The Repulsive Potentials in Alkali Halide Molecules

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On the basis of literature values of various spectroscopic quantities, the "experimental" five derivatives (1st to 5th) of the repulsive functions at the equilibrium distance were evaluated for the 20 alkali halide molecules, retaining the truncated Rittner model for the attractive forces. A self-consistency test showed that the used experimental values are reliable.

Different analytical forms of the repulsive potential were then critically evaluated by comparison with the experimental derivatives. The repulsive functions were characterized by two, three, four or five empirical parameters. It has been shown that only functions with at least three parameters are sufficiently accurate to reproduce spectroscopic quantities such as β_e and γ_e: the classical two parameter functions appeared too crude in this context.

Key words: Repulsive potentials; Derivatives of the repulsive potentials; Alkali halide molecules.

1. Introduction

None of the proposed potentials for the two body interactions within biatomic molecules seems to satisfy a full range of applicability. For this reason the problem was re-examined, taking as a first example the alkali halide molecules. For these compounds, in the gas phase, a large amount of spectroscopic data is available in literature.

The potential energy function $\Phi(r)$ is usually expressed as the sum of an attractive term $A(r)$ formed by a long range coulombic term and two short range terms connected to the dipolar interaction and to the van der Waals (vdW) forces, respectively, and a repulsive short range term $B(r)$:

$$\Phi(r) = A(r) + B(r). \tag{1}$$

The model normally used is the one originally proposed by Rittner [1] and subsequently reviewed by Brumer and Karplus (BK) [2] as "truncated" Rittner (T-Rittner) model:

$$A(r) = -e^2/r - 0.5(\alpha_+ + \alpha_-)/r^4 - c_{+-}/r^6, \tag{2}$$

where r is the interionic distance, e the common absolute value of the ionic charge, α_+, α_- are the ionic polarizabilities and c_{+-} is the dipole-dipole coefficient.

The spectrum of the analytical forms proposed for the repulsive term is particularly wide [3, 4] and involves expressions with two or more parameters. The favorite function appears to be the exponential one, used by Rittner himself:

$$B(r) = a \exp(b\,r), \quad b < 0, \tag{3}$$

although more elaborated functions have been proposed, e.g. the one recently given by Ali and Hasan [5]:

$$B(r) = a\,r^{-2} \exp(b\,r^{1.5}). \tag{4}$$

In order to obtain explicit values for the two parameters a and b, the normal procedure has been to fit the first and second derivatives of (1) at the equilibrium distance r_e (Φ_n is the n-th derivative):

$$\Phi_1(r_e) = 0, \quad \Phi_2(r_e) = k_e, \tag{5}$$

where k_e is the force constant that can be calculated from the experimental vibrational frequency ω_e and the reduced mass μ of the molecule.

Values for the higher derivatives of $\Phi(r)$ at the equilibrium distance can be derived from other spectroscopic quantities (SQ). The required spectroscopic data and the various repulsive functions to which they are connected are summarized in Table 1.

In order to obtain the values of the repulsive functions, one must also evaluate (see (2)) the $A(r)$ term and its derivatives. Thus, apart from the r_e values which are known with high precision [6], figures for the ionic polarizabilities and the van der Waals coefficients are also necessary. Classical values for these quantities are those by Pauling reported in Table III

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Repulsive functions	Connected spectroscopic data
B	D_i
B_1	
B_2	k_e
B_3	k_e, α_e, B_e
B_4	$k_e, \alpha_e, B_e, \omega_e x_e$
or:	$k_e, \alpha_e, B_e, \beta_e$
B_5	$k_e, \alpha_e, B_e, \omega_e x_e, \gamma_e$

Table 1. Connection between spectroscopic quantities and the repulsive function at $r = r_e$.
D_i = dissociation energy in ions,
α_e = rotation-vibration coupling constant,
$\omega_e x_e$ = vibrational anharmonicity constant,
B_e, β_e, γ_e = rotational constants.

of [2]. More accurate values were reported later [7, 8]. The present calculations are based on this latter set*, but it should be noted that the classical Pauling values yield differences that do not appear substantial.

