PCCP

PAPER

View Article Online
View Journal | View Issue

Cite this: *Phys. Chem. Chem. Phys.*, 2022, **24**, 24823

A semiempirical potential for alkali halide diatoms with damped interactions I. Rittner potential

Xiaowei Sheng,[a] Kwong Tin Tang [b] and J. Peter Toennies [*c]

Received 25th July 2022,
Accepted 28th September 2022

DOI: 10.1039/d2cp03405k

rsc.li/pccp

A new semiempirical potential is described for the ground state $X^1\Sigma^+$ of the alkali halide diatoms. The model potential is the first to account for the damping of all the electrostatic and induction potential terms as well as of the long-range dispersion potential. Accordingly, the potential does not have a negative singularity at vanishingly small internuclear distances and is the first Rittner-type model with a realistic dependence of the repulsion at short distances. The new potential is tested by comparing with *ab initio* potentials, which presently are only available in the well region for the molecules LiF, LiCl and CsI. The three parameters of the new potential are determined by fitting the latest experimental parameters for the well depth D_e, bond distance R_e and vibrational frequency ω_e. The new potential is in good agreement with the *ab initio* potentials.

I. Introduction

A. Alkali halides

The alkali halide solids and diatoms are among the most widely studied with ionic bonding. The solids have served as ideal model systems both in the bulk and also at the surface.[1] In 1946 Seitz remarked "In the field of solids, the properties of alkali halides have an enduring interest, since these crystals have continuously yielded to persistent investigation and have gradually provided us with a better and better understanding of the most interesting properties of all solids".[2] The alkali halides also play an important role in many areas of biology and medicine and in industry.[3] The molecules have been important prototype systems in the development of molecular physics[4] and in crossed beam scattering studies of bimolecular reactions.[5] In recent years, due to their large dipole moments, polar molecules have opened up new perspectives in the preparation of ultra-cold gases.[6]

B. Alkali halide diatoms

The understanding of the alkali halide diatoms has a long history essentially because of the simple classical Coulomb interactions between the constituent ions. In 1898 and probably much earlier it was realized that NaCl crystals consisted of a regular periodic array of positive and negative ions.[7,8] In 1917 Kossel, well before the discovery of quantum mechanics, realized that the strong polar bonding of ions could explain the binding in many molecules.[9] Then in 1932 shortly after London published his paper on the dispersion forces, Born and Mayer proposed that the binding in the alkali halide solids could be described by the following simple formula

$$V(R) = Ae^{-R/\rho} - \frac{\alpha e^2}{R} - \frac{C_6}{R^6} + \varepsilon, \quad (1)$$

where A and ρ are Born Mayer parameters for the repulsive potential, α is the Madelung constant[10] and C_6 is the London dispersion coefficient and $\varepsilon = \frac{9}{4}h\upsilon$.[11]

Rittner in 1951 added the classical charge induction and dipole terms already introduced by Born and Heisenberg in 1924.[12] Furthermore, Rittner proposed that the interaction energy between the ions in the dimer is given by (in atomic units)[13]

$$V_{\text{Rittner}}(R) = Ae^{-R/\rho} - R^{-1} - \frac{\alpha_M + \alpha_X}{2R^4} - \frac{2\alpha_M\alpha_X}{R^7} - \frac{C_6}{R^6} + K, \quad (2)$$

where the third and fourth terms are the new Rittner terms, with α_M and α_X, the free ion polarizabilities of the cation and anion, respectively. The last term K is a constant energy term which includes the kinetic energy terms representing the difference in translational, rotational, and vibrational energy between the molecules and the free ions.[13] If the temperature is not considered, the constant K is defined as $h\upsilon_0/2$ and υ_0 is the frequency of vibration.[14] The constant energy term K has no effect on the spectroscopic constants and is therefore not included in the calculations. The repulsive Born Mayer parameters A and ρ were determined by Rittner by fitting eqn (2) to

[a] *Department of Physics, Anhui Normal University, Anhui, Wuhu 24100, China*
[b] *Department of Physics, Pacific Lutheran University, Tacoma, Washington 98447, USA*
[c] *Max-Planck-Institut für Dynamik und Selbstorganisation, Am Fassberg 17, D-37077, Göttingen, Germany. E-mail: jtoenni@gwdg.de*

the experimental equilibrium distance and vibrational frequency of the diatomic molecule. The third, fourth and fifth terms Rittner estimated from the then available polarizabilities and dipole moments.

In 1973 Brumer and Karplus used quantum-mechanical exchange perturbation theory to analyze the interactions in alkali halide diatoms. They demonstrated that higher multipole contributions are quenched by exchange and that a consistent second-order perturbation treatment requires that the $2\alpha_M\alpha_X/R^7$ term in the Rittner potential be neglected.[15,16] The resulting potential, denoted as the truncated Rittner (T-Rittner) model, is given by

$$V_{\text{T-Rittner}}(R) = Ae^{-R/\rho} - R^{-1} - \frac{\alpha_M + \alpha_X}{2R^4} - \frac{C_6}{R^6} + K. \qquad (3)$$

In 1986 Kumar, Kaur and Shankar implemented the T-Rittner model and demonstrated that it reproduced the experimental potential data reasonably well at the equilibrium separation of 25 diatomic alkali halide and the alkali hydride molecules.[16] Although several potential models have since been introduced[14,17,18] the T-Rittner potential model or minor variants thereof are presently considered to be the best models for the diatomic molecules.

A problem with the T-Rittner model and most all of the variant potential models is that they have an unphysical negative singularity at vanishing internuclear distances and fail in describing the repulsive potential which is well known to tend to a large positive value in the limit of $R \geq 0$.[19–21] Therefore, the T-Rittner model is valid only at large R corresponding to the well region. Frequently, the Rittner type potential models, even those for the solid[22] used in connection with high pressure experiments,[23] have an incorrect shape in the repulsive region resulting from the spurious singularity at small internuclear distances.

To a large extent the predominant literature on the potentials is from the previous century. One of the most recent publication is from Walz *et al.* in 2018.[3] In a comprehensive review of the efforts to find a phase transferable force field for all three phases of the alkali halides Waltz *et al.* have used potential models with simple repulsive terms without the Coulomb singularity. These include the well-known, but ultra-simple Lennard-Jones, Buckingham and modified Buckingham potentials. Thus, even today the overall situation in finding a universal potential model is not satisfactory.

In the present article the T-Rittner model is modified by taking account of the damping of the electrostatic, induction and dispersion terms in the T-Rittner model for the potential of the lowest $X^1\Sigma^+$ state. The article is organized as follows. First, it is demonstrated that the values of the available dispersion coefficients and polarizabilities on which previous models have relied differ by large amounts. Then the new model, denoted TTT-R, is introduced. The available experimental data on the bond distance, dissociation energies and vibrational constant on which the TTT-R model is based are surveyed. The more realistic behavior of the TTT-R model in the repulsive region compared to the T-Rittner model is analyzed next. The results are then compared with the available *ab initio* calculations.

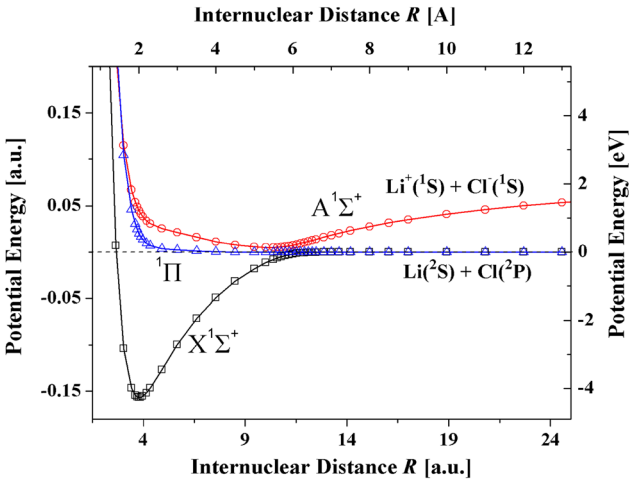

Fig. 1 *Ab initio* potential curves of LiCl showing the avoided crossing between the ionic $X^1\Sigma^+$ state and the $A^1\Sigma^+$ covalent state.[24] In a collision of an alkali atom with an halogen atom at the avoided crossing the outer electron of the alkali atom transfers to the halogen atom thereby producing two oppositely charged ions which attract each other and form a strong ionic bond.

