

Radial Functions of LiH  $X^1\Sigma$  from Vibration–Rotational Spectra

J. F. OGILVIE

*Academia Sinica, Institute of Atomic and Molecular Sciences, P.O. Box 23-166, Taipei 10764, Taiwan  
(electronic mail: cc7b0001@twnmoe10.bitnet)*

The coefficients  $c_j$ ,  $j \leq 7$ , defining the potential-energy  $V(z)$  and coefficients of four other radial functions related to adiabatic and nonadiabatic effects have been determined for LiH in the electronic ground state  $X^1\Sigma$  by a direct fit to the published frequencies and wavenumbers of vibration–rotational transitions. The functions are valid in the range of internuclear distance/  $10^{-10}$  m [1.25, 2.20]. © 1991 Academic Press, Inc.

## INTRODUCTION

There have been published two collections (1, 2) of wavenumbers of vibration–rotational transitions of the diatomic molecule LiH in its four common isotopic variants  ${}^6\text{Li}^1\text{H}$ ,  ${}^6\text{Li}^2\text{H}$ ,  ${}^7\text{Li}^1\text{H}$ , and  ${}^7\text{Li}^2\text{H}$ ; the second collection (2) also included many pure rotational transitions within a few vibrational states. These spectra were measured under conditions such that the reproducibility of the measurements was  $0.1\text{ m}^{-1}$  or better. Complementing these measurements in the infrared region are the previous measurements (3, 4) of several lines in the millimeter-wave region with greater absolute precision. These data provide collectively a valuable source from which information about the fundamental properties of the LiH molecule in its electronic ground state  $X^1\Sigma$  may be deduced.

Attempts have already been made to extract some information. Pearson and Gordy, who measured four lines, one of each isotopic variant, derived a value of the equilibrium internuclear separation  $R_e$  which was claimed to be independent of mass (3); auxiliary data from spectra of poorer quality were included in their analysis. On the basis of the measurement of six further lines, Plummer *et al.* also had recourse to the results of wavenumber analyses of published electronic transitions in their discussion of adiabatic and nonadiabatic effects (4). Following their measurement of about 40 vibration–rotational transitions involving vibrational states  $0 \leq v \leq 3$ , Yamada and Hirota also attempted to determine only a value of  $R_e$  (3). Despite the well known injunctions to impose constraints on the term coefficients  $U_{kl}$  (5, 6) and subsequently also on the associated parameters  $\Delta_{kl}$  (7), in the latter work (3) all these parameters were freely fitted; inconsistencies consequently exist in those results (8). Maki *et al.* made a serious attempt to determine the potential-energy function on the basis of their extensive spectral measurements (4); their fit thereby was significantly less good than when the fit was made to the intermediate parameters  $U_{kl}$  and  $\Delta_{kl}$ . In the latter case, although the formally appropriate constraints were apparently not imposed, that the freely fitted values of both  $U_{0,2}$  and  $\Delta_{0,2}^H$  are near the prospectively constrained values indicates the quality of both the measurements and the fitting procedure. For such constraints

to be applied implies that all physical effects that can be empirically determined must be included in the treatment. Since the work of van Vleck (9) and others who extended his treatment, it is known that account of several factors is required to encompass fully the isotopic effects. Elsewhere we have discussed (10) the basis of the application of these theories; on that basis the combined sets of frequencies and wavenumbers of spectral transitions of isotopic variants to arbitrarily great values of quantum number  $J$  for rotational angular momentum (in the absence of other contributions to total angular momentum except nuclear spin) may be used to determine accurately not only the potential-energy function but also additional radial functions which describe the other effects, specifically the collective adiabatic and nonadiabatic effects that appear to correct for the approximation inherent in the Born–Oppenheimer separation of electronic and nuclear motions. Such radial functions, having as argument the internuclear distance  $R$  or equivalent variable, achieve both the most compact and the most physically meaningful representation of the spectral data (8). Here we report the application of this theory to the analysis of the specified spectral data of LiH, with the objective to determine the maximum information about the molecular properties that the data can yield.