In addition to (5), the relations between the functions Φ_n at $r = r_e$ and the SQ are [3, 10]:

$$\Phi = -D_i\,, \tag{6}$$

$$\Phi_3 = -3\Phi_2(1 + \alpha_e \omega_e / 6B_e^2)/r_e\,, \tag{7}$$

$$\Phi_4 = 5\Phi_3^2/3\Phi_2 - \Phi_2\,\omega_e x_e (64\pi^2 c\,\mu)/h\,, \tag{8}$$

$$\Phi_4 = 57\Phi_2/2r_e^2 + 9\Phi_3/r_e + 1.5\Phi_3^2/\Phi_2 - \beta_e \omega_e^3 \Phi_2/(4r_e^2 B_e^4)\,, \tag{9}$$

$$\Phi_5 = 2\gamma_e \omega_e^2 \Phi_2/(r_e B_e)^3 - 60\Phi_2/r_e^3 - 40\Phi_3/r_e^2 - 10\Phi_3^2/(r_e\Phi_2) - 10\Phi_3^3/(3\Phi_2^2) + 3\Phi_4/r_e + 13\Phi_3\Phi_4/(3\Phi_2)\,, \tag{10}$$

where c is the velocity of light and h Planck's constant.

These equations have been used, as shown later, to obtain the experimental values of the derivatives $B_1 \div B_5$. In particular, the data collected by BK [2], supported by [6], were used for the following SQ: ω_e (to obtain B_2 with (5)), α_e and B_e (to obtain B_3 with (7)), $\omega_e x_e$ (to obtain B_4 with (8)) and γ_e (to obtain B_5 with (10)). On the other hand, these equations can obviously be used also to evaluate the SQ once the analytical expression for $B(r)$ is known. In this way, BK [2] used the exponential function (3), obtained with (5), to calculate the SQ's. They found that: "... the results for α_e and $\omega_e x_e$ are satisfactory ... the calculated values of γ_e and β_e are quite poor, while D_i are almost within the limits of experimental accuracy". They concluded that "... the T-Rittner model, like the Rittner model, gives reasonable results for some spectroscopic properties but is quite poor for others. The origin of these discrepancies is not clear, although they must arise from the failure of one or more of the assumptions ...". Similar conclusions were normally reached in other papers along with doubts on the accuracy of the literature values, so that recently the quantities β_e and γ_e were no longer recalculated.

In this paper the problem to obtain reliable repulsive potentials starting from SQ data was faced focusing on the prevision of the derivatives of the repulsive functions and on the significance of the spectroscopic properties that can be obtained.

2. Test of the SQ Data: Limits of D_i, β_e, γ_e

Equations (5) ÷ (10) with (1) show that, on the basis of the SQ, immediate figures should be available for B and $B_1 \div B_5$ at the equilibrium distance r_e. This is normally so for the derivatives $B_1 \div B_5$, while difficulties arise in the evaluation of the $B(r_e)$ which is connected to the experimental value D_i (see (6)). Experimental D_i values for the alkali halides were reported in [3c] and [2] (see Table 2 columns 2 and 3, respectively), the latter data being constantly larger by about 3.6%. According to Gaydon [11] the experimental error of these quantities is of about 2.5 kcal/mole or higher for the fluorides. Moreover, we found that the $A(r_e)$ and $B(r_e)$ terms represent, on the average, 85% and 15%, respectively, of the absolute value of $\Phi(r_e)$. Thus, with a fixed value for $A(r_e)$, an experimental uncertainty of 4% in D_i, becomes an uncertainty of 18–19% in $B(r_e)$. As a final result, the step $D_i \rightarrow B$ is accompanied by a factor of about 5 in the percentage error.

Since a direct, precise evaluation of $B(r_e)$ could not be performed, an indirect way was attempted: the experimental values of $B_1(r_e) \div B_5(r_e)$ were estimated through (5), (7), (8), (10) and used to obtain the function $B(r)$. The quantities D_i (from (6)) and β_e (from (9)) could then be used to test the fitted model.

As regards the quantity β_e, which ranges from fairly high absolute values to almost zero (see Table 2), it should be underlined that its weight in the $B_4(r_e)$ term (see (9)), averaged on the 20 alkali halides, is 2.7%, ranging from 0.1% (KBr, RbBr, CsBr) to 8.1% (LiF) (see Table 3). Thus in the step $B_4(r_e) \rightarrow \beta_e$ there is an

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* Polarizabilities from the DD model by BK (see [2], Tables VIII, IX) and vdW coefficients calculated with the Slater-Kirkwood equation [8, 9]. A second set of values, based on Shanker's equations and kindly supplied by M. S. Ali (private communication), gives only marginal variations.

Table 2. Comparison between the experimental [2, 3c, 6] and calculated (14) D_i (kcal/mole) and β_e (cm^{-1}) values.