A survey of the literature reveals that only for LiF, and LiCl reliable, reproducible calculations of the potential curves of the $X^1\Sigma^+$ and $A^1\Sigma^+$ states have been reported. Only a single *ab initio* calculation is available for the third system CsI. Fig. 1 shows a recent *ab initio* calculation for the potential curves of both the ground $X^1\Sigma^+$ ion state and the $A^1\Sigma^+$ covalent state of LiCl.[24] The accuracy of the TTT-R model is then evaluated by a quantitative comparison of the reduced potentials with the corresponding *ab initio* potentials for the $X^1\Sigma^+$ state for the three systems. The agreement is better than a few percent. The implications of the TTT-R repulsive potential for which there are no previous model- and *ab initio*-calculations, for analyzing and understanding high pressure experiments is discussed in the concluding section.

C. Dispersion coefficients and polarizabilities

Surprisingly, even presently little is known about the properties of the constituent alkali halide ions. For example, the dispersion coefficients between the constituent ions are not theoretically accurately known, at least compared to the rare gas dimers and solids which have the same electronic structure. In the extensive compilations of Jiang *et al.*[25] and Gould *et al.*[26] the long-range dispersion coefficients between oppositely charged ions are not explicitly included. Table 1 summarizes some of the literature values for the dispersion coefficients. These have been estimated by using various approximations and differ by more than an order of magnitude. The last entry, which is used here, is based on the assumption that the dispersion coefficients are the same as that of the corresponding isoelectronic rare gas dimers created after transfer of the electron from the alkali to the halogen atom, but without consideration of the charges.[27]

The polarizabilities of the ions to be used in the Rittner models are also not accurately known. In the literature there is

Table 1 Comparison of the dispersion coefficients C_6 for LiF, LiCl and CsI from various methods. All numbers are in atomic units. To convert to meV Å^6 multiply by 0.597 × 10^3

LiF	LiCl	CsI	Method and ref.
0.1913	0.7894	140.19	London formula[28]
0.2517	0.9254	119.71	London formula[15]
1.78445	4.5000	700.18	Kirkwood-Muller formula.[16]
3.0319	9.5519	285.87	Isoelectronic rare gas dispersion coeff's[25]

no agreement as to whether the free ion polarizabilities or special polarizabilities, which account for the electric field emanating from the partner ion, are to be used in eqn (3). The long discussion in the literature is concisely summarized by the following discussion between two of the protagonists. Shanker *et al.* have argued that the polarizability depends on the environment of the atom on which there is evidence from condensed systems.[29] This has been questioned by Donald *et al.*[30] in response to which Shanker and Kushwah wrote "a detailed investigation is required to resolve the question of potential dependent polarizability".[31]

Table 2 provides a comparison of recent state of the art *ab initio* calculations of the free ion polarizabilities[32] with some recent literature values of the ion-in-molecule polarizabilities. These recent values for the ion-in-molecule polarizabilities in Table 2 differ also by similar large amounts from earlier published results.[15,16,33] Presently there is no unanimity as to the values of the polarizabities of the ions in the diatoms. Generally the ion-in-molecule polarizabilities are smaller, while in some cases they are about the same or even larger with no obvious trend. One of the aims of the present investigation is the experimental determination of the effective polarizability in the alkali halide molecules under investigation.

II. A new potential model for the alkali halide diatoms with damped interactions

A. Theory

The unphysical shortrange behavior of the Rittner-type potentials can be avoided by introducing a damping function to reduce the R^{-n} terms to zero at small distances. This was first demonstrated for the London dispersion energy in the Tang–Toennies model (TT).[36] The universal damping function introduced by Tang and Toennies is given by

$$f_n(bR) = 1 - e^{-bR}\sum_{k=0}^{n}\frac{(bR)^k}{k!}. \quad (4)$$

It has the advantage that it can be applied to all powers of n and depends only on the exponent of the repulsive Born Mayer term. The TT damping function has been shown to reproduce well the *ab initio* calculated damping of the R^{-6} dispersion potential of two hydrogen atoms by Koide *et al*[37] and Wheatley and Meath.[38] Theoretical calculations have demonstrated that they are remarkably accurate for He_2[39] and HeH.[40] It has also been shown to reproduce the direct calculation of the damping of the R^{-4} induction potential.[41]

The TT damping function for the Coulomb potential is given by

$$f_1(bR) = 1 - e^{-bR}(1 + bR). \quad (5)$$

We are not aware of formal calculations of the damping of the Coulomb potential with which to compare eqn (5) although it has been adopted at least in one other publication.[42] In a related problem Stone in his book *The Theory of Intermolecular Forces* has calculated the correction of the electrostatic multipole energy at short distances, which he denotes the "penetration energy".[43] Accordingly, the energy of a proton as a function of distance from a hydrogen-like atom of nuclear charge Z is given by: $V(R) = -1/2[1 - \exp(-2ZR)(1 + RZ)]$, where the term in brackets is the damping function and $\exp(-2ZR)$ is the charge density of the atom. Substituting $\alpha = 2Z$ the damping function becomes $f_1 = 1 - \exp(-\alpha R)(1-\alpha R/2)$, which is very similar in form to eqn (5). See also Slipchenko and Gordon.[44]

The TTT-R potential model can be written in atomic units compactly as

$$V_{\text{TTT-R}}(R) = Ae^{-bR} - \sum_{n=1}^{6}\left[1 - e^{-bR}\sum_{k=0}^{n}\frac{(bR)^k}{k!}\right]\frac{C_n}{R^n}, \quad (6)$$

where $C_1 = 1$, $C_2 = C_3 = C_5 = 0$, $C_4 = (\alpha_M + \alpha_X)/2$ and C_6 is the dispersion coefficient. Fig. 2 illustrates typical damping functions for $n = 1$, 4 and 6.

Table 2 Some literature values of free ion and molecular state polarizabilities at the equilibrium distance for LiF, LiCl, and CsI. C_4 is calculated from the equation: $C_4 = (\alpha_M + \alpha_X)/2$ the roman numbers in each box are in units of Å^3 or in eV Å^4 and the numbers in italics are in a.u.

LiF			LiCl			CsI			
α_M	α_X	C_4	α_M	α_X	C_4	α_M	α_X	C_4	Ref.
Free ion polarizabilities									
0.0285	2.462	17.931	0.0285	5.356	38.767	2.384	10.400	92.043	32
0.1923	*16.614*	*8.4034*	*0.1923*	*36.144*	*18.168*	*16.088*	*70.183*	*43.135*	
Molecular state polarizabilities									
0.0360	0.6320	4.8095	0.0340	2.1500	15.724	2.9100	5.3700	59.615	34
0.2429	*4.2650*	*2.2539*	*0.2294*	*14.509*	*7.3692*	*19.638*	*36.239*	*27.938*	
0.0530	1.1920	8.9638	0.0530	2.3140	17.042	3.3960	5.3070	62.660	35
0.3577	*8.0440*	*4.2008*	*0.3577*	*15.616*	*7.9867*	*22.917*	*35.813*	29.365	

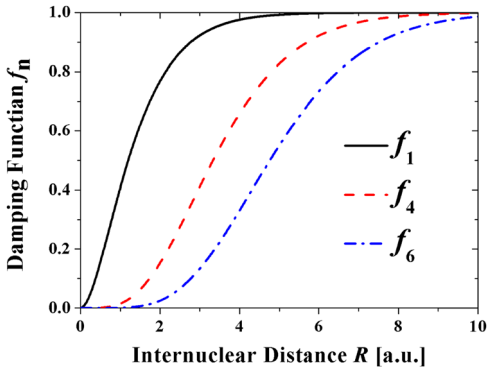

Fig. 2 Typical damping functions used in the present model potential. The parameter b =1.401 a.u.

