

On the additivity of van der Waals radii †

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A review of gas-phase spectroscopic data of van der Waals complexes shows that heteroatomic contacts are systematically longer and their energies lower than the averages for corresponding homoatomic ones. The differences depend on electronic polarisabilities α of contacting atoms, according to empirical formulae $\Delta r_w = c[(\alpha_2 - \alpha_1)/\alpha_1]^{\frac{1}{3}}$ ($\alpha_1 < \alpha_2$) and $\Delta E = a(\alpha_2 - \alpha_1)^n$ ($n = 1-1.2$). A novel system of van der Waals radii, corrected for this effect, is suggested for rare gases, H, N, O, halogens and metals; for di- and poly-atomic molecules as well as for isolated atoms.

The simplest description of a molecular crystal^{1,2} represents each atom as a hard sphere of a certain radius, van der Waals (vdW) radius, and molecules as superpositions of such spheres; these bodies in crystals are packed closely, but without penetrating into or deforming each other. It is implied that the vdW radius is specific for a given atom (element) and remains the same in any contact. Hence any A...B contact distance must be equal to the average of the corresponding homoatomic contacts, A...A and B...B. In fact, such additivity holds only approximately. Several factors are usually considered responsible for the discrepancies. Packing can be affected by forces other than purely vdW, *viz.* electrostatic, dipole, charge-transfer, partially covalent or hydrogen bonding, *etc.* Participation of the contacting atom in covalent bonds affects its electron shells and makes the atomic shape anisotropic.^{3,4} Finally, packing of poly-atomic molecules with complex shapes is always a compromise between many interactions and results in some contacts being longer and some shorter than 'normal', as atomic spheres are not absolutely hard but deformable to some extent.⁵

Recently interatomic distances in vdW molecules (complexes) in the gas phase became available from spectroscopic data, providing an opportunity to study vdW interactions *per se*.⁶⁻¹³ None of the above mentioned sources of perturbation is present here: there is no third particle to complicate the picture, no covalent bonds to cause atomic anisotropy, no static charges or specific interactions. Thus it is possible to check the original suggestion that purely vdW parameters are perfectly additive.

Results and Discussion

Rare gas dimers

Table 1 contains experimental data on interatomic distances in RgRg' (Rg = rare gas) molecules and their dissociation energies. Evidently, the Rg...Rg' distances in heteroatomic molecules are larger than the sums of the vdW radii, determined as half-distances Rg...Rg and Rg'...Rg' in the corresponding homoatomic molecules [equation (1)] and the energies of these

$$d(\text{Rg} \cdots \text{Rg}') > \frac{1}{2}[d(\text{Rg} \cdots \text{Rg}) + d(\text{Rg}' \cdots \text{Rg}')] \quad (1)$$

interactions are smaller [equation (2)]. In both cases, the bigger

$$E(\text{RgRg}') < \frac{1}{2}[E(\text{RgRg}) + E(\text{Rg}'\text{Rg}')] \quad (2)$$

the difference in the atomic sizes between Rg and Rg', the bigger the deviation from additivity.

The observed trend appears even more striking if one takes

into account that for polar heteroatomic compounds (AB) exactly the opposite is true [equations (3) and (4)]. The relations

$$d(\text{AB}) < \frac{1}{2}[d(\text{AA}) + d(\text{BB})] \quad (3)$$

$$E(\text{AB}) > \frac{1}{2}[E(\text{AA}) + E(\text{BB})] \quad (4)$$

(1) and (2) can be rationalised in terms of the dispersion theory of vdW interactions.¹⁵ The energy of London's interactions is given in equation (5) for a heteroatomic A...B contact, while

$$E_{\text{AB}} = \frac{3\hbar v_{\text{A}} v_{\text{B}} \alpha_{\text{A}} \alpha_{\text{B}}}{2(v_{\text{A}} + v_{\text{B}}) d_{\text{AB}}^6} \quad (5)$$

that for the corresponding homoatomic ones A...A and B...B is given in equation (6), where α is the atomic polaris-