Molecule	$D_{i,\,exp}$	$D_{i,\,exp}$	$D_{i,\,calc}$	% Error	$\beta_{e,\,exp}$	$\beta_{e,\,calc}$
LiF	178.3	184.1	180.6	–	−1244.19 ± 30	−1244.40
LiCl	148.0	153.3	148.5	–	−190.13 ± 6.6	−190.44
LiBr	142.9	147.8	140.3	−1.8	–	−108.85
LiI	134.3	138.7	129.7	−3.4	–	59.96
NaF	149.0	153.9	152.6	–	−7.004 ± 24.01	−6.75
NaCl	127.8	132.6	129.6	–	−8.344 ± 1.67	−8.16
NaBr	123.6	127.7	124.2	–	−4.974 ± 0.93	−4.97
NaI	116.6	120.3	115.7	−0.8	−0.474 ± 0.73	−0.50
KF	134.2	139.2	139.1	–	−2.334 ± 8.339	−2.35
KCl	113.2	118.0	116.7	–	−0.834 ± 0.1	−0.81
KBr	109.4	113.6	109.6	–	−0.02 ± 0.07	−0.02
KI	102.3	106.1	104.0	–	0.043 ± 0.06	0.04
RbF	128.9	133.6	135.5	+1.4	−3.669 ± 2.00	−3.82
RbCl	108.8	113.4	111.5	–	0.233 ± 0.133	0.25
RbBr	105.1	109.0	107.3	–	0.00 ± 0.05	0.00
RbI	98.4	101.9	100.5	–	0.0527 ± 0.027	0.05
CsF	125.9	130.5	133.6	+2.4	3.002 ± 0.66	3.30
CsCl	107.8	112.3	109.7	–	0.5 ± 0.067	0.42
CsBr	104.7	108.6	104.4	−0.3	0.002 ± 0.0037	0.00
CsI	97.6	101.1	97.6	–	0.0247 ± 0.005	0.03

Table 3. Percentage weight of the terms containing β_e in $B_{4,\,exp}$ and γ_e in $B_{5,\,exp}$.

Molecule	β_e term	γ_e term
LiF	8.1	15.4
LiCl	5.6	13.7
LiBr	5.6	13.2
LiI	5.8	22.8
NaF	0.7	22.1
NaCl	4.3	15.1
NaBr	6.0	13.5
NaI	1.1	15.9
KF	0.7	13.3
KCl	1.5	12.2
KBr	0.1	14.6
KI	0.4	12.9
RbF	2.1	9.8
RbCl	1.0	11.3
RbBr	0.1	11.7
RbI	2.5	13.6
CsF	2.5	5.9
CsCl	3.7	9.1
CsBr	0.1	8.8
CsI	2.6	10.2

Table 4. Fitted coefficients a (erg/molecule), b (Å^{-1}), c (Å^{-2}), d (Å^{-3}), e (Å^{-4}) for (14).

Molecule	a	b	c	d	e
LiF	$0.1190 \cdot 10^{-7}$	−7.931	2.525	−0.499	0.001
LiCl	$0.3209 \cdot 10^{-8}$	−3.481	−0.537	0.465	−0.101
LiBr	$0.3024 \cdot 10^{-8}$	−3.144	−0.561	0.419	−0.085
LiI	$0.9724 \cdot 10^{-12}$	10.434	−8.690	2.570	−0.291
NaF	$0.1771 \cdot 10^{-10}$	8.696	−11.193	4.422	−0.644
NaCl	$0.6004 \cdot 10^{-8}$	−3.143	−0.772	0.482	−0.085
NaBr	$0.3424 \cdot 10^{-7}$	−5.699	0.879	0.022	−0.036
NaI	$0.1233 \cdot 10^{-9}$	2.769	−3.570	1.048	−0.118
KF	$0.1125 \cdot 10^{-8}$	−0.312	−2.835	1.098	−0.153
KCl	$0.6347 \cdot 10^{-8}$	−2.611	−0.752	0.362	−0.055
KBr	$0.4304 \cdot 10^{-9}$	1.277	−2.668	0.773	−0.083
KI	$0.3567 \cdot 10^{-9}$	1.474	−2.466	0.669	−0.069
RbF	$0.5558 \cdot 10^{-7}$	−7.156	2.019	−0.424	0.026
RbCl	$0.1678 \cdot 10^{-8}$	−0.689	−1.541	0.471	−0.052
RbBr	$0.2727 \cdot 10^{-8}$	−1.008	−1.401	0.463	−0.056
RbI	$0.2207 \cdot 10^{-10}$	5.172	−4.130	0.995	−0.092
CsF	$0.1289 \cdot 10^{-8}$	−0.888	−1.633	0.524	−0.063
CsCl	$0.5100 \cdot 10^{-9}$	1.100	−2.335	0.632	−0.066
CsBr	$0.3606 \cdot 10^{-7}$	−4.230	0.312	0.057	−0.019
CsI	$0.1470 \cdot 10^{-9}$	2.719	−2.742	0.649	−0.059

average factor of 30 ÷ 40 on the percentage error. It is then clear that the β_e test is quite strict since it requires a very precise evaluation of B_4 along with that of B_2 and B_3.