In eqn (6) it is implicitly assumed that the alkali halide diatom is completely ionized. It is however known that the alkali halide molecules have a small covalent character. See for example.[45] The ionicity can be estimated from the ratio of the experimental dipole moment to the theoretical dipole moment calculated assuming a 100% ionic bond. The corresponding ionicities of LiF, LiCl and CsI are 84.2, 73.4 and 73.4%, respectively.[3] Inclusion of the ionicities would require consideration of a corresponding covalent contribution which could compensate the reduction in the ionicity. Since the ionicity was not included in the T-Rittner models it has not been included here.

B. Experimental and TTT-R potential parameters

As in the Rittner model and similar models the potential parameters A and b in eqn (6) are customarily determined by a self-consistent least squares fit of two experimental parameters, usually the bond distance R_e and the vibrational constant ω_e. In the present case considering the uncertainty in C_4 it was also fitted. Since the dispersion term C_6 makes a contribution of at most 1.2% to the total potential in the case of CsI and even less in the lithium containing LiF and LiCl molecules (see Fig. 3) it was assumed to be the same as that of an isoelectronic dimer of rare gas atoms obtained by transferring an electron from the halogen atom to the alkali metal (Table 1, last entry). A, b and C_4 are determined from the experimental values for the well depth D_e in addition to the bond distance R_e and the vibrational frequency ω_e.

The experimental values used in the fit are listed in Table 3. The experimental dissociation energies of LiF and LiCl date back to 1961 from thermodynamic considerations. That of CsI should be more reliable since it was measured directly by photodissociation. Since it is only possible to measure the dissociation energy to atoms D_0, the classical energy for dissociation to ions D_e was calculated from the equation $D_e = D_0 + 0.5\omega_e - 0.25\omega_e\chi_e + (E_{IE} - E_{EA})$, where χ_e is the anharmonicity parameter, E_{IE} is the ionization potential of the neutral alkali atom and E_{EA} is the electron affinity of the neutral halogen atom. The corresponding parameters are listed in the Appendix.

The three unknowns A, b and C_4 of the TTT-R model are determined by simultaneously solving the following three

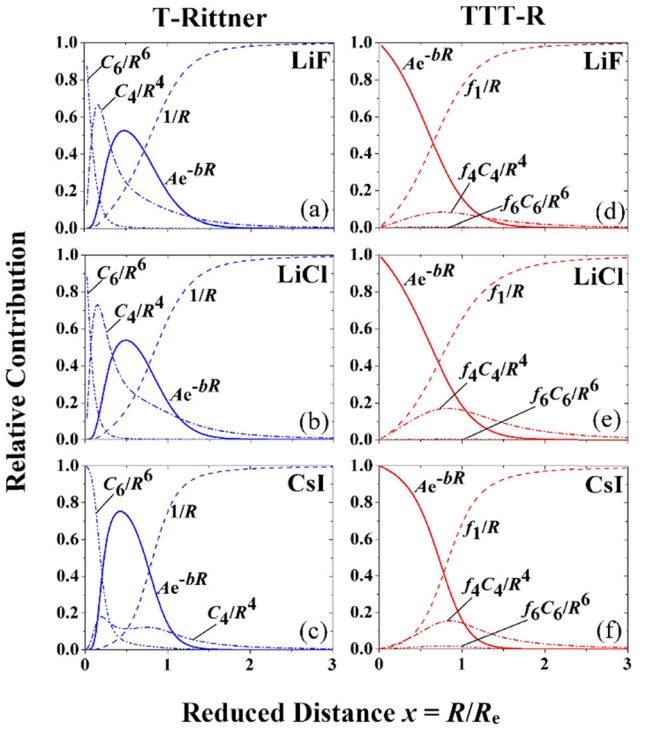

Fig. 3 Diagram showing the effects of damping on the relative contributions to the overall T-Rittner and TTT-R potentials. The frames (a–c) display the relative contributions of the repulsive Born–Mayer term (sold line) and the attractive Coulomb, induction and dispersion terms (broken lines) to the undamped T-Rittner model. Frames (d–f) show the corresponding contributions to the damped TTT-R potential.

equations self-consistently for the experimental values for R_e, D_e and ω_e:

$$V(R_e) = D_e, \tag{7}$$

$$\left.\frac{dV}{dR}\right|_{R=R_e} = 0, \tag{8}$$

and

$$\left.\frac{d^2V}{dR^2}\right|_{R=R_e} = \mu\omega_e^2, \tag{9}$$

where μ is the reduced mass of the isotopomer of the three most abundant isotopomers $^7Li^{19}F$, $^7Li^{35}Cl$, and $^{133}Cs^{127}I$.[46] The program is similar to the one which was used to derive A and b in the TT model with R_e and D_e fixed.[47] One more loop was added to fit eqn (9). All of the possible values (greater than zero) were scanned for C_4 until eqn (7)–(9) are satisfied.

The best fit potential parameters are listed in Table 4 where they are compared with the T-Rittner values based on nearly the same experimental values for R_e and ω_e but with assumed values of C_4. The different approach has a big effect on the TTT-R values for the preexponential factor A. They are reduced to about one half of the T-Rittner values, and the b values are smaller than the T-Rittner values by 6, 14 and 12% for LiF, LiCl and CsI, respectively. Whereas for LiF the present value for C_4 of 3.8800 is close to the T-Rittner value of 3.6407 the TTT-R

Table 3 The experimental values on which the potential parameters of the TTT-R model (Table 4) are based. The classical energy for dissociation to ions, D_e was calculated from the experimentally measured dissociation energy to atoms D_0 using the formula: $D_e = D_0 + 0.5\omega_e - 0.25\omega_e\chi_e + (E_{IE} - E_{EA})$. The corresponding parameters are listed in the Appendix

	Bond distance R_e[47]		Dissociation energy (to atoms) D_0		Classical dissociation energy (to ions) D_e		Vibrational constant[49,50] ω_e		C_6[25]	
Dimer	Å	a.u.	eV	a.u.	eV	a.u.	cm^{-1}	a.u.	eV Å^6	a.u.
$^7Li^{19}F$	1.563	2.955	5.9305[a 51,52]	0.2179	7.9772	0.2931	910.57	0.00415	1.8116	3.0319
$^7Li^{35}Cl$	2.020	3.818	4.8720[a 51,52]	0.1790	6.690	0.2458	642.95	0.00293	5.7076	9.5519
$^{133}Cs^{127}I$	3.314	6.262	3.4670[53]	0.1274	4.3092	0.15836	119.19	0.00054	170.82	285.87

[a] The values are the average of D_0 reported in the two references. The errors are estimated to be ±3%.

values for LiCl and CsI are about a factor two larger than the T-Rittner values.