#### PRINCIPLES OF THE METHOD

The effective potential energy governing the internuclear vibration and rotation (about the center of molecular mass) of a diatomic molecule within a particular electronic state of type  $^1\Sigma$  is expressed (10) as

$$V_{\text{eff}} = c_0 z^2 \left( 1 + \sum_{j=1} c_j z^j \right) + \sum_{j=1} m_e h_j^a z^j / M_a + \sum_{j=1} m_e h_j^b z^j / M_b \\ + B_e J(J+1) \left[ 1 + \sum_{j=0} m_e g_j^a z^j / M_a + \sum_{j=0} m_e g_j^b z^j / M_b \right] R_e^2 / R^2, \quad (1)$$

in which  $m_e$  is the electronic rest mass,  $M_a$  and  $M_b$  are the masses of the separate atoms  $a$  and  $b$ , and the reduced variable  $z$  for displacement of internuclear distance  $R$  from equilibrium at  $R_e$  is defined (11, 12)

$$z = 2(R - R_e) / (R + R_e). \quad (2)$$

The functions involving the coefficients  $h_j^{a,b}$  take empirically into account mostly the adiabatic effects and the nonadiabatic effects related to the vibrational inertia of the electrons because other effects have different dependences on atomic mass which makes them currently negligible with respect to the experimental error of frequency measurements (10). The functions involving the coefficients  $g_j^{a,b}$  take empirically into account certainly the nonadiabatic effects of the rotational inertia of the electrons, and possibly also other effects (10). Defined according to Eq. (1), all coefficients  $c_j$ ,  $g_j^{a,b}$ , and  $h_j^{a,b}$  are formally independent of mass, and dimensionless (except for  $c_0$  and  $h_j^{a,b}$ ). As a consequence of the various contributions to the effective potential energy, the vibration–rotational terms consist also of several contributions; the expression for these terms is an extension of Dunham's form (13):

$$E_{vJ} = \sum_{k=0} \sum_{l=0} (Y_{kl} + Z_{kl}^{h,a} + Z_{kl}^{h,b} + Z_{kl}^{g,a} + Z_{kl}^{g,b}) (v + \frac{1}{2})^k (J^2 + J)^l; \quad (3)$$

in this equation the coefficients  $Y_{kl}$  are supposed to result from purely the internuclear potential energy  $V(z)$  and the centrifugal motion of the nuclei and associated electrons; the remaining coefficients, the four components of  $Z_{kl}$ , reflect respectively the obviously corresponding terms considered as perturbations separately additive in the effective potential energy according to Eq. (1). Analytic expressions of the coefficients  $Y_{kl}$  as functions of the harmonic vibrational coefficient  $k_e$  (implicitly contained within  $U_{1,0}$  or  $\omega_e$ ), the equilibrium separation  $R_e$  (implicitly contained within  $U_{0,1}$  or  $B_e$ ), the reduced mass  $\mu$ , and the potential-energy coefficients  $c_j$  have been published in machine-readable form complete up to  $j = 10$  (14); further expressions containing coefficients up to  $j = 16$  have been generated according to hypervirial perturbation theory (15). The coefficient  $c_0$  in Eq. (1) is defined in terms either of  $U_{1,0}$  and  $U_{0,1}$ ,  $c_0 = U_{1,0}^2/(4U_{0,1})$ , or equivalently of  $k_e$  and  $R_e$ ,  $c_0 = k_e R_e^2/(2ch)$ ; the fundamental physical constants  $c$  and  $h$  enter because  $E_{vj}$ ,  $Y_{kl}$ , and  $Z_{kl}$  are all expressed in wave-number units for spectroscopic applications. Each term coefficient  $Y_{kl}$  and  $Z_{kl}$  consists of a series of contributions,

$$Y_{kl} = Y_{kl}^{(0)} + Y_{kl}^{(2)} + Y_{kl}^{(4)} + \dots, \quad (4)$$

$$Z_{kl} = Z_{kl}^{(0)} + Z_{kl}^{(2)} + \dots, \quad (5)$$

independently of the method of generation of the actual expressions of the coefficients (or of the notation used to distinguish the contributions). Because the coefficients  $Y_{kl}^{(0)}$  are expressed as a product with the reduced (atomic) mass  $\mu = M_a M_b / (M_a + M_b)$ ,