In order to verify the self-consistency of the SQ a repulsive function with 5 parameters has been assumed:

$$B(r) = a\exp(br)\exp(cr^2)\exp(dr^3)\exp(er^4)\,, \quad (13)$$

i.e.

$$\ln(B(r)/a) = br + cr^2 + dr^3 + er^4\,. \quad (14)$$

The five experimental values $B_1(r_e) \div B_5(r_e)$ can then be used to yield the five constants $a \div e$ and thus the function $B(r)$. Table 4 shows the fitted $a \div e$ coefficients while Table 2 reports the D_i and β_e values calculated with (6), (9). The D_i error is taken as zero (dash) when the calculated value is in between the two literature figures: 6 salts fall outside these limits with the largest errors being those of LiI and CsF. The average absolute error is 0.5%. The comparison of the $\beta_{e,\,cal}$ data with the literature ones [2, 6] is quite significant: except for CsCl, where the calculated value (0.42) is very close to the lowest experimental limit (0.433), in all other cases the calculated figures are within the experimental errors. This can be interpreted as evidence of the reliability of the experimental data and of self-consistency of the SQ.

Along with (14), the following function was also studied:

$$B(r) = a\exp(br^m)\exp(cr^n)\,. \quad (15)$$

This potential gives the same β_e values of Table 2 and slightly different D_i ones which anyhow show the same error (0.5%).

In this context, a final remark should be made on the γ_e quantity, which has been so largely discussed in literature. A detailed analysis of this term shows that its weight in $B_5(r_e)$ is on the average 12.8% (with a minimum of 5.9% in the case of CsF and a maximum of 22.8% for LiI). Thus, on going from γ_e to $B_5(r_e)$ there is a reduction of the percentage error of about 1/7 and the figures evaluated for $B_5(r_e)$ should be reliable.

The percentage weights of the terms containing β_e and γ_e in the experimental B_4 and B_5, respectively, for the 20 alkali halides are reported in Table 3.

3. The Repulsive Potentials

The experimental values $B_1 \div B_5$, can now be used to test the precision of different analytical forms for the repulsive function $B(r)$ with an increasing number of parameters.

3.1. Fitting Procedure

If one defines $\varrho = B_1/B$, the following relations are immediately obtained:

$$\begin{aligned} B_1 &= B\varrho\,, \\ B_2 &= B_1\varrho + B\varrho_1\,, \\ B_3 &= B_2\varrho + 2B_1\varrho_1 + B\varrho_2\,, \\ B_4 &= B_3\varrho + 3B_2\varrho_1 + 3B_1\varrho_2 + B\varrho_3\,, \\ B_5 &= B_4\varrho + 4B_3\varrho_1 + 6B_2\varrho_2 + 4B_1\varrho_3 + B\varrho_4\,, \end{aligned} \tag{16}$$

where ϱ_n is the n-th derivative of ϱ.

It should be observed that the number of Eq. (16) required is obviously equal to the number of parameters in the function $B(r)$ to be fitted and that, once the analytical form of $B(r)$ is assumed, the $\varrho_n = f$(parameters) are immediately available. For example, in the case of the simple function (3), only the first two equations (16) are required and $\varrho = b$; $\varrho_1 = 0$. Moreover on the right-hand side of these equations, the first term is always the most important one, the other ones being successively smaller and normally of only a few percent.

The iterative procedure used in the calculations was the following. An initial set of ϱ_n was estimated, e.g. starting from (16-2) with $\varrho_1 = 0$, from (16-3) with $\varrho_2 = 0$ and so on. This set was then cycled, taking into account the relations among the ϱ_n, until convergency was reached on the experimental values B_n. The final set gave the explicit parameter values. This fitting procedure has been tested in many cases against the direct solutions which are, normally, hard to obtain.

