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Anisotropy of van der Waals Radii of Atoms in Molecules: Alkali-Metal and Halogen Atoms

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Abstract

The van der Waals radii of the alkali-metal and halogen atoms in 28 diatomic molecules are estimated theoretically, where the radius is defined as the distance from the nucleus to the surface having a calculated electron density of 0·005 a. u. (0·0337 e Å^{-3}). The anisotropy of their radii is studied. The electron-correlation effect on the electron-density distribution in Na^+ and F^- increases slightly (by 0·01–0·02 Å) the radii calculated at the Hartree–Fock level of theory. A large 'polar flattening' is observed for the Cl and Br atoms bonded to H or halogen atoms. This can arise from the fact that the p_z electrons of the Cl and Br atoms flow into the bonding region in forming the chemical bond. On the other hand, a small 'polar extension' is observed for the K and Na atoms bonded to halogen atoms. This phenomenon is described with a simple model calculation ($Na^+ \cdots -1e$), where the F atom in an NaF molecule is replaced with a negative point charge. The larger repulsion energy of an $(HF)_2$ dimer in a sideways-on contact than in a head-on contact reflects the anisotropy of the electron-density distribution around the F atom in the molecule.

1. Introduction

The van der Waals radii listed in the tables of Pauling (1942) or Bondi (1964, 1968) are often employed as one of the parameters in the analytical potentials (Bohm & Ahlrichs, 1985; Sagarik & Ahlrichs, 1986; Dupuis, 1986; Billeter, Howard, Kuntz & Kollman, 1988) used to compute the interaction energies between molecules. The radii are essentially based on the effective sizes of non-bonded atoms which are assumed to be spherical about their nuclei.

Nyburg & Faerman (1985) recently evaluated the effective van der Waals shapes of several atoms (N, O, F, S, Cl, Br and I) bonded to a single C atom using the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell & Rodgers, 1979). They pointed out that for O and N the shapes are virtually spherical, but for the remainder the shape is more or less spheroidal, always having the shorter radius along the atom-to-carbon bond vector (called 'polar flattening').

Some theoretical papers (Nyburg & Wong-Ng, 1977*a*,*b*; Price & Stone, 1982; Williams & Hsu, 1985; Wiberg & Murcko, 1987) indicating the importance of 'polar flattening' in the computation of exact interaction energies have been published. Stone & Price (1988) recently suggested that the anisotropy is important when considering the potentials which are currently used in simulations of protein structures and intermolecular interactions in crystals.

However, there are only a few theoretical papers (Ikuta, 1990; Ikuta, Ishikawa, Katada & Sano, 1990) which quantitatively discuss the anisotropy of van der Waals radii of atoms in molecules. One of the present authors (Ikuta, 1990) has pointed out that the radii of N, O, P and S atoms *in* molecules, defined as the distance from the nucleus to a surface having an electron density 0·005 a. u., agree well with the effective van der Waals shapes estimated experimentally by Nyburg & Faerman (1985). The r_s and r_h of an N atom, which are perpendicular and parallel to the chemical bond, respectively, are equal to one another. For O and S atoms r_h is smaller than r_s, indicating the presence of polar flattening. The r_h of the H atoms in H*R* molecules are also smaller than r_s and to a large extent are linearly dependent on the

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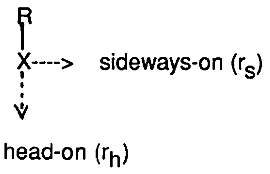
electronegativity (Pearson, 1988*a*,*b*) of the counter atoms *R* (Ikuta, Ishikawa, Katada & Sano, 1990). On the other hand a small 'polar extension' ($r_h > r_s$) is observed for the P atom in the HCP molecule. These results indicate the importance of the electron-density distribution when determining the van der Waals 'shape' of atoms in molecules, although the 'shape' may also be affected by intermolecular forces.