$$Y_{kl}^{(0)} = U_{kl} \mu^{((1/2)k+l)}, \quad (6)$$

the coefficients  $U_{kl}$  become formally independent of mass. Although we have generated some expressions of the contributions  $Y_{kl}^{(6)}$  and  $Y_{kl}^{(8)}$  containing coefficients  $c_j$  up to  $j = 16$ , only the leading term  $Y_{kl}^{(0)}$  and the first two corrections  $Y_{kl}^{(2)}$  and  $Y_{kl}^{(4)}$  are required in this case because the effects of experimental error of wavenumber measurement exceed the magnitudes of further corrections. Analogously, for each of the four components of  $Z_{kl}$  even the first correction  $Z_{kl}^{(2)}$  is negligible for the present data; furthermore additional terms could not be included consistently without account being taken of the interaction of the various effects. Each auxiliary set of coefficients  $Z_{kl}$  is a function of both the potential-energy coefficients  $c_j$  and the respective coefficients either  $g_j$  or  $h_j$  for either nucleus  $a$  or nucleus  $b$ . A few expressions for  $Z_{kl}^h$  in terms of  $c_j$  and  $h_j$  have already been published in a slightly different form (16), which are however readily converted to be consistent with the present definition according to Eq. (1); a larger collection containing  $h_j$  up to  $j = 10$  will be published with the extended set of expressions for  $Y_{kl}$ . Likewise a few expressions for  $Z_{kl}^g$  in terms of  $c_j$  and  $g_j$  have been determined (10); a larger collection containing  $g_j$  up to  $j = 10$  will also be published in machine-readable form.

As we have described elsewhere (10), the method of nonlinear parameter estimation has been applied to determine the applicable coefficients  $c_j$ ,  $g_j^{a,b}$ , and  $h_j^{a,b}$  directly from the frequencies  $\nu$  or wavenumbers  $\tilde{\nu}$  of the pure rotational and vibration-rotational transitions. The transition wavenumbers  $\tilde{\nu}$  are of course the difference of two terms  $E_{vj}$ ; the criterion of the best fit is that the sum of the squares of the residuals between

the measured and calculated values,  $\tilde{\nu}_{\text{obs}} - \tilde{\nu}_{\text{calc}}$ , is a minimum, hopefully the global minimum (apart from possibly the united atom). The algorithm of the fitting process employs the analytic expressions for not only the term coefficients  $Y_{kl}$  and the various components of  $Z_{kl}$  but also the first (partial) derivatives of  $Y_{kl}$  and the  $Z_{kl}$  with respect to the parameters, for instance  $\partial Y_{kl}/\partial c_j$ ,  $\partial Y_{kl}/\partial U_{1,0}$ , and  $\partial Z_{kl}/\partial g_j$ . The analytic expressions for the former derivatives up to  $j = 10$  have already been published in machine-readable form (14); expressions for further derivatives of  $Y_{kl}$  and for the derivatives  $\partial Z_{kl}^k/\partial g_j$  and  $\partial Z_{kl}^h/\partial h_j$  will form part of the large collection to be published subsequently. The different dependences of the residuals on the masses  $M_a$ ,  $M_b$ , and  $J$  make possible the determination of the coefficients  $g_j^a$ ,  $g_j^b$ ,  $h_j^a$ , and  $h_j^b$ .

## APPLICATION TO LiH AND DISCUSSION

From the collection of experimental frequencies (3, 4) and wavenumbers (1, 2) for the pure rotational and vibration-rotational transitions of the specified four isotopic variants we have determined the smallest set of coefficients  $c_j$ ,  $g_j^{\text{Li,H}}$ , and  $h_j^{\text{Li,H}}$  of the corresponding radial functions consistent with an adequate fit of the available data. The most recent values of the fundamental physical constants (17) and the atomic masses (18) were naturally included in the computations. For the fitting process each datum was assigned a weight according to the indication by the various authors of the precision and reproducibility of their data sets. The numerical results are presented in Table I; the estimated (single) standard errors take into account the uncertainties of the fundamental constants if applicable. Various combinations of the coefficients

TABLE I  
Coefficients of the Radial Functions and Other Molecular Properties of LiH  $X^1\Sigma$ ,  
All Independent of Mass

$j$	$c_j$	$g_j^{\text{Li}}$	$g_j^{\text{H}}$	$h_j^{\text{Li}}/\text{m}^{-1}$	$h_j^{\text{H}}/\text{m}^{-1}$
0	(6572688.87 $\pm 0.52$ ) $\text{m}^{-1}$	0 $\pm 0.15$	0 $\pm 0.06$	...	...
1	-0.8974764 $\pm 0.000028$	0.428 $\pm 0.18$	0.763 $\pm 0.051$	5893. $\pm 410.$	-9961. $\pm 44.$
2	0.348587 $\pm 0.00014$		-0.390 $\pm 0.210$	-9868. $\pm 933.$	14825. $\pm 102.$
3	-0.090245 $\pm 0.00080$			7373. $\pm 3670.$	-14654. $\pm 372.$
4	-0.037852 $\pm 0.0035$				15268. $\pm 1192.$
5	0.006865 $\pm 0.0105$				
6	-0.1042 $\pm 0.053$	$U_{1,0} = (131977.723 \pm 0.112) \text{ m}^{-1} \text{ amu}^{\frac{1}{2}}$			
		$U_{0,1} = (662.51879 \pm 0.00107) \text{ m}^{-1} \text{ amu}$			
7	0.286 $\pm 0.115$	$\kappa_e = (102.62468 \pm 0.00018) \text{ N m}^{-1}$			
		$R_e = (1.59514137 \pm 0.00000186) \times 10^{-10} \text{ m}$			