$$E_{\text{AA}} = \frac{3\hbar v_{\text{A}} \alpha_{\text{A}}^2}{4d_{\text{AA}}^6} \text{ and } E_{\text{BB}} = \frac{3\hbar v_{\text{B}} \alpha_{\text{B}}^2}{4d_{\text{BB}}^6} \quad (6)$$

ability, v is the frequency of electron oscillations, and \hbar is the Planck constant. Since the value of v for various atoms differs relatively little, then for atoms of similar size equation (7)

$$\Delta E = \frac{1}{2}(E_{\text{AA}} + E_{\text{BB}}) - E_{\text{AB}} \approx \frac{3\hbar v}{8d^6} (\alpha_{\text{A}}^2 + \alpha_{\text{B}}^2 - 2\alpha_{\text{A}}\alpha_{\text{B}}) \approx c(\alpha_{\text{A}} - \alpha_{\text{B}})^2 \quad (7)$$

applies, wherefrom it is obvious that the energy of a heteroatomic vdW bond is always smaller than its additive expression. However, this is a rather rough approximation. Since actual interatomic distances in heteroatomic vdW molecules always exceed the additive values, the approximation $d_{\text{AA}} \approx d_{\text{BB}} \approx d_{\text{AB}}$ tends to overestimate the denominator in equation (5) and effectively reduces the power of α . Thus, the expression (8),^{7,16}

$$E = K \frac{\alpha^{1.5}}{d^6} \quad (8)$$

proved efficient in calculations of the energy of vdW interactions.

It is noteworthy that interatomic potentials of rare gases derived from experimental data, particularly from low-energy differential cross-sections, second virial coefficients¹⁷ and diffusion coefficients of the binary rare-gas mixtures (measured as a function of temperature),^{17,18} were long known to violate the empirical (essentially additive) 'combining rules', which estimate heteroatomic interactions from homoatomic ones.^{18,19}

In any case it is obvious that the deviation from additivity of

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† Non-SI unit employed: eV $\approx 1.602 \times 10^{-19}$ J.

Table 1 Bond distances and dissociation energies in van der Waals molecules of rare gases*

Molecule	$d_{\text{exp}}/\text{\AA}$	$d_{\text{add}}/\text{\AA}$	$d_{\text{corr}}/\text{\AA}$	$E_{\text{exp}}/\text{meV}$	$E_{\text{add}}/\text{meV}$	$\Delta\alpha$
RgRg'						
HeHe	2.97 ⁶	(2.97)	—	0.91	(0.91)	0
HeNe	3.03 ⁷	3.03	3.07	1.83	2.28	0.189
HeAr	3.48 ^{6,7}	3.36	3.52	2.59	6.62	1.434
HeKr	3.70 ⁶⁻⁸	3.49	3.71	2.67	9.12	2.277
HeXe	3.99 ⁷	3.66	3.97	2.57	12.62	3.837
NeNe	3.09 ^{6,7}	(3.09)	—	3.64	(3.64)	0
NeAr	3.51 ^{7,9b}	3.42	3.52	5.78	7.99	1.245
NeKr	3.66 ^{7,8,9b}	3.55	3.69	6.08	10.49	2.088
NeXe	3.88 ^{7,9}	3.72	3.92	6.22	13.98	3.648
ArAr	3.76 ^{6,7,10}	(3.76)	—	12.34	(12.34)	0
ArKr	3.88 ^{6-8,9b,11}	3.88	3.91	14.42	14.84	0.843
ArXe	4.07 ^{7,9,11,12}	4.06	4.12	16.25	18.33	2.403
KrKr	4.01 ^{6-8,10,11}	(4.01)	—	17.34	(17.34)	0
KrXe	4.19 ^{7,9,11,12}	4.18	4.21	20.12	20.83	1.560
XeXe	4.36 ^{7,12,13}	(4.36)	—	24.33	(24.33)	0

* d is the Rg–Rg' distance, d_{exp} the experimental average (from the refs. specified), $d_{\text{add}} = r_w(\text{Rg}) + r_w(\text{Rg}')$, $d_{\text{corr}} = d_{\text{add}} + \Delta r_w$ (Δr_w is the polarisation correction), E is the bond dissociation energy, E_{exp} the average experimental value (refs. 6 and 14), $E_{\text{add}} = 0.5[E(\text{RgRg}) + E(\text{Rg'Rg'})]$, $\Delta\alpha$ is the polarisation difference, see Table 2.