3.2. The Precision

A reasonable range of the analytical forms of $B(r)$ was analyzed by means of the following 10 types of functions:

a) $B(r)$ with 2 parameters (input: B_1, B_2;
output: B_3, B_4, B_5, B)

This is the easiest and handiest type of repulsive function and thus the most popular in literature. The examined functions are shown in Table 5, i.e. the exponential one (model 1), the gaussian one (model 3), that with $r^{1.5}$ (model 5) and finally the function given by Ali and Hasan [5] (model 7). The same Table gives the % errors of the calculated B_n, while Table 6 reports the parameters fitted for these functions. It can be observed that the best results are those given by functions 1 and 7. The comparison betweeen the absolute and relative errors shows that these models tend to underestimate the value of the repulsive derivatives. Moreover, the errors in the $B_{4,\text{calc}}$ and $B_{5,\text{calc}}$ are generally larger than the weight of the term containing β_e in $B_{4,\text{exp}}$ and γ_e in $B_{5,\text{exp}}$, respectively. This evi-

Model	B_{calc}	$B_{3,\text{calc}}$	$B_{4,\text{calc}}$	$B_{5,\text{calc}}$
1) $a\exp(br)$	3.8 (2.6)	1.9 (−1.2)	6.9 (−5.8)	16.4 (−10.0)
2) $ar^m\exp(br)$	3.8 (2.9)	–	3.1 (−2.2)	11.2 (−3.1)
3) $a\exp(br^2)$	3.9 (−3.3)	18.3 (−18.3)	54.8 (−54.8)	96.6 (−96.6)
4) $ar^m\exp(br^2)$	3.3 (2.1)	–	2.2 (−0.2)	10.1 (5.6)
5) $a\exp(br^{1.5})$	2.9 (−0.7)	9.3 (−9.3)	29.5 (−29.5)	54.9 (−54.9)
6) $ar^m\exp(br^{1.5})$	3.6 (0.0)	–	2.6 (−1.2)	9.8 (1.2)
7) $ar^{-2}\exp(br^{1.5})$	3.5 (2.0)	2.0 (−1.9)	7.6 (−6.7)	16.0 (−9.4)
8) $a\exp(br)\exp(cr^2)$	4.1 (3.2)	–	3.2 (−2.6)	11.1 (−4.3)

Table 5. Absolute and relative (in parentheses) mean % errors for the calculated repulsive functions B_n at $r = r_e$. For B_{calc} in between the two experimental values (obtained from the two $D_{i,\text{exp}}$ sets of Table 2) the error was taken as zero.

Table 6. Fitted coefficients a and b for the two parameter models of Table 5 (r being in Å, $B(r)$ is in erg/molecule).

Molecule	Model 1		Model 3		Model 5		Model 7	
	$a \cdot 10^8$	b	$a \cdot 10^{10}$	b	$a \cdot 10^9$	b	$a \cdot 10^9$	b
LiF	0.1270	−3.787	0.9271	−1.415	0.2270	−2.189	0.1133	−1.334
LiCl	0.1696	−3.165	0.9880	−0.906	0.2604	−1.600	0.2203	−1.028
LiBr	0.1762	−2.986	0.9847	−0.794	0.2631	−1.456	0.2574	−0.943
LiI	0.1946	−2.780	1.0027	−0.669	0.2751	−1.289	0.3284	−0.848
NaF	0.2509	−3.637	1.0909	−1.079	0.3165	−1.872	0.2473	−1.267
NaCl	0.3005	−3.092	1.1326	−0.745	0.3444	−1.434	0.4072	−0.991
NaBr	0.3118	−2.941	1.1421	−0.668	0.3506	−1.324	0.4663	−0.919
NaI	0.2854	−2.686	1.0852	−0.563	0.3290	−1.162	0.5130	−0.803
KF	0.3317	−3.355	1.2589	−0.879	0.3820	−1.622	0.3820	−1.121
KCl	0.4392	−2.926	1.2970	−0.619	0.4274	−1.271	0.6523	−0.907
KBr	0.3501	−2.689	1.1498	−0.539	0.3658	−1.138	0.6216	−0.801
KI	0.4495	−2.600	1.2520	−0.480	0.4206	−1.055	0.8404	−0.758
RbF	0.3908	−3.273	1.3818	−0.818	0.4291	−1.546	0.4707	−1.078
RbCl	0.4288	−2.784	1.2946	−0.564	0.4235	−1.183	0.7050	−0.842
RbBr	0.5481	−2.761	1.3818	−0.526	0.4797	−1.138	0.8985	−0.827
RbI	0.5766	−2.593	1.3785	−0.458	0.4869	−1.029	1.0640	−0.751
CsF	0.3994	−3.126	1.4833	−0.757	0.4533	−1.453	0.5294	−1.007
CsCl	0.6157	−2.806	1.5317	−0.542	0.5340	−1.165	0.9750	−0.847
CsBr	0.6646	−2.705	1.5339	−0.493	0.5482	−1.091	1.1218	−0.799
CsI	0.7124	−2.549	1.5355	−0.430	0.5612	−0.989	1.3409	−0.729

