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Radial functions and the nature of the binding in LiCl and LiBr

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Abstract

The radial functions for the potential energy and the adiabatic and non-adiabatic effects have been determined in the range $1.72 \leqslant R/10^{-10}\ m \leqslant 2.54$ for the gaseous diatomic molecule LiCl and in the range $1.84 \leqslant R/10^{-10}\ m \leqslant 2.73$ for the LiBr molecule, both in the electronic ground state $X^1\Sigma^+$, directly from the published frequencies and wavenumbers of pure rotational and vibration-rotational transitions. The fit of these data using ionic masses was improved insignificantly relative to the fit using atomic masses. The frequency and wavenumber data for transitions among vibration-rotational states up to $0.15D_e$ provide no clear evidence of the strongly polar binding in these molecules.

INTRODUCTION

The internuclear distance R is the particular structural variable of a diatomic molecule upon which the observable properties are taken to depend within the Born–Oppenheimer approximation. The process of reduction of vibration–rotational spectra then leads to the determination of the parameters in the radial functions that pertain to the applicable properties. For data in the form of frequencies or wavenumbers of those spectral lines arising from pure rotational or vibration–rotational transitions in the absence of electromagnetic fields (other than that due to the radiant energy required for the observations), the applicable properties are the potential energy and certain auxiliary radial functions related to the adiabatic and non-adiabatic effects that govern collectively how the total energy of the molecule within a particular electronic state varies as a function of the internuclear distance. The adiabatic effects arise essentially from the fact that the nuclear masses are finite, whereas the non-adiabatic effects result from coupling between electronic states induced by the rotational and vibrational motions. Therefore the ultimate re-

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duction of frequency data from spectra of these types yields the values of the parameters in these radial functions according to some assumed forms [1]. Although the primary structural descriptor of a diatomic molecule is indeed its equilibrium internuclear separation R_e, the radial function for potential energy, of which R_e is merely a particular point, is just as important in relation to the spectral and thermodynamic properties because it governs the population of the states of vibration–rotational energy of the diatomic molecule at thermal equilibrium at any temperature exceeding 0 K. Moreover, without careful determination not only of the potential-energy function but also of the related radial functions for adiabatic and non-adiabatic effects, the value of R_e may only be determined inaccurately.

We have developed a new algorithm to determine the parameters in the applicable radial functions directly from the frequencies and wavenumbers of pure rotational and vibration–rotational transitions of diatomic molecules within an electronic state of the type $^1\Sigma$ [2]. The method makes use of all available data for all known isotopic variants; the existence of a large amount of data for a sufficiently large number of isotopically substituted species, relative to the most abundant set of nuclides, of both atomic types if the molecule is heteronuclear, is essential for complete determination of the applicable functions within a finite range of internuclear distance. Extensive and precise data for the vibration–rotational absorption spectra of gaseous diatomic molecules at equilibrium above the crystalline solid at elevated temperatures have recently been reported for four variants of LiCl, namely $^6\mathrm{Li}^{35}\mathrm{Cl}$, $^6\mathrm{Li}^{37}\mathrm{Cl}$, $^7\mathrm{Li}^{35}\mathrm{Cl}$ and $^7\mathrm{Li}^{37}\mathrm{Cl}$ [3,4], and for four variants of LiBr, namely $^6\mathrm{Li}^{79}\mathrm{Br}$, $^6\mathrm{Li}^{81}\mathrm{Br}$, $^7\mathrm{Li}^{79}\mathrm{Br}$ and $^7\mathrm{Li}^{81}\mathrm{Br}$ [5]. These results complement the previously published pure rotational transitions for the same sets of isotopic variants of LiCl [6–8] and LiBr [9–11]. The vibrational states are sampled up to $v=8$ for LiCl and to $v=9$ for LiBr, and the rotational states up to $J=80$ and $J=90$ respectively. These data provide an excellent opportunity to exploit our algorithm; by this means we have determined for each molecule the coefficients contained within four radial functions that satisfactorily reproduce the measured spectra, within the precision of the measurements and with no systematic deviations. The interpretation of these data enables some discussion of the chemical binding in these polar molecules.