C. The effects of damping on the potential terms

The dramatic effect of damping on the potential parameters is shown in Fig. 3 where the contributions of the individual terms to the T-Rittner potential are compared with the contributions of the damped terms of the TTT-R potential. On the left-hand side of Fig. 3 the three frames (a)–(c) illustrate the relative absolute contributions of the four interaction terms to the original T-Rittner model for LiF, LiCl and CsI, respectively. To facilitate the comparison of the three systems the contributions are plotted against the reduced distance $x = R/R_e$. The T-Rittner contribution from the attractive Coulomb potential gradually decreases with decreasing internuclear distance from 100% at about $x \approx 1.5$ to zero at $x = 0$. At about $x \approx 0.6$ it is overtaken by the repulsive Born–Mayer term which first goes through a maximum and then turns over and also goes to zero. This complete suppression of this important term is caused by the increasingly large negative (attractive) contribution at small internuclear distances from the undamped C_4 term, which also goes through a maximum as it is replaced by the more negative C_6 term. Thus, these two long range undamped negative terms by virtue of their large negative powers n contribute the most at very small distances. Together with the negative Coulomb term they pull the entire potential down to negative infinity.

The corresponding damped TTT-R potential terms are shown in the right-hand frames (d)–(f). Perhaps surprisingly the contribution from the negative Coulomb shows about the same behavior as with the T-Rittner potential. This is attributed to the strong similarity of the damping curve (Fig. 2) and the undamped Coulomb contribution curves in Fig. 3(a)–(c). The damping of the negative long-range terms C_4 and C_6 serves to largely reduce their influence and allows the positive Born Mayer term to dominate the potential at small distances. This provides the overall potential with the usual repulsive wall. The middle frames also show the almost negligible contribution of the C_6 dispersion term referred to in Section II B.

The potential curves based on the two models are shown in Fig. 4. The attractive well regions are nearly identical and there the damping has little effect. Small differences occur at internuclear distance less than the minimum, which are especially apparent in LiF and LiCl. In the repulsive region the damping raises the potentials so that they show the expected behavior. In contrast the T-Rittner potentials pass through a maximum of about 0.2 a.u. (~5.5 eV) and then become strongly negative. CsI behaves differently due to the extended range of the Born–Mayer term (Fig. 3(f)) and in this system the T-Rittner potential turns over at much higher energies.

The potential parameters A, b and C_4 also depend on the damping of each of the attractive terms of the TTT-R model. This is shown in Table 5 where the parameters are listed following successive removal of the damping of the Coulomb potential (second line), removal of damping of the C_4 (third line) and finally removal of all damping functions (last line). The damping of the Coulomb potential does not have a large effect on the potential parameters, but without damping of the attractive C_4 term the preexponential Born Mayer terms A increases significantly and approaches the T-Rittner values. The damping has a much smaller effect on the parameter b and C_4 of LiF but a larger effect on the heavier diatoms LiCl and CsI. It is of interest that the surprisingly large value of C_4 of the present TTT-R potential compared to the assumed T-Rittner value is not affected by damping.

Table 4 Comparison of the best fit values for A, b and C_4 from the damped TTT-R potential model based on the experimental parameters in Table 3 with the T-Rittner model parameters[13]

		A		b		C_4	
Dimer	Potential	eV	a.u.	$Å^{-1}$	a.u.	eV Å^4	a.u.
LiF	TTT-R	419.96	15.433	3.4605	1.8312	8.2796	3.8802
	T-Rittner[13]	728.81	28.768	3.6697	1.9419	7.7686	3.6407
LiCl	TTT-R	411.40	15.119	2.6468	1.4006	46.150	21.628
	T-Rittner[13]	998.25	36.685	3.0211	1.5987	26.776	12.549
CsI	TTT-R	2078.5	76.383	2.3055	1.2200	123.45	57.856
	T-Rittner[13]	4311.4	158.44	2.5880	1.3695	69.118	32.392

III. TTT-R potential curves of LiF, LiCl and CsI

A. Comparison of TTT-R potentials with *ab initio* potential curves

Table 6 provides an overview of the available *ab initio* calculations of the potential curves of LiF, LiCl and CsI, which presently are the only ones available for the alkali halide molecules. The *ab initio* predicted well parameters D_e and R_e

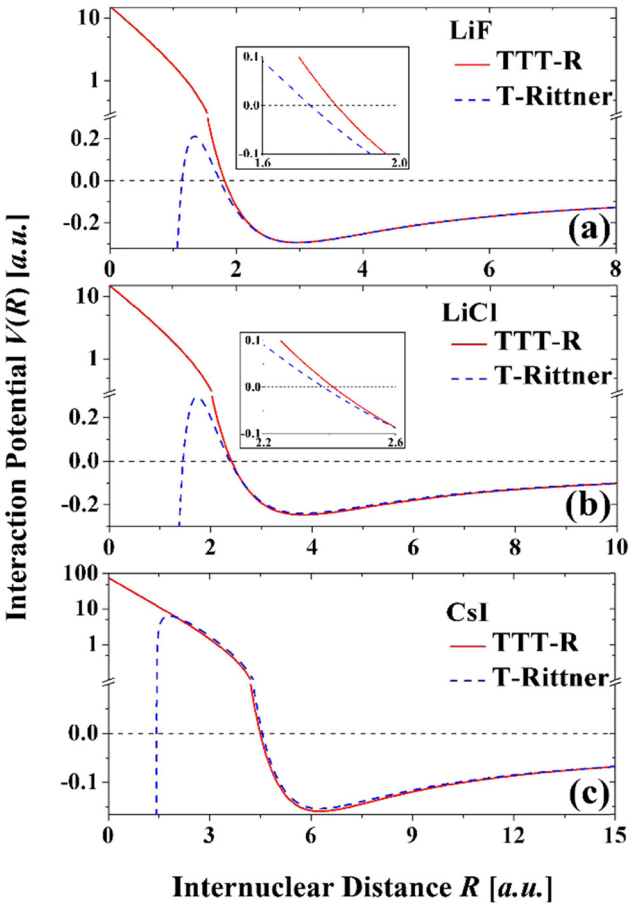

Fig. 4 Comparison of the damped TTT-R with the undamped T-Rittner potential curves for LiF, LiCl and CsI. In the attractive region the potentials are virtually identical. Small differences start to occur at small distances as the potentials become positive. The TTT-R potentials curves display the expected behavior at small distances, whereas the T-Rittner potentials bend over and become negative.

and the vibrational frequencies ω_e are compared with the latest experimental values (Table 3) which are listed in the bottom entry for each system. The most recent theories predict the well parameters D_e and R_e and the vibrational frequencies within a few percent of the experimental values.

Fig. 5(a), 6(a) and 7(a) display comparisons of the present TTT-R reduced potential curves with the corresponding *ab initio* reduced potentials for LiF, LiCl and CsI, respectively. Alternatively the absolute potentials (V in a.u., R in a.u.) could be compared. But in this case each of the different theoretical potential curves would be slightly shifted in both the x- and y-coordinate depending on the corresponding values of D_e and R_e and the comparison would be difficult. For this reason the reduced curves normalized to the corresponding well parameters, which show the shape of the potential, are compared in the following figures. The well parameters are compared separately in Table 6.

For LiF and LiCl the different *ab initio* potentials and the predicted TTT-R potential all follow closely the same potential curve. In the case of CsI there is only one *ab initio* potential from Kurosaki *et al.*[60] In this case the agreement is not so good. In lieu of other calculations the semi-*ab initio* potential of Patil[27] is also shown. In this case the agreement with the TTT-R potential is excellent. This suggests that the TTT-R potential is more reliable than the *ab initio* potentials.