Table 2 Electronic polarisabilities (\AA^3) of isolated atoms

Atom	α_{exp}	Atom	α_{exp}	Atom	$\alpha_{\text{theor}}^{22}$
Li	23.5 ²²⁻²⁴	In	10.2 ²²	H	0.667
Na	23.9 ²²⁻²⁴	Tl	7.6 ²²	F	0.557
K	43.6 ²²⁻²⁴	He	0.207 ²⁷	Cl	2.18
Rb	48.2 ^{22,24}	Ne	0.396 ²²	Br	3.05
Cs	61.3 ^{22,24}	Ar	1.641 ²²	Ag	7.2
Mg	10.9 ^{22,25}	Kr	2.484 ²²	Zn	7.1
Ca	24.5 ^{22,25}	Xe	4.044 ²²	Cd	7.2
Sr	28.6 ^{22,25}	I	4.95 ²⁸	Hg	5.7
Ba	37.9 ^{22,25}	O	0.78 ²⁹	B	3.03
Al	6.8 ²⁶	N	1.21 ²⁹	Si	5.38

E_{AB} and, by implication, of d_{AB} for the vdW bonds can be expressed through the differences of electronic polarisabilities of the contacting atoms, which characterise different influences of closed electron shells upon each other, just as the deviations of bond energy and distance for (polar) covalent bonds are well known to depend on the differences of atomic electronegativities. The actual form of the expression $\alpha = f(E)$ can be determined by a purely empirical approach.²⁰

It was found earlier²¹ that interatomic distances in rare-gas dimers can be described as $d_{\text{corr}} = d_{\text{add}} + \Delta r_w$, where $d_{\text{add}} = r_w(\text{Rg}) + r_w(\text{Rg}')$ and $\Delta r_w = 0.045 [(a_2 - a_1)/a_1]^2$; a_1 being the polarisability of the smaller atom (which has the stronger polarising effect), so that $a_1 < a_2$; r_w are additive radii, obtained as $d/2$ in homoatomic dimers, *viz.* He, 1.485; Ne, 1.545; Ar, 1.88; Kr, 2.005; and Xe, 2.18 Å, d_{corr} , calculated from polarisabilities of isolated rare-gas atoms (see Table 2) show the average discrepancy with the experimental d of only 0.02 Å, against 0.10 Å for the uncorrected d_{add} (see Table 1).

Other diatomic van der Waals complexes

The same method can be applied to vdW molecules of the RgX type (Table 3), where X = H, F, Cl, Br, I, O or N, using formula (9), where $d(\text{Rg–X})$ are the experimental interatomic distances,

$$r_w(\text{X}) = d(\text{Rg–X}) - r_w(\text{Rg}) - \Delta r_w \quad (9)$$

$r_w(\text{Rg})$ are the above mentioned vdW radii of the rare-gas atoms, and the correction Δr_w was calculated as described above. Thus it is expedient to apply this technique to the area most difficult for the traditional approach, namely the vdW radii of metals. In molecular crystals the metal atom is usually 'hidden' inside a complex molecule. When it is exposed, there are often uncertainties whether the intermolecular contacts it participates in are non-bonding or weakly bonding. Unsurprisingly, metals are missing in most tables of vdW radii, and such

Table 3 Experimental interatomic distances (Å) in the RgX molecules and the van der Waals radii of X

RgX	$d(\text{Rg–X})^a$	$r_w(\text{X})$	$\bar{r}_w(\text{X})^b$	r_w^c
NeH	3.15	1.57		
ArH	3.58	1.64	1.56(5)	1.50
KrH	3.62	1.53		
XeH	3.82	1.51		
HeF	3.03	1.48		
NeF	3.15	1.58		
ArF	3.50	1.55	1.52(5)	1.60
KrF	3.65	1.54		
XeF	3.78	1.45		
HeCl	3.49	1.80		
NeCl	3.61	1.94		
ArCl	3.88	1.98	1.90(7)	1.95
KrCl	3.95	1.93		
XeCl	4.06	1.84		
ArBr	3.89	1.97	1.97	2.10
ArI	4.11	2.16	2.16	2.25
KrI	4.20	2.15		
HeO	3.27	1.70		
NeO	3.30	1.71		
ArO	3.60	1.67	1.67(4)	1.65
KrO	3.75	1.67		
XeO	3.90	1.60		
ArN	3.78	1.88	1.84(4)	1.70
KrN	3.86	1.81		