COMPUTATIONAL METHOD FOR DETERMINATION OF THE RADIAL FUNCTIONS

The effective potential energy governing the internuclear vibration and rotation (about the centre of molecular mass) of a diatomic molecule within a particular electronic state of type $^1\Sigma$ we suppose to have the form [2]

$$V_{\mathrm{eff}}=c_0z^2\left(1+\sum_{j=1}c_jz^j\right)+\sum_{j=1}m_\mathrm{e}h_j^\mathrm{a}z^j/M_\mathrm{a}+\sum_{j=1}m_\mathrm{e}h_j^\mathrm{b}z^j/M_\mathrm{b}$$

$$+B_\mathrm{e}J(J+1)\left[1+\sum_{j=0}m_\mathrm{e}g_j^\mathrm{a}z^j/M_\mathrm{a}+\sum_{j=0}m_\mathrm{e}g_j^\mathrm{b}z^j/M_\mathrm{b}\right]R_\mathrm{e}^2/R^2 \tag{1}$$

in which m_e is the electronic rest mass, M_a and M_b are the masses of the separate atoms of types a and b (in this case Li and Cl or Br respectively), and the reduced variable z for displacement of the internuclear distance R from equilibrium at R_e is defined as [12,13]

$$z\equiv2(R-R_\mathrm{e})/(R+R_\mathrm{e}) \tag{2}$$

The functions involving the coefficients $h_j^{\mathrm{a,b}}$ empirically take into account mainly adiabatic effects and non-adiabatic effects related to the vibrational inertia of the electrons, because other effects have different dependencies on the atomic mass which makes them currently negligible with respect to the experimental error of frequency measurement [2]. The functions involving the coefficients $g_j^{\mathrm{a,b}}$ empirically take into account predominantly the non-adiabatic effects related to the rotational inertia of the electrons [2]. Defined according to eqn. (1), all coefficients c_j, $g_j^{\mathrm{a,b}}$ are formally independent of mass, and dimensionless except for c_0 and $h_j^{\mathrm{a,b}}$. As a consequence of the various contributions to the effective potential energy, the vibration–rotational terms consist of several contributions; the expression for these terms is an extension of Dunham's form [14–16]

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

In this equation the coefficients Y_{kl} are supposed to result from the purely mechanical motions of the nuclei and the associated electrons, in the sense that one is able, according to classical mechanics, to at least provide semiquantitative treatment [17] of these motions for the purpose of spectral analysis. The remaining coefficients, the four components of Z_{kl}, reflect respectively the obviously corresponding terms that may be considered as separately additive perturbations in the effective potential energy according to eqn. (1). We have published in machine-readable form analytic expressions [18] of the coefficients Y_{kl} as functions of the harmonic coefficient k_e (implicitly contained within $U_{1,0}$ or ω_e), the equilibrium separation R_e (implicitly contained within $U_{0,1}$ or B_e), the potential-energy coefficients c_j up to $j=10$ and, implicitly, the reduced mass [19]. Further expressions containing coefficients up to $j=16$ have been generated according to hypervirial perturbation theory [20]. The coefficient c_0 in eqn. (1) is defined in terms of either $U_{1,0}$ and $U_{0,1}$, $c_0=U_{1,0}^2/(4U_{0,1})$, or equivalently in terms of k_e and R_e, $c_0=k_\mathrm{e}R_\mathrm{e}^2/(2ch)$ (the fundamental physical constants c and h enter because E_{vJ}, Y_{kl} and Z_{kl} are all expressed in units of wavenumber for spectroscopic applications). Each term coefficient Y_{kl} and Z_{kl} consists of contributions in series [21]

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

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

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

$$Y_{kl}^{(0)} = U_{kl}\mu^{(\frac{1}{2}k+1)} \tag{6}$$

the coefficients U_{kl} become formally independent of mass. Although we have generated some expressions for the contributions $Y_{kl}^{(6)}$ and $Y_{kl}^{(8)}$, containing coefficients c_j up to $j = 16$, only the leading terms $Y_{kl}^{(0)}$ and the first two corrections $Y_{kl}^{(2)}$ and $Y_{kl}^{(4)}$ are required at present because the effects of the experimental errors in wavenumber measurements exceed the magnitudes of further corrections. For each of the four components of Z_{kl} even the first correction $Z_{kl}^{(2)}$ is negligible for the same reason; moreover, additional terms cannot be included consistently without account being taken of the interactions 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 g_j and h_j for nucleus a and nucleus b, in addition to k_e, R_e and μ. A few expressions for Z_{kl}^h in terms of c_j and h_j have already been published in a slightly different form [21]. However, these are readily converted to become consistent with the present definition according to eqn. (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 reported [2]; a larger collection containing g_j up to $j = 10$ will also be published in machine-readable form.

