significance) in terms of the exponential function for potential energy.⁹ Moreover the significant evaluation¹⁰ of the spectral coefficient $U_{4,0}$ implies the significant evaluation of c_6 through the analytic relation specified elsewhere,¹ although a superfluous coefficient h_3^{Li} (essentially equivalent to u_3^{Li} that is absent from table 1) compensated the lack of c_6 in an alternative treatment.⁹ As for HCl,¹ the magnitudes of adiabatic effects (through $u_1^{\text{Li,H}}$) and rotational nonadiabatic effects (through $t_0^{\text{Li,H}}$) in $\Delta_0^{\text{Li,H}}$ are comparable, and correspondingly the magnitudes of adiabatic (through $u_1^{\text{Li,H}}$ and $u_2^{\text{Li,H}}$) and nonadiabatic vibrational (through $s_0^{\text{Li,H}}$) effects in $\Delta^{\text{Li,H}}$ are comparable. Because the latter parameters were estimated explicitly, the coefficients $u_1^{\text{Li,H}}$, $u_2^{\text{Li,H}}$, $t_0^{\text{Li,H}}$, $t_1^{\text{Li,H}}$ and $s_0^{\text{Li,H}}$ retain in this case their original meaning as related to purely adiabatic, nonadiabatic rotational or vibrational effects, whereas the remaining parameters $u_j^{\text{Li,H}}$ or $t_j^{\text{Li,H}}$ necessarily absorb both nonadiabatic vibrational and adiabatic or nonadiabatic rotational effects respectively because the coefficients $s_j^{\text{Li,H}}$ beyond $j=0$ cannot be separately estimated from available

Table 1. Coefficients of Radial Functions and Other Molecular Properties of LiH X $^1\Sigma^+$, all Independent of Mass.^a

j	c_j	t_j^{Li}	t_j^{H}	$u_j^{\text{Li}}/10^6\text{m}^{-1}$	$u_j^{\text{H}}/10^6\text{m}^{-1}$
0	$(6572491.7 \pm 7.5) \text{ m}^{-1}$	0.75335^*	-0.76823^*		
1	-0.8972600 ± 0.0000135	0.511 ± 0.111	0.863 ± 0.029	-5.683 ± 0.046	-5.1892 ± 0.0035
2	0.347982 ± 0.000095		-1.278 ± 0.103	6.977 ± 0.13	8.3021 ± 0.0121
3	-0.08666 ± 0.00042				-10.830 ± 0.26
4	-0.04394 ± 0.0022				9.31 ± 0.84
5	-0.0308 ± 0.0058				
6	0.0758 ± 0.0109				
			$U_{1,0} = (131994.784 \pm 0.117) \text{ m}^{-1} \text{ u}^{\frac{1}{2}}$		
			$U_{0,1} = (662.70996 \pm 0.00042) \text{ m}^{-1} \text{ u}$		
$s_0^{\text{Li}} = 0.7608^* \quad s_0^{\text{H}} = -0.7608^*$			$k_e = (102.65121 \pm 0.00019) \text{ N m}^{-1}$		
range $1.25 \leq R/10^{-10} \text{ m} \leq 2.2$			$R_e = (1.59491127 \pm 0.00000143) \times 10^{-10} \text{ m}$		

^aEach stated uncertainty represents one estimated standard error; the F-value of the fit of 539 data with 17 unconstrained and four constrained* parameters (apart from those set to zero value) is 6.7×10^{13} , and the normalised standard deviation $\hat{\sigma}$ is 1.09.

data. The value of R_e in table 1 differs insignificantly from that evaluated⁹ without explicit account being taken of the rotational g factor because of fortuitous cancellation of the contributions of the merely fitting coefficients $h_1^{\text{H,Li}}$ and $g_1^{\text{H,Li}}$.⁹

The nonhydride species SiS provides results (table 2) that we compare with those of HCl¹ and of LiH in table 1. We fitted 3025 spectral lines of pure rotational and vibration-rotational transitions of $^{28,29,30}\text{Si}^{32}\text{S}$ and $^{28}\text{Si}^{33,34}\text{S}$ in the indicated binary combinations to only twelve independent parameters in the sets indicated in table 2. Since the previous analysis of these spectral data,¹² we incorporated the information from the known rotational g factor¹³ and the molecular electric-dipolar moment¹⁴ to constrain the values of $t_0^{\text{Si,S}}$ to those appearing in table 2; not there indicated, their uncertainties are ± 0.015 . In our previous analysis,¹² we evaluated statistically significant values of twelve parameters, but the value of c_6 (1.351 ± 0.79) attained only marginal significance. As a definitive test whether a truly significant value is derivable from the available data, we fitted the data of only the most abundant isotopic variant $^{28}\text{Si}^{32}\text{S}$, which amounted to 1723 transitions up to $v=10$ and $J=150$. With $g_0^{\text{Si,S}}$ constrained to be consistent with g_1 and only seven varied parameters (k_e , R_e and c_1 - c_5), the fit yielded a normalised standard deviation $\hat{\sigma}=0.854$, whereas the inclusion of c_6 produced the significantly decreased value $\hat{\sigma}=0.790$; as in all cases the weights of individual transitions reflected the estimates of the uncertainties attached to the original measurements, the latter are evidently too conservative, but only the relative values of $\hat{\sigma}$ are pertinent for our analysis. The deduced value of c_6 was -3.3 ± 0.9 , hence significant, and the largest associated correlation coefficient of this parameter, of magnitude 0.91, connected c_6 with c_4 . Moreover when a variable was introduced to take into account any rotational effects additional to those related to the adiabatic potential energy, a value $g'_1 = 0.074 \pm 0.033$ was evaluated and the maximum magnitude of any correlation coefficient connecting this variable with any other was only 0.200; the prime in g'_1 signifies that it, unlike $g_j \approx g_0$, must not be associated with purely nonadiabatic rotational effects. Despite the marginal significance of this value 0.74, this result furnishes further evidence that the additional rotational effects represented by the term coefficients¹ Z_{kl}^r can be evaluated significantly apart from those due to the vibration-rotational effects represented by Z_{kl}^v ; for this reason the dominant term coefficients Y_{kl} should not be regarded as independent fitting parameters but be constrained by means of the known inter-relations.¹⁵ For