The main purpose of the present study is to determine the van der Waals radii and anisotropy ($r_s - r_h$) of the alkali metals (K, Na and Li) and the halogen atoms (Br, Cl and F) in diatomic molecules. In addition the repulsion energy of an $(HF)_2$ dimer in a sideways-on contact is compared with that in a head-on one in order to see the effect of the van der Waals 'shape' of an atom.

2. Method

The bond lengths of molecules were optimized at the Hartree–Fock level of theory with the 6-31G(*d*,*p*) (Hehre, Ditchfield & Pople, 1972; Hariharan & Pople, 1973; Gorden, 1980) or DZP (double-ζ plus polarization, Dunning & Hay, 1977; Guillermo del Conde, Bagus & Baushlicher, 1977; Poirier, Kari & Csizmadia, 1985) basis sets. The optimized bond lengths are summarized in Table 1.

The electron-density distributions around atoms in molecules are calculated in two directions; one is perpendicular to the chemical bond (the r_s direction) and the other is parallel to the chemical bond (the r_h direction). The sideways-on (r_s) and head-on (r_h) radii in these two directions are defined as the distance from the nucleus to the surface having the computed electron density of 0·005 a. u. (Ikuta, 1990; Ikuta, Ishikawa, Katada & Sano, 1990).

To interpret the anisotropy of the radii in alkali-metal halides, simple model calculations are performed; the electron-density distributions around the nuclei Na^+ and Cl^- are calculated based on the supposition that the F atom in an NaF molecule is replaced with a negative point charge and the K atom in a KCl molecule with a positive one. Other model calculations are performed to estimate the environmental effect on the electron-density distribution in the Na^+ and Cl^- ions which are surrounded by six (negative or positive) point charges placed at the octahedral positions.

Table 1. *Optimized bond lengths in RX molecules* (Å)

Hartree–Fock level of theory used with the 6-31G(*d*,*p*) or DZP (only for Br and K) basis set.

R	*X* = K	Na	Li	H	Br	Cl	F
K	4·163						
Na	3·661	3·189					
Li	3·468	2·999	2·807				
H	2·249	1·913	1·630	0·733			
Br	2·913	2·530	2·214	1·407	2·297		
Cl	2·784	2·397	2·072	1·266	2·147	1·990	
F	2·179	1·885	1·555	0·901	1·739	1·613	1·345

The interaction (repulsion) energies of an $(HF)_2$ dimer are calculated at the third-order Møller–Plesset perturbation level of theory (Møller & Plesset, 1934; Krishnan & Pople, 1978) with the 6-311 + G(3*df*,2*p*) basis set (Clark, Chandrasekhar, Spitznagel & Schleyer, 1983). Two conformers, with sideways-on and head-on contacts, are compared.

For calculation of the electron densities, the Hartree–Fock level of theory with the 6-311G(2*d*,*p*) (Krishnan, Binkley, Seeger & Pople, 1980), MC-311G(2*d*,*p*) (McLean & Chandler, 1980) and DZP (only for Br and K) basis sets was used; a diffuse *p* function [$\zeta_p(F) = 0{\cdot}074$, $\zeta_p(Cl) = 0{\cdot}049$ and $\zeta_p(Br) = 0{\cdot}044$] (Wadt & Hay, 1985) is added for each halogen atom. The SDCI calculations (Brooks, Laidig, Saxe, Handy & Schaefer, 1980) are performed in order to clarify the electron-correlation effect on the electron-density distribution around the nuclei in Li^+, F^- and Na^+ ions.

The North Dakota version of *GAMESS* (Dupuis, Spangler & Wendolski, 1980; Schmidt, Boatz, Baldridge, Koseki, Gorden, Elbert & Lam, 1987) and the *GAUSSIAN*86 (Frisch, Binkley, Schlegel, Raghavachari, Melius, Martin, Stewart, Bobrowicz, Bohlfing, Kahn, DeFrees, Seeger, Whiteside, Fox, Fleuder & Pople, 1984) programs were used for the calculations.

