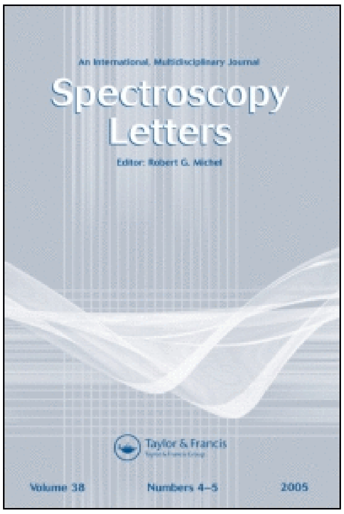

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RADIAL FUNCTIONS OF DIATOMIC LITHIUM HALIDES X $^1\Sigma^+$ FROM VIBRATION-ROTATIONAL SPECTRA

key words - potential-energy functions, lithium halides

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ABSTRACT

The radial functions for potential energy and adiabatic and nonadiabatic effects in the forms of polynomials with coefficients c_j, h_j^{Li}, h_j^X, g_j^{Li} and g_j^X of the reduced variable for internuclear distance $z \equiv 2(R-R_e)/(R+R_e)$ to various non-negative powers have been determined for the family of diatomic molecules of the lithium halides, LiF, LiCl, LiBr and LiI, with the corresponding results of LiH included for purposes of comparison. Trends are evident in the coefficients of lower order, but those of higher order are susceptible not only to the influence of the extent and quality of the data but also to the truncation of the power series in the representations. The various radial functions are valid with the specified ranges of internuclear-

distance depending on the maximum extent of vibrational excitation of the spectra.

INTRODUCTION

Although the binary compounds of lithium with the halogen elements and hydrogen occur as crystalline materials under customary conditions in the laboratory, at sufficiently elevated temperatures the vapours above these solids contain diatomic molecules and possibly aggregates thereof. Under these conditions one may observe the discrete spectra of the diatomic molecules in absorption or emission. For instance when a tube of alumina containing LiF was heated to at least 1200 K, about 1100 emission lines due to vibration-rotational transitions of $^7Li^{19}F$ and $^6Li^{19}F$ in the sequence $\Delta v=1$ were detected in the mid infrared spectral region.[1] Previously a further 37 pure rotational transitions of the same isotopic species had been measured in absorption in the microwave spectral region.[2-4] These combined data provide a basis to determine not only the principal function, the potential energy, that governs the vibrational and rotational motions of the nuclei, but prospectively also other minor functions that take into effect the failure of the discrete molecular energies to follow accurately scaling laws based on the atomic or nuclear masses. The deviations from these laws provide information about the adiabatic effects, arising because the molecular energy depends on not only the internuclear distance, according to the separation of electronic and nuclear motions achieved by Born and Oppenheimer, but also the relative nuclear momenta, and the nonadiabatic effects, arising because the electrons fail to follow perfectly the nuclei during the vibrational and rotational motions of the latter. Because the energies of electronic ground states of most diatomic molecules, within which the observable pure rotational and vibration-rotational transitions occur, are relatively remote from the energies of other electronic states, one can consider these adiabatic and nonadiabatic effects as perturbations such that the corresponding treatment of their functional dependence on internuclear distance, like that of potential energy, becomes feasible.

We have developed an analytic theory that makes practicable the process of spectral inversion, i.e. the extraction by direct reduction, from the frequencies and wavenumbers of the known transitions, of the parameters of the various radial functions.[5] Reduction to this form enables both the most compact and the most chemically and physically meaningful representation of the spectral data.[6] In the application of this theory to several diatomic species,[7,8] we have generated the coefficients of the pertinent functions in sufficient numbers that discernment of trends of the numerical values of the coefficients according to chemical relationships becomes practicable. One chemical family for which sufficient spectral data are available contains the halides of lithium—LiF, LiCl, LiBr and LiI—to which for comparison we add the related species LiH. These diatomic molecules are strongly polar: their permanent electric dipolar moments lie in the range/10^{-30} C m [15, 30].[9]