Table 2. Coefficients of Radial Functions and Other Molecular Properties of SiS X $^1\Sigma^+$, all Independent of Mass.^a

j	c_j	t_j^{Si}	t_j^{S}	$u_j^{\text{Si}}/10^6\text{m}^{-1}$	$u_j^{\text{S}}/10^6\text{m}^{-1}$
0	(66282737.1±52) m ⁻¹	-1.173*	-1.547*		
1	-1.9976298±0.0000124	1.284*	0.906*	0*	0*
2	1.806055±0.000078			81.1±3.3	-13.1±4.1
3	-0.93460±0.0023				
4	-0.18791±0.0181				
5	1.5748±0.089				
6	-3.081±1.03				
			$U_{1,0} = (289563.67 \pm 0.34) \text{ m}^{-1} u^{1/2}$ $U_{0,1} = (452.907092 \pm 0.000017) \text{ m}^{-1} u$ $k_e = (494.01334 \pm 0.00119) \text{ N m}^{-1}$ $R_e = (1.92927313 \pm 0.00000162) \times 10^{-10} \text{ m}$		
range 1.72 < R/10 ⁻¹⁰ m < 2.25					

^aThe F-value of the fit of 3025 data with ten unconstrained and four constrained* parameters (apart from those set to zero value) is 6.22x10¹⁴, and the normalised standard deviation $\hat{\sigma}$ is 0.917.

succeeding fits of data of all the isotopic variants this value of g'_1 was therefore partitioned between Si and S according to the same relation as for g_j under the assumption that the combined effects of $t_1^{\text{Si,S}}$ and $s_0^{\text{Si,S}}$ could be absorbed into effective values of $t_1^{\text{Si,S}}$; specified in table 2 the latter values bear each an associated standard error 0.45 propagated from the generating quantities. By this means we succeed to represent within the precision of their measurement all available spectral data by means of only ten independent parameters-- k_e , R_e , c_1 - c_6 and $u_2^{\text{Si,S}}$ --plus the constrained values of $t_0^{\text{Si,S}}$ from g_j and $t_1^{\text{Si,S}}$ from the surplus rotational effects detected through g'_1 of $^{28}\text{Si}^{32}\text{S}$. These twelve independent parameters clearly embody greater significance, at least due to their direct relation to the rotational g factor, than the parameters of like number separately reported.¹⁶ The statement that the latter work constitutes a direct determination of the potential-energy function is inaccurate because not only is this function an artefact of a particular computational approach (as explained above) but also the inversion of spectral data to the associated nonlinear radial coefficients is an iterative process, hence indirect. The lack of values of $u_1^{\text{Si,S}}$ and $u_2^{\text{Si,S}}$ in table 2 reflects the fact that, as attempted fitted values were equal to nil within their standard errors, so these values were thus constrained in the final fit. The reported¹⁶ parameters other than c_j were all of type $u_j^{\text{Si,S}}$ or equivalent; the magnitudes¹⁶, $\sim 300 \times 10^6 \text{ m}^{-1}$, of $u_2^{\text{Si,S}}$, both being much larger¹ than those in table 2, indicate that our representation is preferable from a statistical point of view, apart from the greater physical significance associated with the parameters related to the rotational g factor. The insignificant magnitudes of $u_1^{\text{Si,S}}$ support the evidence¹⁷ from CO that adiabatic effects of a non-hydride are much smaller than of a hydride, as most contributions to the effective values of $u_1^{\text{Si,S}}$ that would have resulted from their being freely fitted would have reflected adiabatic effects.¹ In table 2 the value of R_e independent of nuclear mass differs from those reported elsewhere¹⁶ by 4-6 standard errors, thus significantly, due to neglect¹⁶ of nonadiabatic rotational effects.

A published analysis¹⁸ of the spectra of the diatomic molecular ion ArH^+ made no use of the reported values of the factors g_j of $^{40}\text{Ar}^1\text{H}^+$ and $^{40}\text{Ar}^2\text{H}^+$ as these values are mutually inconsistent because of faulty measurements or incorrect analysis (R. J. Saykally, private communication, 1992). For this reason the values of the published¹⁸ radial coefficients of ArH^+ have a weaker relation to the corresponding adiabatic and nonadiabatic parameters that might result from direct quantum-chemical calculations than those of LiH and SiS. In general there exists an obvious need of accurate values of not only the rotational g factor but also its rotational and vibrational dependences to yield the most

significant results from inversion of spectral measurements of transition frequencies and wavenumbers.

For the purpose of qualitative and quantitative analysis of the constituents of gaseous samples by spectral measurements at high resolution, for instance in the upper terrestrial atmosphere, there is a need to maintain either an extensive list of frequencies and wavenumbers of spectral lines of likely substances or a rapid method of generating such observable quantities from a small set of parameters by means of an efficient and generally applicable algorithm. The analytic relations reported¹ provide a means to effect the latter approach; the expressions are relatively simple, can be readily converted to machine-readable instructions and can then be rapidly executed with modest computational resources. Analogous expressions exist in relation to the intensities of spectral lines in vibration-rotational transitions.¹⁹ As spectral atlases expand so much as to tax the limits of current computational resources, the latter approach commends itself to further development.

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