3. Results and discussion

Van der Waals radii of ions

The computed electron densities around the nuclei in several ions (Li^+, Na^+, K^+, F^-, Cl^- and Br^-) are plotted in Fig. 1 as a function of distance from their nuclei. The predicted radii of their ions are 0·79, 1·10, 1·46, 1·46, 1·78 and 1·90 Å, respectively, which are similar to the corresponding Goldschmidt ones (Pauling, 1942), 0·78, 0·98, 1·33, 1·33, 1·81 and 1·96 Å. Electron correlation increases the Hartree–Fock radius of Na^+ only by 0·005 Å and that of F^- by 0·016 Å. Boyd & Wang (1989) and Wang & Boyd (1989) also reached the same conclusion that electron correlation has a very small effect on the electron-density distribution, particularly in the region of van der Waals radii.

Table 2. *r_s and r_h of alkali-metal atoms* (*A*) *in molecules* (*AR*) *and their anisotropies* (Å)

6-311G(2*d*,*p*) basis set used for first-row atoms, MC-311G(2*d*,*p*) for second-row atoms and DZP for K and Br atoms. For each halogen atom one diffuse *p* function is added.

R	r_s	r_h	$r_s - r_h$	Atomic charges
A = Li				
K	0·915	0·826	0·089	−0·436
Na	0·895	0·817	0·078	−0·087
Li	0·894	0·813	0·081	0·000
H	0·835	0·805	0·030	0·332
Br	0·829	0·807	0·022	0·551
Cl	0·827	0·808	0·019	0·588
F	0·827	0·813	0·014	0·721
(Li$^+$)	0·794	0·794	0·000	1·000
A = Na				
K	1·208	1·168	0·040	−0·363
Na	1·190	1·156	0·034	0·000
Li	1·190	1·153	0·037	0·087
H	1·134	1·134	0·000	0·392
Br	1·115	1·121	−0·006	0·676
Cl	1·113	1·124	−0·011	0·727
F	1·110	1·126	−0·016	0·861
(Na$^+$)	1·100	1·100	0·000	1·000
A = K				
K	1·510	1·500	0·010	0·000
Na	1·497	1·492	0·005	0·363
Li	1·491	1·492	−0·001	0·436
H	1·469	1·483	−0·014	0·734
Br	1·466	1·473	−0·007	0·950
Cl	1·463	1·473	−0·010	0·959
F	1·464	1·478	−0·014	0·972
(K$^+$)	1·460	1·460	0·000	1·000

Electronegativities in eV*

K	Na	Li	H	Br	Cl	F
2·42	2·85	3·01	7·18	7·59	8·30	10·41

* Pearson (1988*a*,*b*).

Table 3. *r_s and r_h of halogen atoms* (*X*) *in molecules* (*RX*) *and their anisotropies* (Å)

6-311G(2*d*,*p*) basis set used for first-row atoms, MC-311G(2*d*,*p*) for second-row atoms and DZP for K and Br atoms. For each halogen atom one diffuse *p* function is added.

R	r_s	r_h	$r_s - r_h$	Atomic charges
X = Br				
K	1·894	1·853	0·041	−0·950
Na	1·876	1·828	0·048	−0·676
Li	1·868	1·814	0·054	−0·551
H	1·838	1·643	0·195	−0·117
Br	1·827	1·600	0·227	0·000
Cl	1·827	1·580	0·247	0·102
F	1·822	1·523	0·299	(0·425)*
Br$^-$	1·900	1·900	0·000	−1·000
X = Cl				
K	1·777	1·739	0·038	−0·959
Na	1·758	1·717	0·041	−0·727
Li	1·748	1·700	0·048	−0·588
H	1·715	1·556	0·159	−0·164
Br	1·700	1·523	0·177	−0·102
Cl	1·696	1·510	0·186	0·000
F	1·696	1·439	0·257	0·287
Cl$^-$	1·778	1·778	0·000	−1·000
X = F				
K	1·456	1·428	0·028	−0·972
Na	1·443	1·418	0·025	−0·861
Li	1·433	1·397	0·036	−0·721
H	1·376	1·300	0·076	−0·366
Br	1·353	1·303	0·050	(−0·425)*
Cl	1·362	1·300	0·062	−0·287
F	1·344	1·241	0·103	0·000
F$^-$	1·459	1·459	0·000	−1·000

* In order to avoid the convergence problem in BrF, the 6-31G(*d*) basis set is used for F.