$c_j$ ,  $g_j^{\text{Li}}$ ,  $g_j^{\text{H}}$ ,  $h_j^{\text{Li}}$ , and  $h_j^{\text{H}}$  and varied extents of truncation of the five polynomials were tested; the shown results represent the best (smallest standard deviation of the fit and generally smallest standard errors of the individual parameters) and most compact (smallest total number of parameters leading to an acceptably small sum of squared residuals) fit. The transitions available from the four sources (1-4) number 585 in total, with some vibration-rotational transitions overlapping from the two sources (1, 2). Only one transition,  $R(8)$  of the band ( $v' = 3 \leftarrow v'' = 2$ ) of  $^7\text{Li}^1\text{H}$ , was rejected as an outlier, because its residual was almost seven times the standard deviation of the fit. As for this line the residual was exceptionally large also in the previous fit (4); presumably the assignment or the measurement may be incorrect, but we suggest no alternative assignment. The standard deviation of the fit is  $0.0947 \text{ m}^{-1}$ , slightly smaller than (2) the root-mean-square deviation (which neglected the millimeter-wave measurements) of the previous fit (2). However in that case the best fit was obtained when the parameters determined numbered 22 (with two other coefficients having constrained values not zero), of the type  $U_{kl}$  and  $\Delta_{kl}^{\text{Li,H}}$  in the expression for the vibration-rotational terms originated by Ross *et al.* (19). Unlike the radial functions (even if composite) to which the coefficients  $c_j$ ,  $g_j^{\text{Li,H}}$ , and  $h_j^{\text{Li,H}}$  pertain, the parameters  $U_{kl}$  and  $\Delta_{kl}^{\text{Li,H}}$  have no particular physical significance (20), merely serving as empirical fitting parameters. Moreover, the significant determination of only 19 parameters in the present work, with no parameters constrained to have values other than zero, sufficed to reproduce satisfactorily the spectral data. The matrix of correlation coefficients contained only a small fraction of values exceeding in 0.9 in magnitude, in fact proportionately smaller than in typical results of fitting potential-energy coefficients to the intermediate spectral coefficients  $Y_{kl}$  according to the traditional method (21); in combination with the relatively small estimated standard errors of most parameters, this fact indicates that the calculation has proceeded to produce statistically meaningful results.

Some comments on the particular values follow. Although fits with  $g_0^{\text{Li}}$  and  $g_0^{\text{H}}$  unconstrained were tried, the resulting converged values were less than two (small) standard errors different from zero; for this reason in further fits these values were constrained to zero. However, the other coefficients  $g_j^{\text{H}}$  and  $g_j^{\text{Li}}$  were determined significantly without unduly large magnitudes of correlation coefficients connecting them. No previous determinations of the coefficients  $g_j^{a,b}$  from purely vibration-rotational data have been reported. Coxon attempted to determine an equivalent radial function for only one atomic type, H, in his work on HCl which involved purely numerical computations (i.e., without analytic relationships) (22); furthermore he constrained to zero the value of the leading coefficient corresponding to  $g_0^{\text{H}}$ , although the latter quantity may be related to the rotational magnetogyric ratio of HCl for which a nonzero value certainly exists (23). There appear to exist no other data for LiH with which might be compared the few values of  $g_j^{\text{Li,H}}$  here determined. With due allowance for the different definitions, the magnitudes of the coefficients  $h_j^{\text{Li,H}}$  differ from those estimated previously (7), although the orders of magnitudes and signs remain consistent; because in previous analyses of the data for the spectral frequencies and wavenumbers the effects of the rotational inertia of the electrons were not included explicitly, the values of the parameters  $h_j^{\text{Li,H}}$  or their precursors  $\Delta_{kl}^{\text{Li,H}}$ , and to some extent also the potential-energy coefficients  $c_j$ , of necessity absorbed some effects due to the absence