dence, tested for each salt, prevents the evaluation of β_e and γ_e and thus discourages the use of these functions when precision is needed down to this level; in particular it was observed that β_e could not be calculated in 74 (and γ_e in 64) out of the 80 examined cases, while the few favorable ones were always connected with models 1 and 7. It can then be concluded that, in general, values for β_e and γ_e cannot be calculated since the two parameter repulsive potentials appear too crude for the evaluation of these quantities.

Finally, it should be observed that, owing to (16), for each molecule the parameters of Table 6 are connected to each other. For example, with the values for a and b of the exponential model 1, the corresponding a_G and b_G parameters of the gaussian model 3 can be calculated by means of the relations

$$a_G = a\,b(b - r_e^{-1})^{-1} \exp(0.5\,b\,r_e + 0.5)\,,$$
$$b_G = 0.5\,r_e^{-1}(b - r_e^{-1})\,. \qquad (17)$$

Moreover, the following approximate relation can also be applied:

$$b\,b_G(b_{1.5})^{-2} = 1.12\,, \qquad (18)$$

where $b_{1.5}$ refers to model 5.

b) $B(r)$ with 3 parameters (input: B_1, B_2, B_3; output: B_4, B_5, B).

Three of the previously used functions are modified by the introduction of the pre-exponential term r^m: models 2, 4 and 6 are thus obtained. For comparison, the function

$$B(r) = a \exp(b\,r) \exp(c\,r^2) \qquad (19)$$

was also taken into account.

Tables 5 and 7 summarize the results. It can be observed that the best results are those given by models 4 and 6, where the pre-exponential term yields marked improvements. In this case β_e could not be calculated in 43 (and γ_e in 23) out of 80 cases. In considering these numbers one must refer to Table 3 which, for example, shows that nine molecules require a precision higher than 1.5% in $B_{4,\,\mathrm{calc}}$ in order to allow the evaluation of β_e.

Also in this case, the parameters reported in Table 7 are for each molecule interconnected. Useful approximate relations are:

$$b\,b_G(b_{1.5})^{-2} = 1.27\,, \qquad (20)$$
$$(m - m_{1.5})/(m_{1.5} - m_G) = 1.99\,,$$

where b, m refer to model 2, while subscripts 1.5 and G refer to models 6 and 4, respectively.

Table 7. Fitted coefficients a, b and m (or c) for the three parameter models of Table 5 (r being in Å, $B(r)$ is in erg/molecule).