Van der Waals radii of atoms in molecules

The calculated r_s and r_h of alkali-metal atoms (*A*) in various diatomic molecules (*AR*) are summarized in Table 2. The difference between the two radii ($r_s - r_h$, the anisotropy), the electronegativity (Pearson, 1988*a*,*b*) of the counter atoms (*R*) and the Mulliken atomic charge (Mulliken, 1955*a*–*d*) on the alkali-metal atoms (*A*) are also included. The r_h of the alkali-metal atoms in these molecules show a negligible dependence on the counter atoms *R*, remaining almost constant, while the r_s for each alkali-metal atom vary by three times as much as the corresponding r_h values.

The r_s, r_h, the anisotropy of the halogen atoms (*X*) in *RX* molecules and the Mulliken atomic charge on the halogen atoms (*X*) are summarized in Table 3. In contrast with the results for alkali-metal atoms in molecules, the r_h of the halogen atoms depend on the counter atoms *R* more than the corresponding r_s. The anisotropy of the F atom is very small in KF. The r_s (1·46 Å) of F nearly equals the theoretical radius of the F$^-$ anion, since the ionic bond character in K—F is almost complete. In fact, the Mulliken atomic charge on the F atom is −0·973.

Nyburg & Faerman (1985) estimated the van der Waals radii using crystallographic data for atoms bonded to a single C atom. The present r_s and r_h of the F atom in HF are equal to their estimated values of 1·38 and 1·30 Å, respectively; the calculated radii for the F atom in HF agree well with those for FCH_3 (S. Ikuta & G. Bacskay, unpublished results). Effective van der Waals radii estimated by Nyburg & Faerman (1985) are 1·78 (r_s) and 1·58 Å (r_h) for Cl and 1·84 (r_s) and 1·58 Å (r_h) for Br, which again agree well with the present theoretical values (1·72

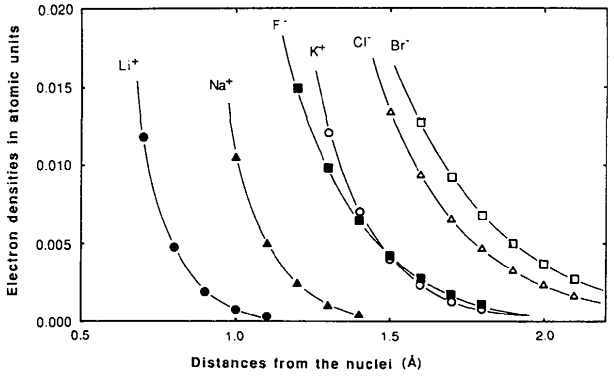


Fig. 1. Computed electron densities around the nuclei of several ions as a function of the distance from the nuclei.

and 1·56 Å for Cl and 1·84 and 1·64 Å for Br) for HCl and HBr. These results indicate that the present definition of the van der Waals radius as the distance from the nucleus to the surface having an electron density of 0·005 a.u. really is useful. Thus the present theoretical study on *isolated molecules* provides us with a useful guide for estimating the van der Waals radii in *crystals*, although the environmental effect of the surrounding atoms and molecules may have to be taken into consideration in more detailed investigations.

Anisotropy of van der Waals radii

The anisotropy of the alkali-metal atoms in molecules is small indicating that they are nearly spherical. A small 'polar extension' ($r_s < r_h$) is found for the K atoms in KH, KBr, KCl and KF, and for the Na atoms in NaBr, NaCl and NaF. The anisotropy of Li is a little larger, being between 0·01 and 0·09 Å, where ordinary 'polar flattening' is observed.