PRINCIPLE OF THE METHOD

The salient features of the procedure we recall here as a basis to understand the results of our calculations on the lithium compounds. The effective potential energy governing the internuclear vibration and rotation (about the centre of molecular mass) of a diatomic molecular species LiX within a particular electronic state of type $^1\Sigma$ contains at most five determinable radial functions, expressed

$$V_{eff} = c_0 z^2 (1 + \sum_{j=1} c_j z^j) + \sum_{j=1} m_e h_j^{Li} z^j / M_{Li} + \sum_{j=1} m_e h_j^X z^j / M_X$$

$$+ B_e J(J+1)[1 + \sum_{j=0} m_e g_j^{Li} z^j / M_{Li} + \sum_{j=0} m_e g_j^X z^j / M_X] R_e^2/R^2 \qquad (1)$$

in which m_e is the electronic rest mass, M_{Li} and M_X are the masses of the separate atoms of types Li and X distinguished by their atomic numbers, and the reduced variable z for displacement of internuclear separation R from the equilibrium distance R_e is defined[10,11]

$$z \equiv 2\ (R - R_e)/(R + R_e) \qquad (2)$$

The functions involving the coefficients $h_j^{Li,X}$ take empirically into account collectively the vibrational adiabatic effects and the nonadiabatic effects associated with vibrational inertia of the electrons, because other effects have different dependences on atomic mass which make them currently negligible with respect to the experimental error of frequency measurements.[12] The functions involving the coefficients $g_j^{Li,X}$ embody the nonadiabatic effects of the rotational inertia of the electrons, and to some extent also the nonadiabatic effects of the vibrational inertia of the electrons. The two nonadiabatic effects may be considered to arise from interactions between electronic states induced by the vibrational and rotational motions of the nuclei respectively. Defined according to equation 1, all coefficients c_j, $g_j^{Li,X}$ and $h_j^{Li,X}$ are formally independent of mass, and dimensionless (except c_0 and $h_j^{Li,X}$ having units m^{-1}).

Because for LiF and LiI data of F and I of only one nuclidic type each are available, we consider no further the effects of variation of the latter nuclear masses; hence we specify g_j^{Li} and h_j^{Li} as the parameters to treat the features of the spectra of LiF and LiI that depend on the mass of the Li nuclei. For the other molecules, even though data exist for transitions involving isotopic variants of each nuclide, these data may prove of insufficient quality and quantity to allow the significant determination of parameters of all five functions. 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 systematic form,[13]

$$E_{vJ} = \sum_{k=0} \sum_{l=0} (Y_{kl} + Z_{kl}^{h,Li} + Z_{kl}^{h,X} + Z_{kl}^{g,Li} + Z_{kl}^{g,H}) (v+\tfrac{1}{2})^k [J(J+1)]^l \quad . \qquad (3)$$

In this equation in which the explicit isotopic dependence of E_{vJ} and the coefficients Y_{kl} and Z_{kl} has been suppressed to simplify the notation, the coefficients Y_{kl} are supposed to reflect purely the internuclear potential energy V(z) and the centrifugal motion of the nuclei and associated electrons; the remaining coefficients, Z_{kl} of four varieties, pertain respectively to the obviously corresponding terms considered as perturbations separately additive in the effective potential energy according to equation 1. The distinction between $Z_{kl}^{h,Li}$ and $Z_{kl}^{g,Li}$, and equivalently for the other two coefficients $Z_{kl}^{h,X}$ and $Z_{kl}^{g,X}$ of each partner X, is practicable only because of the structure within each coefficient Z_{kl}, i.e. its dependence on the parameters in the various radial functions containing coefficients g_j and h_j;[12] hence the latter expressions are effective functions in terms of the more fundamental but difficultly separable adiabatic and nonadiabatic effects.

The method of estimation of nonlinear parameters we apply to determine the applicable coefficients c_j,

g_j and h_j directly from the wavenumbers $\tilde{\nu}$ of the pure rotational and vibration-rotational transitions as in each case pure rotational transitions have been measured in the microwave region and vibration-rotational transitions in the mid infrared region. Each wavenumber $\tilde{\nu}$ of a transition is the difference of the two terms E_{vJ} of the combining states; the criterion of convergence of a fit to a particular model is that the sum of the squares of the weighted residuals between the measured and calculated values, $\tilde{\nu}_{obs} - \tilde{\nu}_{calc}$, is a minimum, hopefully the global minimum (apart from possibly the united atom), with the weights being the squared reciprocals of the estimated uncertainties of the measurements. All uncertainties in the tables represent one estimated standard error; for R_e and the force coefficient k_e the stated uncertainties take into account also the error in the pertinent fundamental constants.[14] The atomic masses of H, Li, F, Cl, Br and I are drawn from the latest consistent set.[15]

RESULTS AND DISCUSSION

The set of input data for LiH differs from that in previous determinations of the radial functions in that only 539 unduplicated transitions are included from measurements of pure rotational lines in the millimetre-wave region[16,17], and pure rotational and vibration-rotational lines in the infrared region,[18,19] for the isotopic variants $^6Li^1H$, $^6Li^2H$, $^7Li^1H$ and $^7Li^2H$. Almost all data of Yamada and Hirota[18] were excluded because the residuals between those measured wavenumbers and the ones calculated from the parameter sets in tables 1 and 2 generally significantly exceeded the estimated uncertainties of those measurements,