Molecule	Model 2			Model 4			Model 6			Model 8		
	$a \cdot 10^8$	b	m	$a \cdot 10^9$	b	m	$a \cdot 10^9$	b	m	$a \cdot 10^8$	b	c
LiF	0.0251	−2.077	−2.262	0.0491	−0.400	−3.661	0.0733	−0.808	−3.190	0.3968	−5.500	0.675
LiCl	0.1203	−2.708	−0.797	0.1329	−0.389	−3.211	0.2122	−0.911	−2.400	0.2501	−3.607	0.130
LiBr	0.1521	−2.767	−0.411	0.1638	−0.368	−3.071	0.2565	−0.896	−2.178	0.2151	−3.197	0.058
LiI	0.2034	−2.864	0.174	0.2155	−0.343	−2.878	0.3245	−0.880	−1.853	0.1788	−2.700	−0.020
NaF	0.0679	−1.988	−2.757	0.1341	−0.302	−4.436	0.1913	−0.687	−3.873	0.9998	−5.286	0.507
NaCl	0.2515	−2.763	−0.683	0.2859	−0.334	−3.598	0.4270	−0.852	−2.621	0.4194	−3.412	0.079
NaBr	0.3101	−2.929	−0.027	0.3268	−0.332	−3.316	0.4801	−0.875	−2.214	0.3160	−2.953	0.003
NaI	0.2870	−2.704	0.044	0.3933	−0.283	−3.244	0.5290	−0.777	−2.142	0.2793	−2.668	−0.004
KF	0.2011	−2.595	−1.447	0.2488	−0.343	−3.954	0.3781	−0.837	−3.114	0.6759	−4.100	−0.200
KCl	0.4282	−2.844	−0.194	0.5201	−0.301	−3.611	0.7180	−0.821	−2.467	0.4828	−3.006	0.017
KBr	0.3159	−2.171	−1.286	0.6676	−0.219	−4.025	0.8262	−0.612	−3.107	0.6587	−3.195	0.104
KI	0.4488	−2.728	0.346	0.7376	−0.251	−3.412	0.8858	−0.735	−2.154	0.3798	−2.476	−0.023
RbF	0.2934	−2.793	−0.960	0.3173	−0.350	−3.795	0.4862	−0.878	−2.845	0.6255	−3.742	0.120
RbCl	0.3870	−2.319	−1.144	0.7265	−0.236	−4.042	0.9189	−0.657	−3.072	0.7521	−3.238	0.094
RbBr	0.5526	−2.873	0.296	0.7730	−0.273	−3.536	0.9717	−0.787	−2.253	0.4744	−2.651	−0.021
RbI	0.5558	−2.850	0.729	0.9288	−0.250	−3.381	1.0664	−0.750	−2.006	0.4042	−2.344	−0.045
CsF	0.3575	−2.924	−0.417	0.3566	−0.354	−3.487	0.5468	−0.904	−2.458	0.4894	−3.322	0.048
CsCl	0.6244	−2.941	0.347	0.8144	−0.283	−3.524	1.0433	−0.810	−2.229	0.5197	−2.676	−0.026
CsBr	0.6566	−2.956	0.689	0.9516	−0.268	−3.436	1.1442	−0.791	−2.056	0.4751	−2.461	−0.045
CsI	0.6537	−2.852	0.900	1.2176	−0.239	−3.402	1.3196	−0.734	−1.963	0.4593	−2.255	−0.050

c) $B(r)$ with 4 parameters (input: $B_1 \div B_4$; output: B_5, B)

Two functions of this type were taken into account:

$$B(r) = a \exp(b r) \exp(c r^2) \exp(d r^3), \tag{21}$$

$$B(r) = a\, r^m \exp(b r^n). \tag{22}$$

The following results were obtained: $B_5(r_e)$ can be calculated with an absolute error of 3.9 and of 4.6 from (21), (22), respectively. The calculated $B(r_e)$ shows an error of 3.4 and 3.1, respectively. As expected, the β_e values calculated by these functions are identical to those reported in Table 2, which represent the figures consistent with the fitted experimental $\omega_e x_e$. The calculated γ_e show an error which is about 7 times that of $B_{5,\,\mathrm{calc}}$.

4. Conclusions

The data in Table 5, along with those obtained with the 4-parameter functions, give a quantitative picture of how the precision of the $B_{n,\,\mathrm{calc}}$ increases with the number of fitted parameters in the assumed $B(r)$ function, and also of how, given a repulsive function, the precision of its calculated derivatives decreases as the order of the derivation increases. A comparative analysis of the functions with 2 and 3 parameters is reported in Figs. 1 and 2 for the LiF molecule. As can be observed, the 2 parameter functions are rather scattered, while the 3-parameter ones are clustered. This is in agreement with the figures reported in Table 5: the choice of a 2-parameter function is much more critical than that of a multiparameter one.

Moreover it should be observed that an estimate of the errors in the calculated SQ based on the errors in the $B_{n,\,\mathrm{calc}}$ is rather complicated: for example, when γ_e is calculated by means of a 2-parameter function, the final expression (see (10)) includes the calculated B_3, B_4 and B_5, each being burdened with its own error. A direct relation is present only between the error of the first of the calculated derivatives and that of its connected SQ: e.g. for α_e (from $B_{3,\,\mathrm{calc}}$) with a 2-parameter function there is a constant factor of 2.2, for $\omega_e x_e$ (from $B_{4,\,\mathrm{calc}}$) with a 3-parameter function a constant factor of 0.63.