In Fig. 2, r_s, r_h and the anisotropy of the alkali-metal atoms (A) in diatomic molecules (AR) are plotted against the electronegativity of counter atoms R. The r_s and r_h of the alkali-metal atoms bonded to H or halogen atoms do not vary much, whereas the radii of counter atoms bonded to alkali-metal atoms vary with the counter-atoms electronegativity. The radii of K, Na and Li bonded to F atoms approach the values of the corresponding cations K^+, Na^+ and Li^+, respectively (see Table 2). The r_s and r_h of the K atom show a negligible dependence on the counter halogen atoms R, indicating that the K atom is almost spherical in these molecules. This comes from the fact that the electronegativity of K is very small and a completely ionic bond ($K^+ \cdots R^-$) is formed.

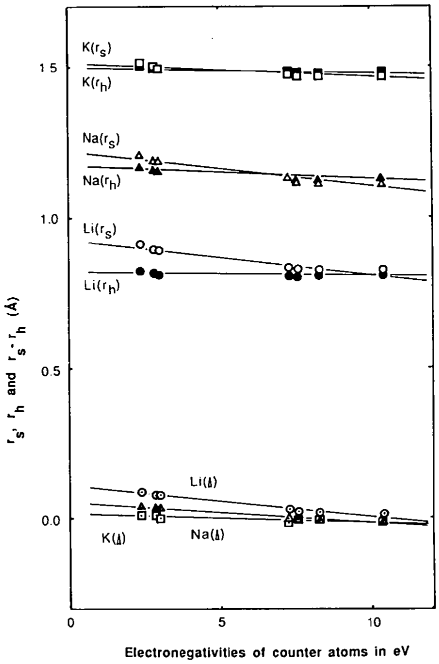


Fig. 2. Sideways-on (r_s) and head-on (r_h) radii and their anisotropies ($r_s - r_h$) for the alkali-metal atoms in molecules as a function of the electronegativity of the counter atoms.

In Fig. 3, r_s and r_h are plotted against Mulliken atomic charge on the alkali-metal atoms in molecules. Mulliken atomic charge varies considerably with the basis sets used, but it is often useful when considering the electron distribution in molecules. The r_h values for each alkali-metal atom lie on a straight line, while the r_s values lie on two separate lines; one for the molecules with counter alkali-metal atoms, the other for those with halogen atoms. Separation of the two lines is most conspicuous in r_s for Li atoms, since both covalent and ionic bonds are formed in the molecules with an Li atom.

In Fig. 4, r_s and r_h and the anisotropy of the halogen atoms (X) in molecules (RX) are plotted against the electronegativity of the counter atoms R. r_s and r_h both vary linearly with the electronegativity of the counter atoms R. The slope for the r_h is steeper than that for the corresponding r_s, indicating that r_h depend more on the counter atoms R. It is worth noting that the slopes for the r_s of F, Cl and Br are almost equal, and have no dependence on the halogen atoms themselves. On the other hand, the slopes for r_h become steeper with decreasing electronegativity of the halogen atoms; the slope for the r_h of Br is steepest.

The anisotropy of the halogen atom (X) in molecules RX (X = F, Cl or Br) increases with increasing electronegativity of the counter atoms R (K < Na < Li < H < Br < Cl < F). The anisotropy for the Br atom (0·30 Å) in BrF amounts to about 20% of the r_h. The large anisotropy for both Cl and Br in the molecules reflects the ability to form a covalent

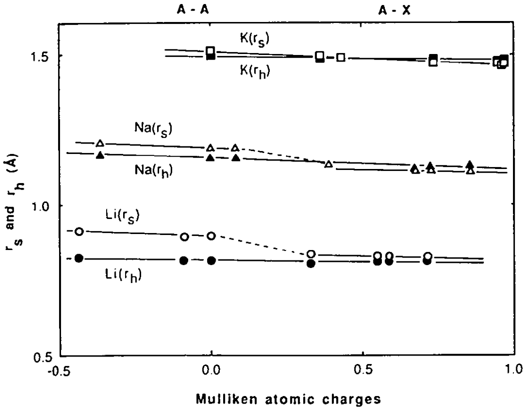


Fig. 3. r_s and r_h for the alkali-metal atoms in molecules as a function of the Mulliken atomic charge.

bond. The r_s and r_h of the halogen atoms bonded to a counter atom having a small electronegativity (for example, K and Na) both approach the radii of the corresponding anions (F^-, Cl^- and Br^-, respectively).