Since the differences between the TTT-R and the *ab initio* potential curves are too small to be clearly resolved in Fig. 5(a), 6(a) and 7(a) they are shown in the bottom parts of each of the figures. In the case of LiF and LiCl the agreement with the *ab initio* potentials is better than about 2% and mostly about 1%. The only exception is the 1974 CI potential of Kahn *et al.*[54] for LiF. The large differences in the case of CsI and the fact that there is only one *ab initio* potential for this system appears to be related with the large spin–orbit (SO) coupling which leads to a splitting between the $^2P_{1/2}$ and $^2P_{1/2}$ states of the halogen atom. Iodine stands out among the halogen atoms by having the largest splitting of 7603 cm^{-1} compared to 404 cm^{-1} and 881 cm^{-1} for fluorine and chlorine, respectively. As stated by Kurosaki *et al.* in their article:[60] "The atomic SO splittings greatly affect the nature of the potential energy curves especially around the avoided crossing point. Also substantial are the relativistic effects on the inner shell electrons in heavy elements." This illustrates another advantage of the model potentials, which are not affected by these complications.

As indicated by Fig. 4 similarly good agreement with the *ab initio* potentials in the well region is also expected for the T-Rittner potentials based on the parameters in Table 4. Since most of the modern *ab initio* potentials have appeared in the present century and the model calculations are mostly from the end of the last century the good agreement provides belated justification of the T-Rittner model for the attractive well region of the potentials.

IV. Summary and discussion

The present article describes the effects of the damping due to charge overlap at short distances on the popular T-Rittner

Table 5 The effect of damping on the TTT-R potential parameters (in a.u.) is tabulated by comparing the calculated best fit values with successive eliminations of the damping functions f

	LiF			LiCl			CsI		
Model	A	b	C_4	A	b	C_4	A	b	C_4
Present	15.432	1.8312	3.8802	15.119	1.4006	21.628	76.382	1.2200	57.856
$f_1 = 1$	18.098	1.8411	3.8352	17.165	1.4064	21.519	78.078	1.2200	58.038
$f_4 = f_1 = 1$	27.909	1.9404	3.3099	37.469	1.5388	18.703	96.562	1.2370	57.379
$f_6 = f_4 = f_1 = 1$	31.104	1.9757	3.1130	39.822	1.5538	18.375	107.232	1.2489	56.847

Table 6 The reported *ab initio* calculations of LiF, LiCl and CsI potential curves are summarized. For each calculation the method used and the predicted well parameter values R_e, D_e and ω_e values are listed. The entries for each system are in chronological order with the latest experimental values at the bottom of each system list

	Method	R_e (Å)	R_e (a.u)	D_e (eV)	D_e (a.u.)	ω_e (cm)	Ref.
LiF	GVB/IVO-CI[a]	1.5637	2.9550	7.1875	0.2487	—	Kahn *et al.*[54]
	EDC-SSD[b]	1.5000	2.8346	8.0225	0.2948	1010 ± 20	Kim and Gordon[55]
	MCSCF[c]	1.5890	3.0028	7.8305	0.2878	896.1	Werner and Meyer[56]
	CIR-VB[d]	1.6000	3.0236	8.0605	0.2962	—	Zeiri and Balint-Kurti[57]
	MRCI[e]	1.5991	3.0219	7.7864	0.2861	—	Varandas[58]
	Expt.	1.563	2.995	7.9772	0.2931	910.57	Table 3
LiCl	EDC-SSD[b]	1.9400	3.6661	6.2532	0.22980	690 ± 10	Kim and Gordon[55]
	CIR-VB[d]	2.0000	3.7795	6.5489	0.24067	—	Zeiri and Balint-Kurti[57]
	MRSDCI[f]	2.0215	3.832	6.7742	0.24894	644.09	Weck *et al.*[59]
	MRSDCI[f]	2.0327	3.8112	6.3672	0.2340	630.62	Kurosaki and Yokoyama[24]
	Expt.	2.0207	3.8185	6.690	0.2458	642.95	Table 3
CsI	QMEPT[g]	3.2650	6.170	4.3267	0.15900	—	Patil[27]
	MRSDCI[f]	3.4000	6.4251	3.6679	0.13479	116.6	Kurosaki *et al.*[60]
	Expt.	3.3142	6.2629	4.3092	0.15836	119.19	Table 3

[a] CI with generalized valence-bond orbitals from ground state MCSCF calculation. [b] Coulomb energy calculated from electron density of the combined system assumed as the sum of the separate ionic electron densities. Non-Coulombic energy calculated from electron gas approximation. [c] MCSCF with optimized wave functions. [d] Covalent-ionic resonance model together with valence-bond method. [e] Multireference CI based on complete-active-space SCF wave functions. [f] Multireference single-and double-excitation CI. [g] Quantum mechanical exchange perturbation theory similar to used in ref. 15.

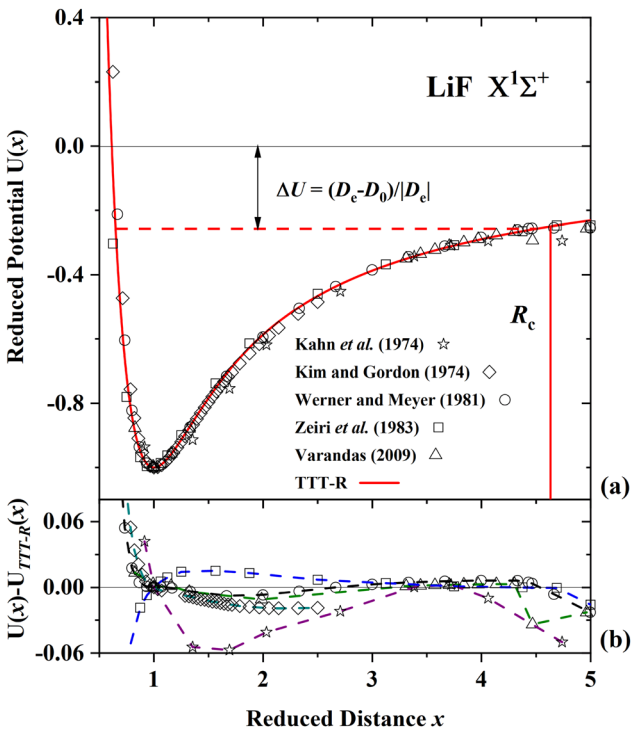

Fig. 5 Comparison of the present reduced potential (red line curve) with five *ab initio* reduced potential curves for LiF in the ground state.[54–58] (a) Shows the *ab initio* energy-distance points on a reduced scale. The zero reduced potential corresponds to dissociation to ions, the dashed red line corresponds to dissociation to atoms. ΔU denotes the difference between the two dissociation limits. R_c denotes the reduced distance at which the covalent and Coulombic potentials cross each other. (b) The differences in the *ab initio* reduced potentials with respect to the present potential are plotted as a function of the reduced distance. The agreement among the *ab initio* potentials and with the present potential is better than 3% with the exception of the potential of ref. 53 and the agreement with the TTT-R potential is better than about 2%.

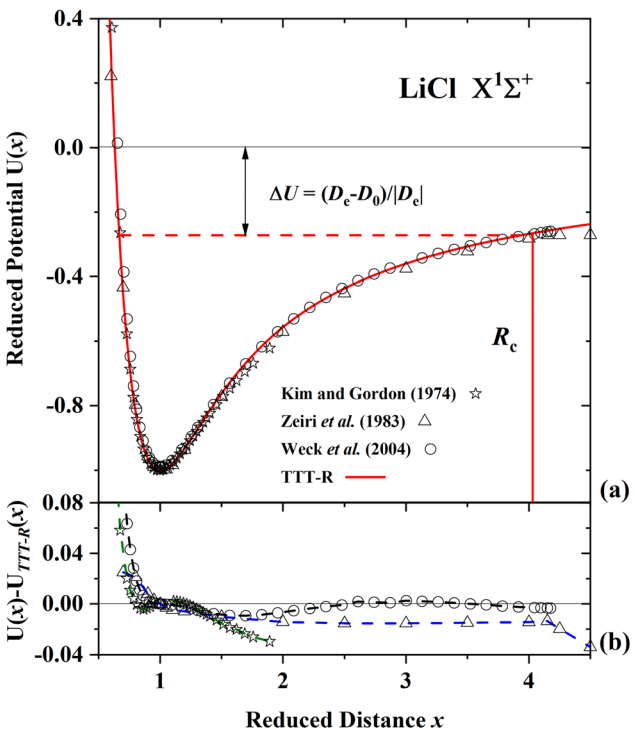

Fig. 6 Comparison of the present reduced potential (red line curve) with 3 *ab initio* reduced potential curves for LiCl in the ground state.[55,57,59] (a) Shows the *ab initio* energy-distance points on a reduced scale. The zero reduced potential corresponds to dissociation to ions, the dashed red line corresponds to dissociation to atoms. ΔU denotes the difference between the two dissociation limits. R_c denotes the reduced distance at which the covalent and Coulombic potentials cross each other. (b) The differences in the *ab initio* reduced potentials with respect to the present potential are plotted as a function of the reduced distance. The present potential agrees with the latest *ab initio* potential of Weck *et al.*[59] to better than 1% and agrees to better than 2% with the earlier potential of Zieri *et al.*[57]