of the parameters  $g_j^{\text{LiH}}$ . Both the values of  $U_{1,0}$  and  $U_{0,1}$  and their associated estimated standard errors in the table differ only slightly from those in the previous successful fit (2). The values of the potential-energy coefficients  $c_j$  converted from the coefficients  $a_j$  of the Dunham equation previously reported (2) are  $c_1 = -0.89723 \pm 0.00007$ ,  $c_2 = 0.3459 \pm 0.00055$ ,  $c_3 = -0.0957 \pm 0.0022$ ,  $c_4 = 0.046 \pm 0.005$ ,  $c_5 = -0.279 \pm 0.043$ ,  $c_6 = 0.34 \pm 0.15$ , and  $c_7 = 0.57 \pm 0.32$ . Of these values the first three agree closely with those in the table, consistent with the expectations of the previous authors (2), but the others diverge increasingly. In all cases the estimated standard errors in the present results are significantly smaller than those determined from the previous results (2). This effect is entirely consistent with the previous discussion (2) in which the difficulty of fitting transition wavenumbers of LiH directly to the coefficients  $a_j$  was emphasized. Furthermore although they were unable to effect the required modifications of their analysis, Maki *et al.* understood the necessity to include further rotational dependence into the effective potential-energy function; this lack is fulfilled by the present work in which the functions  $\sum g_j^{a,b} z^j m_e / M^{a,b}$  in Eq. (1) serve precisely this purpose.

#### CONCLUSION

Directly from the frequencies and wavenumbers of the published pure rotational and vibration-rotational transitions of LiH in the electronic ground state  $X^1\Sigma$ , we have determined the coefficients of five radial functions which are independent of mass. The range/ $10^{-10}$  m, approximately [1.25, 2.20], of validity of these functions corresponds to the classical turning points of the state  $v = 3$  of  ${}^6\text{Li}^1\text{H}$ , the vibrational state of greatest energy in the available transitions. These functions may serve as tests of the accuracy of quantum computations on this relatively simple molecular species.

#### ACKNOWLEDGMENT

This research was supported by the National Science Council of the Republic of China.

RECEIVED: February 28, 1991

#### REFERENCES

1. C. YAMADA AND E. HIROTA, *J. Chem. Phys.* **88**, 6702-6706 (1988).
2. A. G. MAKI, W. B. OLSON, AND G. THOMPSON, *J. Mol. Spectrosc.* **144**, 257-268 (1990).
3. E. F. PEARSON AND W. GORDY, *Phys. Rev.* **177**, 59-61 (1969).
4. G. M. PLUMMER, E. HERBST, AND F. C. DE LUCIA, *J. Chem. Phys.* **81**, 4893-4897 (1984).
5. J. K. G. WATSON, *J. Mol. Spectrosc.* **80**, 411-421 (1980).
6. V. G. TYUTEREV AND T. I. VELICHKO, *Chem. Phys. Lett.* **104**, 596-604 (1984).
7. J. F. OGILVIE, *Spectrosc. Lett.* **22**, 477-488 (1989).
8. J. F. OGILVIE, *Spectrochim. Acta Part A* **46**, 43-46 (1990).
9. J. H. VAN VLECK, *J. Chem. Phys.* **4**, 327-338 (1936).
10. J. F. OGILVIE, to be published.

11. J. F. OGILVIE, *Proc. R. Soc. London A* **378**, 287–300 (1981); *Proc. R. Soc. London A* **381**, 479 (1982).
12. J. F. OGILVIE, *J. Chem. Phys.* **88**, 2804–2808 (1988).
13. J. L. DUNHAM, *Phys. Rev.* **41**, 721–731 (1932).
14. J. F. OGILVIE, *Comput. Phys. Commun.* **30**, 101–109 (1983).
15. F. M. FERNANDEZ AND J. F. OGILVIE, *Phys. Rev. A* **42**, 4001–4007 (1990).
16. J. F. OGILVIE, *Chem. Phys. Lett.* **140**, 506–511 (1987).
17. E. R. COHEN AND B. N. TAYLOR, *Rev. Mod. Phys.* **59**, 1121–1148 (1987).
18. A. H. WAPSTRA AND G. AUDI, *Nucl. Phys. A* **432**, 1–54 (1985).
19. A. H. M. ROSS, R. S. ENG, AND H. KILDAL, *Opt. Commun.* **12**, 433–438 (1974).
20. P. NIAY, P. BERNAGE, C. COQUANT, AND A. FAYT, *Can. J. Phys.* **55**, 388–394 (1977).
21. J. F. OGILVIE AND D. KOO, *J. Mol. Spectrosc.* **61**, 332–336 (1976).
22. J. A. COXON, *J. Mol. Spectrosc.* **117**, 361–387 (1986).
23. F. H. DE LEEUW AND A. DYMANUS, *J. Mol. Spectrosc.* **48**, 427–445 (1973).