TABLE 1

Coefficients of the Potential-energy Function and Related Molecular Properties of Diatomic Lithium Compounds X $^1\Sigma^+$

Parameter	LiH	LiF	LiCl	LiBr	LiI
c_0/m^{-1}	6572489.4 ±7.2	15409075.2 ±4.8	14627923.7 ±14.7	14231154.8 ±19.7	13926628.3 ±17.0
c_1	-0.8972750 ±0.0000130	-1.7012917 ±0.0000163	-1.7196467 ±0.0000125	-1.714944 ±0.000053	-1.723039 ±0.000054
c_2	0.3481105 ±0.000092	1.751183 ±0.000087	1.693281 ±0.000065	1.67871 ±0.00036	1.64130 ±0.00026
c_3	-0.086493 ±0.00041	-1.09714 ±0.00032	-0.94901 ±0.00031	-0.95979 ±0.00194	-0.85051 ±0.00196
c_4	-0.0473 ±0.0021	0.12398 ±0.00136	-0.11548 ±0.00163	-0.0214 ±0.0199	-0.2032 ±0.0148
c_5	-0.0257 ±0.0056	0.3279 ±0.0045	0.8323 ±0.0053	0.5647 ±0.067	0.8890 ±0.048
c_6	0.0939 ±0.0106	1.1474 ±0.0113	-0.4777 ±0.025	-0.354 ±0.171	-0.439 ±0.143
$k_e/N\ m^{-1}$	102.65118 ±0.00019	250.30698 ±0.00019	142.32917 ±0.00010	120.02315 ±0.00021	96.69858 ±0.00019
$R_e/10^{-10}m$	1.5949112 ±0.0000014	1.5638869 ±0.0000015	2.0206817 ±0.0000022	2.1704066 ±0.0000019	2.3920293 ±0.0000021

TABLE 2

Coefficients of Other Radial Functions of Diatomic Lithium Compounds X $^1\Sigma^+$

Parameter	LiH	LiF	LiCl	LiBr	LiI
$h_1^{Li}/10^6 m^{-1}$	-0.723 ±0.045	5.64 ±0.14	4.761 ±0.083	[-3.0]	13.4 ±2.3
$h_2^{Li}/10^6 m^{-1}$	0.294 ±0.126	-16.84 ±0.50	-15.41 ±0.29		
$h_3^{Li}/10^6 m^{-1}$		7.57 ±2.5	16.92 ±1.76		
$h_1^{X}/10^6 m^{-1}$	-10.2387 ±0.0034		-15.14 ±1.22		
$h_2^{X}/10^6 m^{-1}$	15.1529 ±0.0117				
$h_3^{X}/10^6 m^{-1}$	-14.630 ±0.25				
$h_4^{X}/10^6 m^{-1}$	13.255 ±0.81				
g_1^{Li}	0.384 ±0.107	0.869 ±0.047	1.196 ±0.065		
g_1^{X}	0.777±0.028				
g_2^{X}	-0.490±0.100				

although the residuals showed no systematic trend of signs, i.e. generally positive or generally negative differences between observed and calculated values; the removal of transitions that duplicated measurements in the larger set of data[19] led to an improved normalised standard deviation $\bar{\sigma}$= 1.061, negligibly larger than the uncertainties attached to the various measurements. For this reason also the values of the corresponding parameters in tables 1 and 2 differ, although only slightly, from those previously reported,[20] but are determined more significantly. The maximum range of validity of the radial functions of LiH is $1.25 \leqslant R/10^{-10}$ $m \leqslant 2.18$.

The 1152 data of LiF include 37 pure rotational transitions in the microwave region,[2-4] and 1115 vibration-rotation transitions in the infrared region[21,1] in the sequence $\Delta v=1$ up to $v'=8$, for the isotopic variants $^{6}Li^{19}F$ and $^{7}Li^{19}F$. As the uncertainties of measurement associated with most infrared data were estimated conservatively,[1] the resulting normalised standard deviation of the fit, 0.707, was significantly less than unity. The previous fit[1] of the major collection of data was not applied to produce a potential-energy function. In our fit all parameters of that function were well determined; of the four parameters to describe the adiabatic and nonadiabatic effects h_3^{Li} exhibited only moderate significance. The maximum range of validity of the radial functions of LiF is $1.32 \leqslant R/10^{-10}$ $m \leqslant 2.03$.