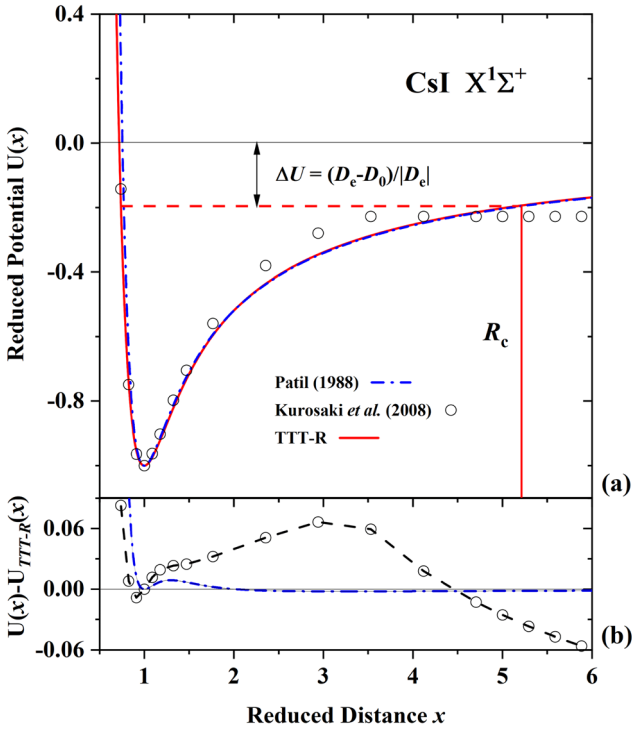

Fig. 7 Comparison of the present reduced potential (red line curve) with the *ab initio* reduced potential of Kurosaki *et al.*[60] and the semi-*ab initio* reduced potential of Patil[27] for CsI in the ground state. (a) Shows the *ab initio* energy-distance points on a reduced scale. The zero reduced potential corresponds to dissociation to ions, the dashed red line corresponds to dissociation to atoms. ΔU denotes the difference between the two dissociation limits. R_c denotes the reduced distance at which the covalent and Coulombic potentials cross each other. (b) The differences in the *ab initio* reduced potentials with respect to the present potential are plotted as a function of the reduced distance. The present potential differs by up to 6% with the *ab initio* potential[60] and differs only by less than 0.5% with the semi-*ab initio* potential of Patil.[27]

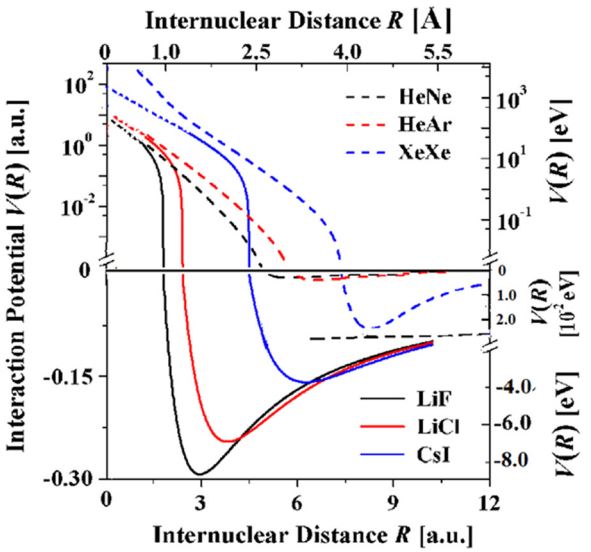

Fig. 8 Comparison of the TTT-R potentials of the three alkali halide diatoms with the corresponding isoelectronic rare gas diatoms. The rare gas potentials are highly accurate and have recently been shown to be conformal.[61] Their repulsive potentials extend to R = 0 since the proper united atom limit has been taken into account.[61]

potential[13] for the alkali halide diatoms. The damping function used is based on the original damping function of Tang and Toennies which was developed and tested first for the London dispersion potential. Without damping the long range negative R^{-4} induction and R^{-6} dispersion terms are shown to dominate the T-Rittner potential at the expense of the Born–Mayer repulsion so that the potential tends to minus infinity at distances below the zero crossing point. Thus the damping of the attractive Coulomb potential, induction and dispersion terms has the important effect that it eliminates the negative singularity at short distances. Instead, at short ranges the new potential with damping, denoted TTT-R, exhibits the expected increase of the repulsive potential with decreasing internuclear distances.

In addition to having the proper short range behavior it is demonstrated that the TTT-R potential curve also agrees within a few percent over the full range of distance from the zero passage distance R_0 out to very large distances with the *ab initio* potentials for LiF and LiCl. Since the damping affects only the potential at short distances near the zero crossing point the 1973 T- Rittner potential on which the TTT-R potential is based provides a nearly equally good agreement with the *ab initio* potentials over most of the well region. The comparison with the only *ab initio* potential for CsI is not satisfactory, but this could be due to inaccuracies of the *ab initio* potential related to the large spin–orbit coupling and relativistic effects. On the other hand comparison with a *semi ab initio* perturbation calculation[26] appears to provide confirmation of the model potentials.

In the early T-Rittner-type investigations the C_4 induction term was assumed to be known. In view of the wide range of the polarizabilities of the ions in the many previous reports the C_4 term was also fitted in the present investigation. Thus the parameters of TTT-R model are based on a fit not only of the well distance R_e, and vibrational frequency ω_e but also of the experimental determined well depth D_e. Whereas the so determined value for C_4 in the case of LiF is in reasonable agreement with an earlier theoretical value for the ion-in-molecule polarizabilities[35] the best fit C_4 value for LiCl is about a three times larger and CsI is about twice larger as the theoretical values in the early literature.[34,35] Compared to the free ion polarizabilities for LiF they are about one half as large and for LiCl about the same and about 50% larger for CsI. Also in view of the uncertainties of the theory in treating the effects of strong Coulomb forces on the ion polarizabilities, further work is necessary.

With the availability of realistic potentials it is possible to compare the potentials for the three systems with the potentials of the isoelectronic rare gas diatoms HeNe, HeAr, and XeXe[61] over nearly the full range of internuclear distances (Fig. 8). The much wider attractive bowls of the alkali halide potentials derive from the damped Coulomb and induction C_4 terms. The strong attraction of these terms can also explain that the bond distances are smaller by 51, 58 and 76% and that the dissociation energies are much greater by factors of 10^3 to 10^2.