^a Refs. 7–9. ^b Estimated standard deviations in parentheses. ^c Ref. 3.

estimates as are available are based on indirect data (*e.g.* those by Bondi,³⁰ on critical volumes) and were found to be generally unsatisfactory.³¹

Moreover, the problem is by no means irrelevant. Stereochemical interpretation of 'secondary' co-ordination in organometallic compounds and 'agostic' metal–hydrogen bonding, which have received increasing interest recently, strongly demand the metal atom radius as a reliable reference point. Equally, molecular mechanics modelling techniques are the least developed for organometallic compounds³² and improved parametrisation for metal atoms (including equilibrium radii) would be useful.

Using the interatomic distances in vdW molecules of a MRg type (M = metal), known radii of the rare-gas atoms and polarisation corrections discussed above, metal atom radii can be calculated easily (see Table 4).

Complexes with diatomic molecules

So far we have been dealing only with the radii of individual atoms. When the latter are incorporated into molecules, the

Table 4 Interatomic distances in metal–rare gas molecules (MRg) and van der Waals radii of metal atoms (Å)

M	$d(\text{M-Rg})^* [r_w(\text{M})]$				
	MNe	MAr	MKr	MXe	Mean $r_w(\text{M})$
Li	5.01 [2.79]	4.86 ^{7,33} [2.73]	4.84 [2.65]	4.84 [2.53]	2.7
Na	5.14 ^{7,34} [2.91]	5.02 ^{35,36} [2.88]	4.93 ^{37,38} [2.74]	5.01 ^{38,39} [2.70]	2.8
K		5.15 [2.88]	5.15 [2.85]	5.22 [2.84]	2.9
Rb			5.29 [2.97]		3.0
Cs		5.50 [3.13]	5.44 [3.06]	5.47 [3.03]	3.1
Ag		4.0 ⁴⁰ [2.0]			2.0
Mg	4.40 ³⁶ [2.45]	4.49 ³⁶ [2.47]		4.56 ⁴¹ [2.32]	2.4
Zn		4.18 ³⁶ [2.20]	4.20 ³⁶ [2.13]		2.2
Cd	4.27 ^{7,36,42} [2.42]	4.28 ^{7,36,42} [2.30]	4.36 ^{43,44} [2.29]	4.55 [2.33]	2.3
Hg	3.91 ^{7,32,41} [2.11]	3.98 ^{45,46} [2.02]	4.04 ^{43,46} [1.98]	4.20 ^{46,47} [2.00]	2.0
B		3.61 ⁴⁸ [1.69]			1.7
Al		3.64 ^{49,50} [1.66]	3.81 ^{49,51} [1.74]		1.7
In		3.86 ⁵² [1.84]	3.9 ⁵² [1.8]		1.8
Tl		4.35 ⁵³ [2.36]	4.34 ⁵³ [2.26]	4.27 ⁵³ [2.05]	2.2
Si		4.0 ⁵⁴ [2.0]			2.0

* Average experimental values; from ref. 7, except where specified.