As described elsewhere [2], we have applied the method of non-linear parameter estimation to determine directly the applicable coefficients c_j, $g_j^{a,b}$ and $h_j^{a,b}$ from the frequencies ν 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 best fit is that the sum of the squares of the 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). The algorithm of the fitting process employs the analytic expressions not only for the term coefficients Y_{kl} and the various components of Z_{kl} but also for the first (partial) derivatives of Y_{kl} and Z_{kl} with respect to the parameters, for instance $\partial Y_{kl}/\partial c_j$, $\partial Y_{kl}/\partial U_{1,0}$ and $\partial Z_{kl}/\partial h_j$. The analytic expressions for the former derivatives up to $j = 10$ have already been published in machine-readable form [19]; expressions for further derivatives of Y_{kl} and for the derivatives $\partial Z_{kl}^g/\partial g_j$ and $\partial Z_{kl}^h/\partial h_j$ will form part of the large collection to be published subsequently. That the dependencies of the residuals on the masses M_a, M_b and on J differ makes possible the determination of the coefficients g_j^a, g_j^b, h_j^a and h_j^b.

APPLICATION TO THE FREQUENCY AND WAVENUMBER DATA OF LiCl AND LiBr

The available data of LiCl consist of 68 pure rotational transitions, involving rotational states up to $J=11$ in the vibrational states $0 \leqslant v \leqslant 3$ [6–8], 93 vibration–rotational lines up to $v=5$ and $J=59$ [3], and 2509 vibration–rotational transitions up to $v=8$ and $J=80$ [4]. The correction $-0.03\ \mathrm{m}^{-1}$ was applied to all the latter data [4]. All but eight lines in the smaller set of data [3] duplicated transitions in the larger set [4]; for this reason we used these eight lines to supplement the 2509 lines, to make a total of 2585 independent transitions. With the 17 independent parameters of LiCl given in Table 1, the standard deviation of the fit of the 2577 lines was $0.0289\ \mathrm{m}^{-1}$, equivalent to the uncertainties attached to the infrared measurements [4]. However, the average magnitude of the deviation between the observed and calculated values of the eight additional lines [3] was five such standard deviations, with no systematic trend; for this reason the wavenumbers of these eight lines were given small weights, such that their values had essentially no effect on the values of the parameters. These 17 parameters provide a fit to all the data that is worse than the 19 freely fitted parameters of types U_{kl} and Δ_{kl}, with a further nine parameters of type U_{kl} constrained in the previous fit of the large data set [4], and even slightly worse than the 13 parameters of type U_{kl}, Δ_{kl} and a_j (potential-energy coefficients in the Dunham function [14]). Jones and Lindenmayer were unable to determine the mass-independent parameters in their work [3]; they fitted the wavenumbers of $^{7}\mathrm{Li}^{35}\mathrm{Cl}$, $^{7}\mathrm{Li}^{37}\mathrm{Cl}$ and $^{6}\mathrm{Li}^{35}\mathrm{Cl}$ separately to the coefficients Y_{kl}, requiring 27 parameters to fit their 93 lines with a standard deviation $0.13\ \mathrm{m}^{-1}$. Although the latter is almost the same value as the average deviation of the eight unduplicated lines calculated with the parameters in the Table, the fact that this standard deviation is based on a much smaller data set naturally tends to augment its size. With respect to the set of 13 parameters [4], the set of potential-energy coefficients c_j, $0 \leqslant j \leqslant 8$, in the Table exceeds the set of related coefficients a_j, $0 \leqslant j \leqslant 7$, although from the determination of a significant value of $U_{5,0}$ or $Y_{5,0}$ we infer that a significant value of a_8 could have been determined [4]. Although the value of $c_8 = -7.686 \pm 2.6$ appears poorly determined, its presence in the set of parameters decreases the variance of the fit, and the correlation coefficients (covariances) connecting c_8 to the other parameters lack unduly large magnitudes. The coefficients $h_j^{\mathrm{Li,Cl}}$ are related to the spectral parameters $\Delta_{kl}^{\mathrm{Li,Cl}}$, of which five were previously determined [4]; the one further parameter $h_4^{\mathrm{Li}}/10^6\ \mathrm{m}^{-1} = 82.06 \pm 12.1$ is required, like c_8, and the magnitudes of its correlation coefficients are not near