The 2577 data of LiCl consist of 68 pure rotational transitions in the microwave region,[2,22,23] and 2509 vibration-rotational transitions[24,25] in the infrared region in the sequence $\Delta v=1$ up to $v'=8$, for the isotopic variants $^{6}Li^{35}Cl$, $^{6}Li^{37}Cl$, $^{7}Li^{35}Cl$ and

$^7Li^{37}Cl$. The normalised standard deviation of the fit, 0.993, is essentially unity, as a result of both the careful weighted constituent data and an efficient fit. By means of our improved fitting program we achieved this fit by means of only 13 independent parameters, all significantly determined, compared with 16 independent parameters in the results previously reported.[26] The maximum range of validity of the radial functions of LiCl is $1.72 \leqslant R/10^{-10}\ m \leqslant 2.54$.

The 1018 data of LiBr consist of 14 pure rotational lines in the microwave region,[2,27,28] and 1004 vibration-rotational lines[29] in the infrared region in the sequence $\Delta v=2$ up to $v'=9$, for the isotopic variants $^6Li^{79}Br$, $^6Li^{81}Br$, $^7Li^{79}Br$ and $^7Li^{81}Br$. The normalised standard deviation of the fit was 1.0052 with only nine independent parameters; although h_1^{Li}, previously undetermined,[26] was only marginally determined here, the related parameter $\Delta_{0,1}^{Li}$ appeared well determined in that fit to the coefficients U_{kl} and $\Delta_{0,1}^{Li}$.[29] We obtained a value of h_1^{Li} not by a direct fit but rather by separate trials with varied values to discover which set of parameters yielded the maximum value of the F statistic. The maximum range of validity of the radial functions of LiBr is $1.84 \leqslant R/10^{-10}\ m \leqslant 2.73$.

The 116 data of LiI include seven pure rotational transitions in the microwave region,[2,27] and 109 vibration-rotational lines in the infrared region in the sequence $\Delta v=2$ up to $v'=10$;[30] of all these data only two microwave transitions belong to $^6Li^{127}I$, the remainder pertaining to the dominant isotopic variant $^7Li^{127}I$. Being based on only these two measurements, determination of the coefficient h_1^{Li} proved difficult; after its value was found reasonably precisely in a preliminary fit, this value was constrained in later fits to determine the potential-energy coefficients with decreased correlation coefficients. According to this strategy, the normalised standard deviation of the fit became 0.774, indicating conservative estimation of the uncertainties of the infrared data.[30] The maximum range of validity of the radial functions of LiI is $2.03 \leqslant R/10^{-10}\ \mathrm{m} \leqslant 3.00$.

CONCLUSION

On the basis of the generated sets of coefficients of the radial functions (within the specified ranges) of diatomic molecules in this family of the lithium halides, some trends are discernible in the values of the parameters. For instance, according to table 1 the magnitudes of c_0, c_2, c_3 and k_e decrease systematically from LiF to LiI, whereas the magnitudes of R_e and c_1 increase in the same order. Trends for c_4-c_6 are less evident because these coefficients are more susceptible both to the extent and quality of the data sets and to the truncation of the polynomials in the representation. In table 2 the values of h_1^{Li}, h_2^{Li} and g_1^{Li} of LiF and LiCl are comparable. These similarities and trends indicate the physical and chemical significance of the results in the forms of these effective radial functions.[6] Even though according to some chemical and physical properties LiH might be considered to resemble the lithium halides, there are more contrasts than similarities in the corresponding spectral data appearing in tables 1 and 2.

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REFERENCES

1. Hedderich H G, Frum C I, Engleman R, Bernath P F. Infrared Emission Spectra of LiF and HF. Can. J. Chem. 1991; 69: 1659-1671.

2. Honig A, Mandel M, Stitch M L, Townes C H. Microwave Spectra of the Alkali Halides. Phys. Rev. 1954; 96: 629-642.

3. Wharton L, Klemperer W, Gold L P, Strauch R, Gallagher J J, Derr V E. Microwave Spectrum, Spectral Parameters and Electric Dipole Moment of Lithium Fluoride. J. Chem. Phys. 1963; 38: 1203-1210.

4. Pearson E F, Gordy W. Millimetre- and Submillimetre-wave Spectra and Molecular Parameters of LiF and LiCl. Phys. Rev. 1969; 177: 52-58.

5. Ogilvie J F. Radial Functions of LiH X $^1\Sigma^+$ from Vibration-rotational Spectra. J. Mol. Spectrosc. 1991; 148: 243-249.

6. Ogilvie J F. The Physical Significance of Energy Coefficients of Diatomic Molecules. Spectrochim. Acta 1990; 46A: 43-46.