Whereas the attractive wells of the rare gas dimers are much smaller Fig. 8 shows that the repulsive potentials are similar. In particular, in the case of CsI and XeXe this trend is in agreement

with high pressure equation of state studies which reveal that at pressures above 15 GPa the volumes per atom are nearly identical.[62] Fig. 8 suggests that this may also be true for the lighter alkali halide and isoelectronic rare gas dimers. The comparison of the repulsive regions in Fig. 8 suffers somewhat from the fact that the united atom limit has not been accounted for in the TTT-R potentials but have been included in the rare gas dimers. Thus, the extent of agreement of the repulsive potentials at distance less than 1.5 a.u. is only approximate. More accurate models and experiments are required before it can be shown that the alkali halide reduced potentials are conformal as it has been recently shown for the rare gas diatoms.[61]

In future investigations several improvements of damped T-Rittner models can be envisaged. The polarizabilities of the cations and anions can be improved by accounting for the large differences in the free anion and cation polarizabilities and their different internuclear distance dependencies. The T-Rittner type models including the present TTT-R model have the disadvantage that they are based on experimental parameters related only to the minimum of the potential. By including additional *ab initio* parameters such as the distance dependence of the dipole moments better models could be developed. The repulsive region can also be improved by taking account of the united atom limit.[20,61] Future refined models will provide accurate force field models for treating condensed systems such as solids and liquid alkali halides.

Author contributions

Xiaowei Sheng carried out the calculations and made the figures. K. T. Tang had the idea and made valuable advice. Peter Toennies wrote the final version.

Conflicts of interest

There are no conflicts of interest.

Appendix

Table 7 The energy differences for the dissociation to ions and atoms in the LiF, LiCl, and CsI. The ionization energies and electron affinities are corresponding to the cation (Li and Cs) and anion (F, Cl and I), respectively. Here the ionization energies and the electron affinities are taken from NIST[47] and the ref. 63

	$\omega_e\chi_e$[48]		Ionization energies E_{IE}[47]		Electron affinities E_{LA}[63]		$\Delta E = E_{IE} - E_{EA}$	
Dimer	cm^{-1}	a.u.	eV	a.u.	eV	a.u.	eV	a.u.
LiF	8.2080	3.74×10^{-5}	5.392	0.1981	3.401	0.1250	1.991	0.07314
LiCl	4.4725	2.04×10^{-5}	5.392	0.1981	3.613	0.1328	1.779	0.06538
CsI	0.2542	1.16×10^{-6}	3.894	0.1431	3.051	0.1124	0.8349	0.03068

Acknowledgements

X. W. S. acknowledges and appreciates the support of the National Natural Science Foundation of China (No. 12174003) and the Anhui Provincial Natural Natural Science Foundation (No. 2008085MA25). J. P. T. thanks his colleagues for generous support: He also thanks Katrin Glormann for careful assistance in preparing the manuscript. Open Access funding provided by the Max Planck Society.

References

1 G. Benedek and J. P. Toennies, *Atomic Scale Dynamics at Surfaces*, Springer, New York, 2018.
2 F. Seitz, Color Centers in Alkali Halide Crystals, *Rev. Mod. Phys.*, 1946, **18**(3), 384.
3 M. M. Walz, M. M. Ghahremanpour, P. J. van Maaren and D. van der Spoel, Phase-Transferable Force Field for Alkali Halides, *J. Chem. Theory Comput.*, 2018, **14**(11), 5933.
4 C. W. Townes and A. L. Schawlow, *Microwave Spectroscopy McGraw Hill*, New York, 1955.
5 D. Herschbach, Molecular collisions, from warm to ultracold, *Faraday Discuss.*, 2009, **142**, 9.
6 P. D. Gregory, J. A. Blackmore, S. L. Bromley, J. M. Hutson and S. L. Cornish, Robust storage qubits in ultracold polar molecules, *Nat. Phys.*, 2021, **17**(10), 1149.
7 W. Barlow, The Architecture of Molecules, *Z. Kristallogr*, 1898, **29**, 433.
8 L. Pauling, The theoretical prediction of the physical properties of many-electron atoms and ions. Mole refraction, diamagnetic susceptibility, and extension in space, *Proc. R. Soc. A.*, 1927, **114**, 181.
9 W. Kossel, *Sitzungsbericht d. Bayr. Akad., meth.-naturw. Kl.*, 1917, 127.
10 E. Madelung, Das elektrische Feld in Systemen von regelmäßig angeordneten Punktladungen, *Phys. Z.*, 1918, **19**, 524.
11 M. Born and J. E. Mayer, Zur Gittertheorie der Ionenkristalle, *Z. Phys.*, 1932, **75**, 1.
12 M. Born and W. Heisenberg, Über den Einfluß der Deformierbarkeit der Ionen auf optische und chemischen Konstanten, *Z. Phys.*, 1924, **23**, 388.
13 E. S. Rittner, Binding Energy and Dipole Moment of Alkali Halide Molecules, *J. Chem. Phys.*, 1951, **19**(8), 1030.
14 B. T. Gowda, B. S. Sherigara and S. W. Benson, Potential Functions for Alkali-Halide Molecules, *J. Comput. Chem.*, 1985, **6**(2), 93.
15 P. Brumer and M. Karplus, Perturbation-Theory and Ionic Models for Alkali-Halide Systems. 1. Diatomics, *J. Chem. Phys.*, 1973, **58**(9), 3903.
16 M. Kumar, A. J. Kaur and J. Shanker, Spectroscopic Constants of Alkali-Halides and Hydrides Using Modified T-Rittner Model, *J. Chem. Phys.*, 1986, **84**(10), 5735.
17 M. J. L. Sangster and M. Dixon, Interionic Potentials in Alkali-Halides and Their Use in Simulations of Molten-Salts, *Adv. Phys.*, 1976, **25**(3), 247.
18 R. N. Yardley and G. G. Balintkurti, Ab-Initio Valence-Bond Calculations on HF, LiH, LiH+ and LiF, *Mol. Phys.*, 1976, **31**(3), 921.