TABLE 1

Coefficients of the radial functions and other properties of the diatomic molecules LiZ (Z = Cl or Br) in the state $X^1\Sigma^+$

j	c_j	g_j^{Li}	g_j^Z	$h_j^{Li}/10^6\,m^{-1}$	$h_j^Z/10^6\,m^{-1}$
LiCl					
0	$(14627863.54 \pm 10.3)\ m^{-1}$	0	0	-	-
1	-1.7195628 ± 0.0000154	1.098 ± 0.063	0	4.915 ± 0.083	-15.25 ± 1.20
2	1.692992 ± 0.000088	0	0	-15.144 ± 0.300	
3	-0.949478 ± 0.00071			1.422 ± 2.34	
4	-0.10895 ± 0.0048			82.06 ± 12.1	
5	0.8553 ± 0.025				
6	-0.8349 ± 0.170				
7	0.827 ± 0.86				
8	-7.686 ± 2.6				
$U_{1,0} = (155425.969 \pm 0.066)\ m^{-1}\ amu^{1/2}$					
$U_{0,1} = (412.857730 \pm 0.000052)\ m^{-1}\ amu$					
$k_e = (142.32849 \pm 0.00012)\ N\ m^{-1}$					
$R_e = (2.02068244 \pm 0.00000217) \times 10^{-10}\ m$					
LiBr					
0	$(14231429.8 \pm 22.8)\ m^{-1}$	0	0	-	-
1	-1.715007 ± 0.000061	0	0	0	0
2	1.678978 ± 0.00042	0	0	0	
3	-0.96077 ± 0.0023				
4	-0.02137 ± 0.0231				
5	0.5723 ± 0.078				
6	-0.304 ± 0.199				
$U_{1,0} = (142727.369 \pm 0.137)\ m^{-1}\ amu^{1/2}$					
$U_{0,1} = (357.854097 \pm 0.000115)\ m^{-1}\ amu$					
$k_e = (120.02316 \pm 0.00024)\ N\ m^{-1}$					
$R_e = (2.1704275 \pm 0.00000186) \times 10^{-10}\ m$					

unity. The microwave data [6–8] prove important for sensitively determining the coefficients $h_j^{Li,Cl}$ (or equivalently $\Delta_{kl}^{Li,Cl}$); in their absence these coefficients are only poorly defined. The parameter $g_1^{Li} = 1.098 \pm 0.063$ is of a new type [2], not previously used in these fits of vibration–rotational spectral data to analytic functions. The relatively small standard error of this parameter indicates its great significance, such that in its absence small but significant systematic deviations in the previous fit to the potential-energy function could have been discerned [4]. Such effects in the spectra of various isotopic variants of LiH [22] were eliminated by the corresponding inclusion of g_1^{Li}, g_2^{Li} in the parameter set for the direct fit [23] of the pertinent microwave and IR data.

Although the IR data of LiBr extend over a larger range of both v and J than those of LiCl, the parameters required to fit the data are fewer for LiBr; eight parameters sufficed to provide a fit of the frequencies of the 14 microwave lines [9–1] and wavenumbers of the 1004 IR transitions [5] with a standard deviation 0.29 m^{-1}, comparable to the estimated precision 0.25 m^{-1} of the IR measurements [5]. No standard deviation of the previous fit was explicitly stated [5], but comparison of the former values of $U_{0,1}$, $U_{1.0}$ and $U_{1,1}$ with the present values of $U_{0,1}$, $U_{1,0}$ and c_1 indicates that the present fit may be a slight improvement. The previous fit required 12 parameters of the type U_{kl} and only one coefficient $\Delta_{0,1}^{\mathrm{Li}}$, whereas during the present fit we significantly determined a value of neither coefficients $h_j^{\mathrm{Li,Br}}$ nor g_1^{Li}. The extent of the potential-energy coefficients c_j, $0 \leqslant j \leqslant 6$, is consistent with the significant determination of the spectral parameters U_{kl} up to $U_{4,0}$ in the previous fit [5].

