General and Inorganic Chemistry

Van der Waals radii of metals from spectroscopic data

S. S. Batsanov

Center for High Dynamic Pressures, All-Russian Scientific and Research Institute for Physico-Mechanical and Radio-Technical Measurements, Russian Academy of Sciences, 141570 Mendeleevo, Moscow Region, Russian Federation. Fax: +7 (095) 533 7386

The lack of information about the van der Waals radii of metals can be compensated for by using the results of spectroscopic investigations of van der Waals molecules. It has been shown that the interatomic distances in these molecules obey an additive scheme if one allows for the polarization effects. The van der Waals radii of the alkali metals, Ag, Mg, Zn, Cd, Hg, B, Al, In, and Si, have been determined from the interatomic distances in their heteroatomic molecules with atoms of noble gases. Use of the obtained radii for crystal chemistry is discussed.

Key words: van der Waals molecules, van der Waals radii of metals, polarizability, dissociation energy, interatomic distances.

Typical metals are the least represented elements[1–8] in the published systems of van der Waals radii (r_W), mainly because of the fact that in the crystal state they form no compounds that have a metal atom "on the surface" of the molecule, *i.e.*, not completely sterically shielded by the atoms valent-bonded to it. For this reason the r_W of metals ($r_W(M)$) have been calculated, e.g. by Bondi,[2] using indirect methods, *viz.*, from critical volumes, from correlations with the ionization energies of the atoms or with their covalent radii. However, a comparison of these values with the structural data indicates a systematic underestimation of $r_W(M)$.[7,9,10] Evidently, new information is needed in order to make a more reliable estimation of the van der Waals radii of metals.

This information can be gained from spectroscopic measurements of interatomic distances in MIg type van der Waals molecules (where Ig is an inert gas atom) assuming that the interatomic distances in these molecules obey additive correlations. This paper reports the possibilities of using this approach.

Methods of calculation of van der Waals radii

Checking on the applicability of the additivity principle for the calculation of interatomic distances in van der Waals molecules we begin with the molecules of inert gases. Table 1 gives all the values known at present for equilibrium interatomic d_e distances in homo- and heteronuclear molecules of the IgIg′ type that have been determined experimentally (spectroscopically).

From the values of d_e in the Ig_2 homoatomic molecules we have the van der Waals radii ($r_W(Ig) = d_e(Ig_2)/2$) for the inert gases: r_W for He = 1.485, Ne — 1.545, Ar — 1.88, Kr — 2.005 and Xe — 2.18 Å. For the heteroatomic IgIg′ molecules simple addition of these

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Table 1. Spectroscopically determined equilibrium interatomic distances (Å) in the molecules of inert gases

IgIg'	d_e^{exp}	Σr_W	$d_e-\Sigma r_W$	Δr_W	$\Sigma r_W+\Delta r_W$
HeHe	2.967[11]	2.97	—	—	2.97
HeNe	3.03[12]	3.03	0.00	0.04	3.07
HeAr	3.48[12]	3.36	0.12	0.16	3.52
HeKr	3.70[12]	3.49	0.21	0.23	3.72
HeXe	3.99[12]	3.66	0.33	0.32	3.98
NeNe	3.087[11], 3.09[12]	3.09	—	—	3.09
NeAr	3.50[12]	3.42	0.08	0.09	3.51
NeKr	3.66[12], 3.70[13]	3.55	0.13	0.14	3.69
NeXe	3.88[12], 3.879[14]	3.72	0.16	0.20	3.92
ArAr	3.759[11], 3.76[12]	3.76	—	—	3.76
ArKr	3.88[12]	3.88	0.00	0.03	3.91
ArXe	4.07[12], 4.094[14]	4.06	0.02	0.06	4.12
KrKr	4.012[11], 4.01[12], 4.017[15]	4.01	—	—	4.01
KrXe	4.17[12], 4.203[14]	4.18	0.01	0.03	4.21
XeXe	4.36[12], 4.362[16]	4.36	—	—	4.36