Table 5 Geometry of the RgX₂ type van der Waals complexes

X	Parameter ^{a/} Å	Rg					Mean $r_w(\text{X})/\text{Å}$
		He	Ne	Ar	Kr	Xe	
H	$d_{\text{cm}}(\text{Rg-H}_2)$	3.24	3.30	3.58	3.72	3.94	
	$d(\text{Rg-H})$	3.26	3.32	3.60	3.74	3.96	
	$r_w(\text{H})$	1.68	1.73	1.67	1.66	1.67	1.68(2)
O	$d_{\text{cm}}(\text{Rg-O}_2)$	3.52	3.62	3.72	3.88	4.02	
	$d(\text{Rg-O})$	3.57	3.67	3.77	3.93	4.065	
	$r_w(\text{O})$	1.93	2.03	1.88	1.89	1.82	1.91(7)
N	$d_{\text{cm}}(\text{Rg-N}_2)$	3.69	3.72	3.72	3.84	4.05 ^b	
	$d(\text{Rg-N})$	3.73	3.76	3.76	3.88	4.09	
	$r_w(\text{N})$	2.07	2.11	1.87	1.85	1.86	1.95(11)
Cl	$d_{\text{cm}}(\text{Rg-Cl}_2)^c$	3.67	3.57	3.72			
	$d(\text{Rg-Cl})$	3.80	3.71	3.85			
	$r_w(\text{Cl})$	1.97	1.95	1.90			1.94(3)
Br	$d_{\text{cm}}(\text{Rg-Br}_2)^d$	3.84	3.67				
	$d(\text{Rg-Br})$	4.00	3.84				
	$r_w(\text{Br})$	2.08	2.02				2.05(3)
I	$d_{\text{cm}}(\text{Rg-I}_2)$	4.47 ^c					
	$d(\text{Rg-I})$	4.66					
	$r_w(\text{I})$	2.54					2.54

^a $d_{\text{cm}}(\text{Rg-X}_2)$ is the experimental distance between Rg and the center of mass of X₂, from ref. 7, unless otherwise specified; $r_w(\text{X})$ is the van der Waals radius of X, corrected for polarisation effects. ^b Ref. 55. ^c Ref. 56. ^d Ref. 57.

formation of covalent bonds affects their electron structures and, consequently, their vdW radii.

The vdW complexes comprising a rare-gas atom and a dinuclear homoatomic molecule, RgX₂, adopt a T-shaped configuration. Thus the Rg...X distances can be easily calculated using known X–X distances in isolated X₂ molecules, which alter insignificantly on complexation (see Table 5). Then the vdW radii of the X atoms can be calculated using the Rg radii presented above and the polarisation corrections calculated in the same manner as for individual atoms, but using the electronic polarisabilities of molecules (Table 6). The resulting $r_w(\text{X})$ for molecules are systematically larger than for atoms.

This result can be understood as, according to Pauling,³ $r = a_0(n^*)^2/Z^*$, where r is the atomic radius, a_0 is the Bohr hydrogen radius, n^* is the effective principal quantum number and Z^* is the effective nuclear charge. The overlap of the atomic electron shells upon the formation of a covalent bond X–X increases the electron density around each X atom which screens the nucleus, thus reducing Z^* and increasing r .

Complexes of rare gases with heteroatomic or polyatomic molecules present a much more difficult problem, deserving further investigation. Here one must take into account the

Table 6 Electronic polarisabilities (α) of molecules*

Molecule	$\alpha/\text{Å}^3$	Molecule	$\alpha/\text{Å}^3$
H ₂	0.803	I ₂	11.16
O ₂	1.566	CH ₄	2.553
N ₂	1.741	C ₆ H ₆	10.31
Cl ₂	4.527	SF ₆	4.48
Br ₂	6.414		

* Ref. 58.

complicated shapes of the molecules, polarity of the covalent bonds and consequent alteration of the electron density (and size) of the atoms, *etc.*

The relationship between van der Waals radii and polarisability

Returning to the additivity of the vdW energy E , it has been suggested that the correction ΔE depends linearly on the difference of polarisabilities, $\Delta E = 0.4 \Delta \alpha$ (for α in Å³, E in meV). However, a more extensive study⁵⁹ proved that equation (10)

$$\Delta E = 0.2 (\Delta \alpha)^{1.2} \quad (10)$$

gives a better agreement with the experimental data for a variety of vdW contacts, including rare-gas dimers (all possible combinations), rare gas–metal (Mg, Ca, Sr, Zn, Cd or Hg) and vdW metal–metal complexes, as well as complexes of molecules (H₂, O₂, N₂ or CH₄) with rare gases and metals. Theoretical explanations of these (energy) relations and their connection with the above mentioned relations concerning distances, need further investigation.