In Fig. 5, r_s and r_h of the halogen atoms (*X*) in molecules (*RX*) are plotted against Mulliken atomic charge on the halogen atom. The r_s of the halogen atoms in each *RX* series fit a single straight line, while the r_h fit two separate lines; one for the molecules with the alkali-metal atom and the other with the halogen atoms. These results are in contrast with those for the alkali-metal atoms, where the r_h of the alkali-metal atom (Li, Na or K) in molecules fit a single straight line, but the r_s do not. The atomic orbital of a halogen atom which forms a chemical bond is a p_z-type atomic orbital in diatomic molecules, while that of the alkali-metal atom is an *s*-type. The direct result of these differences can be seen in the different behavior of the electron-density distribution around the atoms. The p_z electrons of a halogen atom flow into a bonding region to form a chemical bond, thus the electon density in the head-on direction parallel to the chemical bond decreases significantly. r_h, therefore, varies very much with the electronegativity of the counter atoms *R*. The anisotropy of the halogen atoms increases with increasing electron attraction of the counter atom *R*. On the other hand, the alkali-metal atoms share the *s* electrons to form a chemical bond. Thus the anisotropy of the alkali-metal atom in molecules is expected not to become so large, since an *s* orbital is natively spherical.

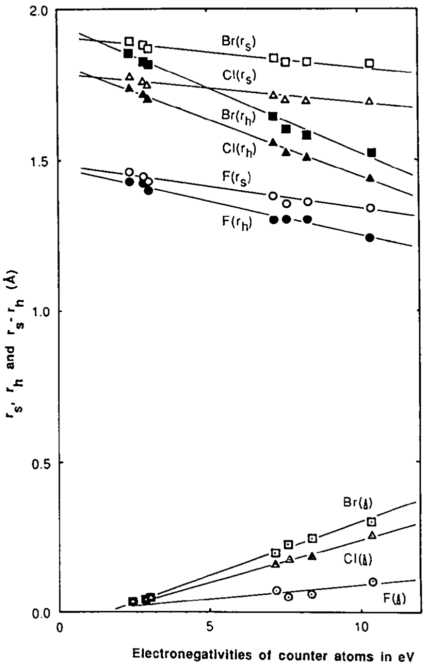


Fig. 4. r_s, r_h and $r_s - r_h$ for the halogen atoms in molecules as a function of the electronegativity of the counter atoms.

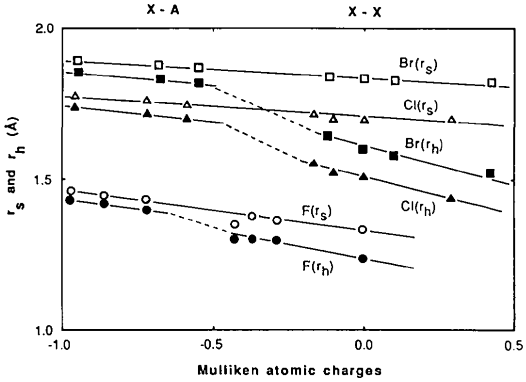


Fig. 5. r_s and r_h for the halogen atoms in molecules as a function of the Mulliken atomic charge.

In Fig. 6, the correlations between the r_s and r_h of atoms in molecules are shown. The data for the Li^+, Na^+, K^+, F^-, Cl^- and Br^- ions lie on a straight line since the electron-density distribution is spherical; the slope is unity.

The radii in the hydrogen halides and bihalides with a strong covalent bond deviate from the straight line, since the large anisotropy of the electron-density distribution is present. On the other hand, the radii for the molecules (*AR*) with the strong ionic bond lie nearer to the line, because the molecule can be considered, as a first approximation, to be $A^+ \cdots R^-$; the r_s and r_h (of *A* and *R* atoms) both approach those in the corresponding ions.