19 R. A. Buckingham, The Repulsive Interaction of Atoms in S States, *Trans. Faraday Soc.*, 1958, **54**(4), 453.
20 S. Warnecke, K. T. Tang and J. P. Toennies, Communication: A simple full range analytical potential for H(2)b(3)Sigma(+)(u), H-He (2)Sigma(+), and He-2 (1)Sigma(+)(g), *J. Chem. Phys.*, 2015, **142**, 13.
21 R. K. Pathak and A. J. Thakkar, Very Short-Range Interatomic Potentials, *J. Chem. Phys.*, 1987, **87**(4), 2186.
22 A. J. Kaur, W. N. Bhende, P. S. Bakhshi and J. Shanker, Analysis of the Short-Range Repulsive Potential in Alkali-Halides, *Phys. Status Solidi B*, 1984, **123**(1), 71.
23 A. Dewaele, A. B. Belonoshko, G. Garbarino, F. Occelli, P. Bouvier, M. Hanfland and M. Mezouar, High-pressure high-temperature equation of state of KCl and KBr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**(21), 214105.
24 Y. Kurosaki and K. Yokoyama, Ab initio MRSDCI study on the low-lying electronic states of the lithium chloride molecule (LiCl), *J. Chem. Phys.*, 2012, **137**(17), 064305.
25 J. Jiang, J. Mitroy, Y. Cheng and M. W. J. Bromley, Effective oscillator strength distributions of spherically symmetric atoms for calculating polarizabilities and long-range atom-atom interactions, *At. Data Nucl. Data Tables*, 2015, **101**, 158.
26 T. Gould and T. Bucko, C-6 Coefficients and Dipole Polarizabilities for All Atoms and Many Ions in Rows 1-6 of the Periodic Table, *J. Chem. Theory Comput.*, 2016, **12**(8), 3603.
27 S. H. Patil, Interionic Potentials in Alkali-Halides, *J. Chem. Phys.*, 1987, **86**(1), 313.
28 Y. P. Varshni and R. C. Shukla, Potential Energy Functions for Alkali Halide Molecules, *J. Mol. Spectrosc.*, 1965, **16**(1), 63.
29 J. Shanker, G. G. Agrawal and N. Dutt, Electronic Polarizabilities and Photoelastic Behavior of Ionic-Crystals, *Phys. Status Solidi B*, 1986, **138**(1), 9.
30 K. J. Donald, W. H. Mulder and L. von Szentpaly, Comment on "A potential dependent polarizability?" [J. Chem. Phys. 96, 5289 (1992)], *J. Chem. Phys.*, 2000, **113**(8), 3477.
31 J. Shanker and S. S. Kushwah, Response to "Comment on A potential dependent polarizability?" [J. Chem. Phys. 113, 3477 (2000)], *J. Chem. Phys.*, 2000, **113**(8), 3479.
32 A. S. McNeill, K. A. Peterson and D. A. Dixon, Polarizabilities of neutral atoms and atomic ions with a noble gas electron configuration, *J. Chem. Phys.*, 2020, **153**(17), 174304.
33 J. Shanker and H. B. Agrawal, Electronic Polarizabilities, Ionic-Radii, and Repulsive Potential Parameters for Diatomic Alkali-Halide Molecules, *Can. J. Phys.*, 1980, **58**(7), 950.
34 M. Kumar and J. Shanker, Electronic Polarizabilities, Potential Functions, and Spectroscopic Constants for Diatomic-Molecules of Alkali-Halides and Alkali Hydrides, *J. Chem. Phys.*, 1992, **96**(7), 5289.
35 S. Hati, B. Datta and D. Datta, Polarizability of an ion in a molecule. Applications of Rittner's model to alkali halides and hydrides revisited, *J. Phys. Chem.*, 1996, **100**(51), 19808.
36 K. T. Tang and J. P. Toennies, An Improved Simple-Model for the van der Waals Potential Based on Universal Damping Functions for the Dispersion Coefficients, *J. Chem. Phys.*, 1984, **80**(8), 3726.
37 A. Koide, W. J. Meath and A. R. Allnatt, 2nd Order Charge Overlap Effects and Damping Functions for Isotropic Atomic and Molecular-Interactions, *Chem. Phys.*, 1981, **58**(1), 105.
38 R. J. Wheatley and W. J. Meath, Dispersion Energy Damping Functions, and Their Relative Scale with Interatomic Separation, for (H,He,Li)-(H,He,Li) Interactions, *Mol. Phys.*, 1993, **80**(1), 25.
39 M. Gutowski, J. Verbeek, J. H. Vanlenthe and G. Chalasinski, The Impact of Higher Polarization Functions on 2nd-Order Dispersion Energy - Partial-Wave Expansion and Damping Phenomenon for He-2, *Chem. Phys.*, 1987, **111**(2), 271.
40 W. Meyer and L. Frommhold, Long-Range Interactions in H-He: *ab-initio* Potential, Hyperfine Pressure Shift and Collision-Induced Absorption in the Infrared, *Theor. Chim. Acta*, 1994, **88**(3), 201.
41 K. T. Tang and J. P. Toennies, Asymptotic Theory of the Chemical-Bond in H-2+ Based on a Simple Physical Model, *J. Phys. Chem.*, 1990, **94**(20), 7880.
42 R. Nikhar and K. Szalewicz, Reliable crystal structure predictions from first principles, *Nat. Commun.*, 2022, **13**, 3095.
43 A. J. Stone, *The Theory of Intermolecular Forces*, Clarendon Press, Oxford, 1996.
44 L. V. Slipchenko and M. S. Gordon, *Electrostratic Energy in the Effective Fragment Potential Method: Theory and Application to Benzene Dimer*, I. Wiley Periodicals, 2006.
45 K. Jug, E. Fasold and A. M. Koster, Charge and Valence in Lithium Compounds, *Chem. Phys. Lett.*, 1992, **188**(3–4), 294.
46 The atomic masses for these isotopes are m(7Li) = 7.016004 u, m(19F) = 18.993105 u, m(35Cl) = 34.968852729 u, m(127I) = 126.904070 u, m(133Cs) = 132.905433 u.
47 K. T. Tang and J. P. Toennies, New Combining Rules for Well Parameters and Shapes of the van der Waals Potential of Mixed Rare-Gas Systems, *Z. Phys. D – Atoms Molec. Clusters*, 1986, **1**(1), 91.
48 Online available at **https://physics.nist.gov/cgi-bin/MolSpec/diperiodic.pl**.
49 K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, IV Constants of Diatomic Molecules*, Van Nostrand Rheinhold Co., New York, 1979.
50 K. K. Irikura, Experimental vibrational zero-point energies: Diatomic molecules, *J. Phys. Chem. Ref. Data*, 2007, **36**(2), 389.
51 L. Brewer and E. Brackett, The Dissociation Energies of Gaseous Alkali Halides, *Chem. Rev.*, 1961, **61**(4), 425.
52 E. M. Bulewicz, L. F. Phillips and T. M. Sugden, Determination of Dissociation Constants and Heats of Formation of Simple Molecules by Flame Photometry.8. Stabilities of Gaseous Diatomic Halides of Certain Metals, *Trans. Faraday Soc.*, 1961, **57**(6), 921.
53 T. M. R. Su and S. J. Riley, Alkali-Halide Photofragment Spectra.1. Alkali Iodide Bond-Energies and Excited-State Symmetries at 266 Nm, *J. Chem. Phys.*, 1979, **71**(8), 3194.
54 L. R. Kahn and P. J. Hay, Theoretical Study of Curve Crossing - Ab-Initio Calculations on 4 Lowest 1sigma+ States of Lif, *J. Chem. Phys.*, 1974, **61**(9), 3530.
55 Y. S. Kim and R. G. Gordon, Ion-Ion Interaction Potentials and Their Application to Theory of Alkali-Halide and

Alkaline-Earth Dihalide Molecules, *J. Chem. Phys.*, 1974, **60**(11), 4332.

56 H. J. Werner and W. Meyer, Mcscf Study of the Avoided Curve Crossing of the 2 Lowest Sigma-1+ States of Lif, *J. Chem. Phys.*, 1981, **74**(10), 5802.

57 Y. Zeiri and G. G. Balint-kurti, Theory of Alkali-Halide Photofragmentation - Potential-Energy Curves and Transition Dipole-Moments, *J. Mol. Spectrosc.*, 1983, **99**(1), 1.

58 A. J. C. Varandas, Accurate ab initio potential energy curves for the classic Li-F ionic-covalent interaction by extrapolation to the complete basis set limit and modeling of the radial nonadiabatic coupling, *J. Chem. Phys.*, 2009, **131**(12), 124128.

59 P. F. Weck, K. Kirby and P. C. Stancil, Ab initio configuration interaction study of the low-lying (1)Sigma(+) electronic states of LiCl, *J. Chem. Phys.*, 2004, **120**(9), 4216.

60 Y. Kurosaki, L. Matsuoka, K. Yokoyama and A. Yokoyama, Ab initio study on the ground and low-lying excited states of cesium iodide (CsI), *J. Chem. Phys.*, 2008, **128**(2), 024301.

61 X. W. Sheng, J. P. Toennies and K. T. Tang, Conformal Analytical Potential for All the Rare Gas Dimers over the Full Range of Internuclear Distances, *Phys. Rev. Lett.*, 2020, **125**(25), 253402.

62 A. N. Zisman, I. V. Aleksandrov and S. M. Stishov, X-Ray Study of Equations of State of Solid Xenon and Cesium Iodide at Pressures up to 55-Gpa, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1985, **32**(1), 484.

63 T. Andersen, H. K. Haugen and H. Hotop, Binding energies in atomic negative ions: III, *J. Phys. Chem. Ref. Data*, 1999, **28**(6), 1511.