All uncertainties in the Table represent one estimated standard error, and the uncertainties in k_e and R_e also take into account the error in the appropriate fundamental constants [24]. The ranges of validity of the radial functions defined by the coefficients in the Table correspond approximately to those $(1.72–2.54) \times 10^{-10}$ m for LiCl and $(1.84–2.73) \times 10^{-10}$ m for LiBr between the classical turning points for the highest vibrational state, $v=8$ and $v=9$ respectively, to which transitions were measured.

RELATION TO THE CHEMICAL BINDING IN LiCl AND LiBr

Both LiCl and LiBr are strongly polar molecules; the equilibrium values of the molecular electric dipole moments ($\times 10^{-29}$ C m) are 3.23748 [25] and 3.47739 [11] respectively. The latter values correspond to roughly 73% and 69%, respectively, of the dipole moments that would result from the separation of unit positive and negative electronic charges separated by the appropriate distance R_e. On this basis one wonders whether the effects of this polarity might be discerned in, for instance, the potential-energy function in the vicinity of R_e.

Kratzer [26] designed the first potential-energy function to treat polar molecules, specifically HF, HCl and HBr, which he supposed ionic; this potential-energy function, in which the term with the negative sign reflects the supposed coulombic attraction between the ions, is, in its simplest form,

$$V(R) = \omega_e^2 [1 - R_e/R]^2 / (4B_e) \tag{7}$$

When this function is transformed to the form $V(z)$ which corresponds to the first term of $V_{\mathrm{eff}}(z)$ in eqn. (1), the coefficients c_j take the values $c_1 = -1$, $c_2 = 3/4$, $c_3 = -1/2$, $c_4 = 5/16$, and in general $c_j = (-1)^j (j+1)/2^j$. Because these values obviously differ markedly from the values in Table 1, the applicability of this functional form for the potential energy of LiCl and LiBr is at least questionable. The present vibration–rotational transitions are between states that lie in the region of the minimum of potential energy, extending to only about 15% of the dissociation limit at D_e. The effects of the coulombic attraction, which undoubtedly exists at internuclear distances much greater than R_e, may hence be more directly discernible from transitions to states nearer the dissociation limit.

A different test of the effects of ionic binding is available through the effective masses of the atoms. According to the contemporary interpretation of the (classical) motions of a diatomic molecule [2] in relation to its vibration–rotational spectra, the nuclei vibrate and rotate with respect to the centre of molecular mass, their motions being perturbed by the influence of the electrons, which follow the nuclei imperfectly [27]. The applicable masses in eqns. (1) and (implicitly) (3) should in principle be the nuclear masses, not the atomic masses. Because the latter are much more accurately known than the former and because the resulting error is relatively much smaller than the error inevitably associated with the determination of the small corrections containing the coefficients $g_j^{\mathrm{Li,Z}}$ and $h_j^{\mathrm{Li,Z}}$ (Z = Cl or Br), atomic masses suffice in practice for the present purpose [2]. If however, the binding in the vicinity of R_e were essentially ionic, then it would be appropriate to use the ionic masses of Li^+ and Cl^- or Br^-. Such an effect has been demonstrated for BaCl [28], for which deviations from mass relations of isotopic variants were partially overcome by use of the reduced mass calculated from the masses of the ions Ba^+ and Cl^- rather than from the neutral atoms Ba and Cl. When we repeated the calculations on LiCl using the ionic masses of Li^+ and Cl^- rather than the atomic masses of Li and Cl, the fit was significantly worse than when we used the atomic masses. As would be expected from the formal lack of dependence on mass of the potential-energy coefficients c_j, their values differed negligibly between the two calculations; there were small but significant variations in both $U_{1,0}$ and $U_{0,1}$, and g_1^{Li}, h_j^{Li} and h_j^{Cl} also varied only slightly. In the case of LiBr the standard deviation of the fit with the ionic masses was much worse than that of the corresponding fit with the atomic masses. Because these tests disclosed no clear superiority of fit resulting from the use of the ionic masses instead of the atomic masses, we have maintained the conventional usage of the latter for the results presented in Table 1.

In summary, the frequency and wavenumber data of the pure rotational and vibration–rotational transitions involving states near the minimum of potential energy for both LiCl and LiBr yield no clear evidence of the nature of the binding in these molecules. In contrast, the intensities and Stark shifts of the rotational transitions, which directly reflect the electric dipole moment, strongly indicate the polar status of these molecules [6,9,25].

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