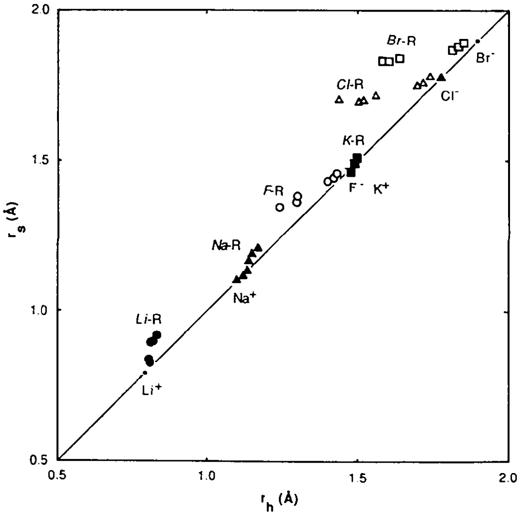


Fig. 6. Correlation between r_s and r_h of atoms in molecules.

Table 4. *Electron-density distribution around the* Na *atom*

Contracted [6*s*5*p*1*d*] basis set (Poirier, Kari & Csizmadia, 1985) used.

	$(Na^+\cdots -1e)$* electron densities‡		
l (a.u.)†	Sideways-on	Head-on	Na^+
1·5	0·0510	0·0520	0·0508
1·6	0·0337	0·0344	0·0334
1·7	0·0223	0·0229	0·0221
1·8	0·0148	0·0153	0·0147
1·9	0·0099	0·0103	0·0098
2·0	0·0066	0·0069	0·0066
2·1	0·0044	0·0047	0·0044
2·2	0·0030	0·0032	0·0030
2·3	0·0020	0·0022	0·0020
2·4	0·0014	0·0015	0·0013
2·5	0·0009	0·0010	0·0009

*A point negative charge is placed 1·885 Å from the Na nucleus.
†Distances from the Na nucleus.
‡In atomic units. 1 a.u. = 6·7483 e Å^{-3}.

Table 5. *Electron-density distribution around the* Cl *atom*

Contracted [6*s*5*p*2*d*] basis set (Poirier, Kari & Csizmadia, 1985) used with a diffuse *p* function.

	$(Cl^-\cdots +1e)$* electron densities‡		
l (a.u.)†	Sideways-on	Head-on	Cl^-
2·5	0·0253	0·0225	0·0254
2·6	0·0208	0·0185	0·0210
2·7	0·0171	0·0153	0·0173
2·8	0·0141	0·0126	0·0143
2·9	0·0116	0·0104	0·0118
3·0	0·0096	0·0086	0·0098
3·1	0·0079	0·0072	0·0081
3·2	0·0065	0·0060	0·0067
3·3	0·0054	0·0050	0·0056
3·4	0·0045	0·0042	0·0047
3·5	0·0037	0·0036	0·0039
3·6	0·0031	0·0030	0·0033
3·7	0·0026	0·0026	0·0028
3·8	0·0022	0·0022	0·0023
3·9	0·0018	0·0019	0·0020
4·0	0·0015	0·0016	0·0017

*A point positive charge is placed 2·784 Å from the Cl nucleus.
†Distances from the Cl nucleus.
‡In atomic units. 1 a.u. = 6·7483 e Å^{-3}.

Environmental effects of the point charges

The electron-density distribution around the Na atom, calculated in two directions along r_s and r_h, where a negative charge ($-1e$) is placed 1·885 Å from the Na nucleus is summarized in Table 4. The value of 1·885 Å is the optimized bond length in an NaF molecule. The electron-density distribution of an isolated Na^+ ion is also summarized in the table. The electron densities in the r_s direction do not vary at all from those in the isolated Na^+ ion, indicating that the negative (point) charge does not affect the electron density in the r_s direction. On the other hand, the electron densities in the r_h direction are a little bit larger than those along r_s owing to the electrostatic repulsion between the negative point charge and the electrons on the Na^+ ion. These results clearly show that a 'polar extension' exists in the present model system ($Na^+\cdots -1e$) as in the real system of NaF. Although the 'polar extension' (0·007 Å) in this model system is somewhat smaller than that (0·016 Å) in the real NaF molecule, it can be qualitatively described by simple model calculations.