7. Ogilvie J F. Radial Functions of SiS X $^1\Sigma^+$ from Vibration-rotational Spectra. Chem. Phys. Lett. 1991; 183: 40-44.

8. Ogilvie J F. Radial Functions of the Diatomic Metal Hydrides AgH, GaH, InH and TlH from Vibration-rotational Spectra. Chem. Phys. Lett. 1992; 191: 592-598.

9. McClellan A L. *Tables of Experimental Dipole Moments* vol. 3. El Cerrito, U.S.A.: Rahara, 1989.

10. Ogilvie J F. A General Potential-energy Function for Diatomic Molecules. Proc. Roy. Soc. London 1981; A378: 287-300, 1982; A381: 479.

11. Ogilvie J F. Extension of a General Potential-energy Function for Diatomic Molecules. J. Chem. Phys. 1988; 88: 2804-2808.

12. Fernandez F M, Ogilvie J F. An Analytic Treatment of Adiabatic and Nonadiabatic Effects on the Vibration-rotational Energies of Diatomic Molecules. Chin. J. Phys. 1992; 30: 177-193.

13. Dunham J L. The Energy Levels of a Rotating Vibrator. Phys. Rev. 1932; 41: 721-731.

14. Cohen E R, Taylor B N. The 1986 Adjustment of the Fundamental Physical Constants. Rev. Mod. Phys. 1987; 59: 1121-1148.

15. Wapstra A H, Audi G. The 1983 Atomic Mass Evaluation; I. the Atomic Mass Table. Nucl. Phys. 1985; A432: 1-54.

16. Pearson E F, Gordy W. Millimetre-wave Spectra and Molecular Parameters of ^{6}LiD and ^{7}LiD. Phys. Rev. 1969; 177: 59-61.

17. Plummer G M, Herbst E, DeLucia F C. Submillimetre-wave Spectra and Molecular Parameters of ^{6}LiH, ^{7}LiH, ^{6}LiD and ^{7}LiD. J. Chem. Phys. 1984; 81: 4893-4897.

18. Yamada C, Hirota E. Infrared Diode-laser Spectroscopy of Lithium Hydride. J. Chem. Phys. 1988; 88: 6702-6706.

19. Maki A G, Olson W B, Thompson G. Infrared Measurements of the Rotational and Vibrational Spectra of LiH and LiD. J. Mol. Spectrosc. 1990; 144: 257-268.

20. Ogilvie J F. Radial Functions of LiH X $^{1}\Sigma^{+}$ from Vibration-rotational Spectra: Correction and Extension. J. Mol. Spectrosc. 1992; 154: in press.

21. Maki A G. Infrared Spectra by Tunable Diode Laser of Lithium Fluoride at High Temperatures. J. Mol. Spectrosc. 1983; 102: 361-367.

22. Lide D R, Cahill P, Gold L P. Microwave Spectrum of Lithium Chloride. J. Chem. Phys. 1964; 40: 156-159.

23. Story T. L. *Dipole Moments of Alkali Halides by the Method of Electric Deflection*. Ph. D. Dissertation, University of California, Lawrence Radiation Laboratory, Berkeley, U.S.A. 1968.

24. Jones H, Lindenmayer J. Diode-laser Spectroscopy of Lithium Chloride at Elevated Temperatures. Chem. Phys. Lett. 1987; 135: 189-192.

25. Thompson G A, Maki A G, Olson W B, Weber A. High-resolution Infrared Spectrum of the Fundamental Band of LiCl at 830 °C. J. Mol. Spectrosc. 1987; 124: 130-138.

26. Ogilvie J F, Ho M C C. Radial functions and the Nature of the Binding in LiCl and LiBr. J. Mol. Struct. 1991; 263: 167-175.

27. Rusk J R, Gordy W. Millimetre-wave Spectroscopy of Molecular Beams of Alkali Bromides and Iodides. Phys. Rev. 1962; 127: 817-830.

28. Hebert A J, Breivogel F W, Street K. Radiofrequency and Microwave Spectra of LiBr by the Method of Molecular Beam and Electric Resonance. J. Chem. Phys. 1964; 41: 2368-2376.

29. Brazier C R, Oliphant N H, Bernath P F. Spectra of Lithium Bromide with a Diode Laser. J. Mol. Spectrosc. 1989; 134: 421-432.

30. Thompson G, Maki A G, Weber A. Infrared Spectroscopy by Tunable Diode Laser of the $\Delta v=2$ Sequence of $^7Li^{127}I$. J. Mol. Spectrosc. 1986; 118: 540-543.

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