Table 8 summarizes the % absolute errors obtained in the SQ calculated by the models 1 and 7 for the 2-parameter and 4 and 6 for the 3-parameter functions (see Table 5) and (21), (22) in the case of the 4 parameters. The β_e values in the 2-parameter models are given as "non computable" (NC) since limited, for each equation, to only 3 cases out of 20 on the basis of the previously discussed criteria. In the 3-parameter models, for each equation, 10/20 cases could be taken into account: here a zero error was assumed

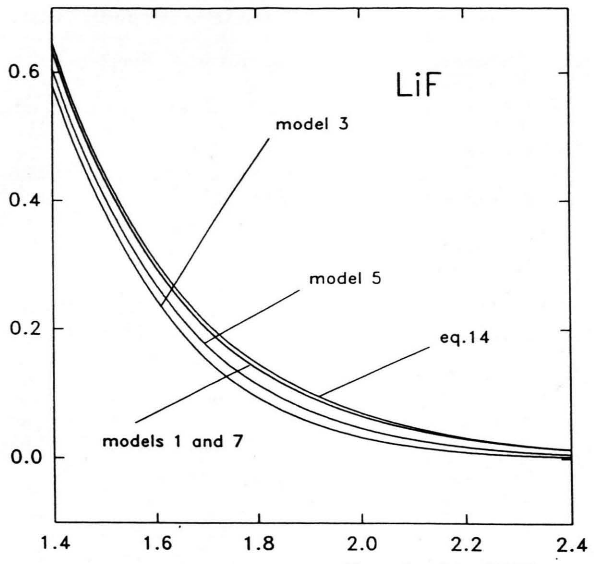

Fig. 1. Repulsive potentials (erg 10^{11}/molecule) of LiF vs. r (Å) as calculated by the two parameter models. For comparison, (14) is also reported.

Table 8. Mean absolute % errors in the calculated spectroscopic quantities. The models are those of Table 5.

SQ	2-parameters		3-parameters		4-parameters	
	model 1	model 7	model 4	model 6	Eq. (21)	Eq. (22)
α_e	4.2	4.3	–	–	–	–
$\omega_e x_e$	5.9	4.9	3.3	4.1	–	–
β_e	NC		24.3*	41.1*	0.0	0.0
γ_e	NC		39.0**	43.1**	27.2	32.9

* Average on 10/20 cases.
** Average on 15/20 cases.

when the $\beta_{e,\text{calc}}$ was within the experimental error of $\beta_{e,\text{exp}}$. Finally, in the 4-parameter models, the $\beta_{e,\text{calc}}$ values coincide with the experimental ones (see Table 2). The γ_e with a 2-parameter model could be obtained, for each equation, in 8/20 cases with an average error of 58.9%; in the 3-parameter model they could be calculated in 15/20 cases.

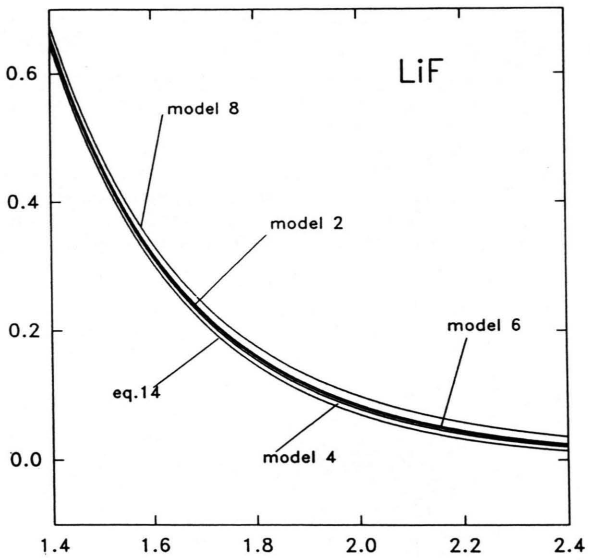

Fig. 2. Repulsive potentials (erg 10^{11}/molecule) of LiF vs. r (Å) as calculated by the three parameter models. For comparison, (14) is also reported.

It can thus be concluded that the analysis of different analytical expressions for the repulsive potential and mainly that of the significance and limits of the generated SQ has brought light into the problem of the prevision of the β_e and γ_e values. In order to be able to evaluate these quantities, one must deal with functions that are sufficiently precise and however compatible with the weight of the terms containing β_e and γ_e in the $B_{4,\text{exp}}$ and $B_{5,\text{exp}}$ of the chosen molecule (see Table 3). Thus, in the case of Na (F, I), K (F, Cl, Br, I), Rb (Cl, Br) and CsBr molecules, β_e can be properly calculated only by a 4-parameter function.

The choice of a proper analytical expression for the repulsive potential $B(r)$ must accomodate the desired precision with the difficulties inherent to the use of a multiparameter function.*

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* Further details on the results not reported in this paper can be obtained from the authors.

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