The electron-density distribution around the Cl atom in the model system, $Cl^-\cdots +1e$, is summarized in Table 5. The electron densities for an isolated Cl^- anion are also summarized. The positive charge is placed 2·784 Å from the Cl nucleus which is the optimized bond length for a KCl molecule. The electron densitities along r_s, which are similar to those in the isolated Cl^- anion, are larger than the corresponding r_h ones. Thus normal 'polar flattening' is observed in this model system. The point charge attracts the electrons on the Cl atom mainly along the head-on direction.

These results obtained with the simple models indicate that the anisotropy in the molecules with a strong ionic bond character can be qualitatively described with an electrostatic contribution due to a negative or positive charge on a counter atom. To quantitatively describe the electron-density distribution in such molecules some contribution of a covalent-bond character should be taken into consideration.

The environmental effects on the electron-density distribution around the nuclei in Na^+ and Cl^- ions are evaluated by using another type of simple model calculation, where six (negative or positive) point charges are placed at the octahedral positions. The distances between the ion and the point charges were fixed at 2·81 Å, the internuclear distances in the NaCl crystal (Pauling, 1942). The electron-density distribution around the central nucleus does not vary from that in the corresponding isolated one, indicating no expansion or contraction of the radii of the

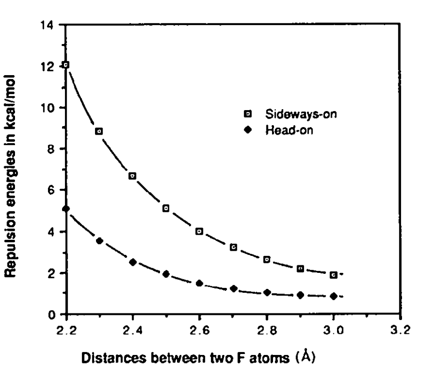
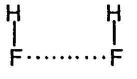


Fig. 7. Calculated repulsion energies of the $(FH)_2$ dimer in the sideways-on and head-on contacts as a function of distance between the two F atoms. 1 kcal mol^{-1} = 4·1868 kJ mol^{-1}.

central ions. These results again indicate that the van der Waals radii predicted in an isolated molecule can be used as the radii in the crystals.

Repulsion energies in the $(HF)_2$ *dimer*

In Fig. 7, the calculated interaction energies of the $(HF)_2$ dimer are shown as a function of the distance between two F atoms, where two conformers, sideways-on and head-on contacts, are considered.



sideways-on

head-on

The interaction energies in the head-on contact are always less repulsive, reflecting the electron-density distribution around the *F* atoms (polar flattening). The energy decomposition analysis (Morokuma, 1971; Kitaura & Morokuma, 1976) of the hydrogen-halide dimer in these two conformers indicated that the interaction energy difference comes from the energy difference resulting from electroexchange repulsion (S. Ikuta & C. Bacskay, unpublished results).

The r_s and r_h of the F atom in HF predicted theoretically in this study are 1·38 and 1·30 Å, respectively. From Fig. 7, one can estimate the interaction (repulsive) energies for the $(HF)_2$ dimer at the internuclear distances of the two F atoms being 2·76 (2 × 1·38) and 2·60 (2 × 1·30) Å in the sideways-on and head-on contacts, respectively. The repulsive energy in the sideways-on contact at 2·76 Å is 11·72 kJ mol^{-1}, 5·44 kJ mol^{-1} larger than that in the head-on one at 2·60 Å. Thus the larger repulsion energy in the sideways-on contact reflects both the anisotropy of the electron-density distribution around the F atom in HF and the additional electroexchange repulsions between the σ(H—F) bonds. This type of σ-bond repulsion is negligible in the head-on contact.

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