The meaning of the new van der Waals radii

Finally, it is necessary to discuss the physical meaning of the new system of vdW radii and their place among other systems. It is noteworthy that the deviations from additivity, discussed in the present paper, have nothing to do with ‘specific interactions’. Mutual polarisation of atoms is not something external to vdW forces, but is the essence of them. However, to find the net effect of electrostatic interactions, hydrogen bonding, *etc.*, one should first eliminate the polarisation-induced Δr_w , which is comparable in magnitude with the former effects.

Physically, the present system of radii, which can be called ‘ideal vdW radii’, corresponds to the pure vdW interaction between two isolated atoms or molecules. In this, they are close to Allinger’s equilibrium radii⁵ (see the comparison in Table 3). However, the latter (as any other previously suggested system) were calculated without accounting explicitly for the polarisation interactions between atoms of different types. Instead,

Table 7 van der Waals radii of elements in various states

State	Ne	Ar	Kr	Xe
Gaseous $R_{g_2}^a$	1.545	1.88	2.005	2.18
Solid R_g^b	1.578	1.874	1.996	2.167
State	F	Cl	Br	I
Gaseous R_{gX}^c	1.52	1.90	1.97	2.16
Liquid X_2^d	1.54	1.89	2.03	2.23

^a From Table 1. ^b Ref. 62. ^c From Table 3. ^d Ref. 63.

this correction is 'hidden' inside the values of the radii themselves, which were adjusted to compensate for the (unrecognised) effect.

After the described approach had been outlined,²¹ the same gas-phase data were used to derive a system of vdW radii, assuming the simple additive scheme.⁶⁰ The assumption was based on the observation that interatomic distances in heteroatomic dimers involving Ar, Kr and Xe are closely additive, and then generalised for all elements. In fact, the near-additivity of the vdW radii of these three elements occurs only because their polarisabilities are of the same order of magnitude. Even for them, small but *systematic* deviations of heteroatomic contacts from the sums of radii towards longer distances are evident (see Table 3 in ref. 60). The difference $\Delta r_w = d_{AB} - (r_A + r_B)$ becomes much more conspicuous if one takes into consideration Ne and He (for HeXe, $\Delta r_w = 0.33$ Å); for metal-rare-gas complexes, Δr_w can be comparable with the interatomic distance itself, e.g. 0.9 Å for MgNe.

Certain combinations of atomic polarisabilities can produce a paradoxical effect: interatomic distances *contracting* when one of the atoms is replaced by an apparently larger one, e.g. from 3.99 Å in HeXe to 3.88 Å in NeXe. A similar anomaly has been noticed recently⁶¹ in the series Zn^+Rg ($Rg = He, Ne$ or Ar) and explained by progressively larger 'back-polarisation' of the metal core electrons as the polarisability of the Rg atom increases. However, this is not necessarily the case. Thus, in the succession ArXe, KrXe, XeXe, the interatomic distances behave 'normally', increasing from 4.07 to 4.19 to 4.36 Å; the effect depends on relative rather than absolute magnitudes of polarisabilities.

On the other hand, ideal radii (as well as equilibrium radii) need not necessarily coincide with the 'crystallographic' vdW radii. The latter are derived from shortest contacts between polyatomic molecules in crystal structures. When such molecules contact, most interatomic distances have to be much longer than the equilibrium distance (corresponding to the minimum of the potential curve) and the resulting interactions are attractive. For the system to be in equilibrium, some contacts must be well below the equilibrium distance, giving rise to repulsive interactions. These shortest contacts are normally used to calculate crystallographic vdW radii, so the latter tend to be shorter than Allinger's equilibrium radii for most organo-gen elements (elements common for organic molecules, e.g. C, H, N, O, etc.).⁵ However, this reasoning is not valid for the crystals of rare gases, which are monoatomic. Indeed, for these elements the ideal (gas phase) and crystal radii^{21,60} are practically coincident (see Table 7). For other elements, ideal radii ought to exceed the crystallographic ones, but the polarisation corrections can be applied to the latter radii, using the same philosophy as described in the present paper. Of course, for larger molecules the actual technique of the correction will be more complex.

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