Table 2. Experimental interatomic distances (Å) in the IgX molecules[11,12] and the values of the van der Waals radii of X obtained from them

IgX	r(IgX)	r_W(X)	IgX	r(IgX)	r_W(X)
HeF	3.03	1.48			
NeF	3.15	1.58	NeH	3.15	1.57
ArF	3.50	1.56	ArH	3.58	1.65
KrF	3.65	1.55	KrH	3.62	1.54
XeF	3.78	1.46	XeH	3.82	1.52
HeCl	3.49	1.82	HeO	3.27	1.70
NeCl	3.61	1.96	NeO	3.30	1.72
ArCl	3.88	1.98	ArO	3.60	1.68
KrCl	3.95	1.93	KrO	3.75	1.68
XeCl	4.06	1.84	XeO	3.90	1.62

radii gives markedly smaller values than the experimentally found d_e values (on the average, by 0.1 Å, Table 1.) The difference in the d_e and Σr_W values increases monotonically as the differences in the atomic numbers of Ig and Ig′ increase.

In our opinion, the contribution of the polarization interaction is the main reason for this difference: the more hard Ig atom (with a smaller atomic number) will loosen the electron shells of the less hard atom, thus increasing the effective size of the latter.

If one assumes the electron polarizability (α) to be the measure of atomic hardness, then the empirical correction Δr_W for the size increase will be given by

$$\Delta r_w = a[(\alpha_2-\alpha_1)/\alpha_1]^{2/3}, \quad (1)$$

where $a = 0.045$ and $\alpha_1 < \alpha_2$. The results of calculations using Eq. (1) and the α values from Ref. 17 are given in Table 1 as well. As can be seen, the average difference between the calculated and experimentally found interatomic distances in the heteronuclear molecules of inert gases, taking into consideration the polarization interaction, is decreased to 0.003 Å (0.01 — 0.04 Å).

We tested the validity of Eq. (1) on IgX molecules, where X = H, F, Cl, O. Table 2 gives the definite experimental interatomic distances in these molecules[12,13] and the r_W values of the above elements calculated by the equation

$$\Delta r_W(X) = r_e(IgX) - r_W(Ig) - \Delta r_W \ , \quad (2)$$

As can be seen, the additive method of calculating the interatomic distances also operates for these molecules rather well. The average values of the van der Waals radii obtained for F, Cl, H and O are 1.53±0.05, 1.90±0.08, 1.57±0.06, 1.68±0.04 Å, respectively, which are close to the corresponding values of Allinger:[4] 1.60, 1.95, 1.50, and 1.65 Å. This similarity is explained by the fact that Allinger calculated his r_W from the values corresponding to the minimum potential energy of van

Table 3. Experimental interatomic distances in the molecules of MIg (Å)[12] and the van der Waals radii of M calculated from them

MIg	r(MIg)	r_W(M)	MIg	r(MIg)	r_W(M)
LiNe	5.01	2.82	ZnAr	4.18[18]	2.20
LiAr	4.84	2.71	ZnKr	4.20[18]	2.13
LiKr	4.78, 4.90	2.66	CdNe	4.26, 4.1[22]	2.37
LiXe	4.80, 4.88	2.54	CdAr	4.33, 4.31[18], 4.30[22]	2.34
NaNe	4.82, 5.29	2.83	CdKr	4.40[22]	2.34
NaAr	5.05, 5.01[18], 4.991[19]	2.88	CdXe	4.55	2.34
NaKr	4.92, 4.918[20]	2.72	HgNe	3.87, 3.92[18], 3.95[23]	2.13
NaXe	5.06	2.75	HgAr	3.99[18], 4.01	2.04
KAr	5.05, 5.07, 5.34	2.87	HgKr	4.07	2.02
KKr	4.84, 5.24, 5.36	2.85	HgXe	4.25, 4.10[24], 4.23[25]	1.99
KXe	5.20, 5.25	2.83	BAr	3.606[26]	1.68
RbKr	5.29	2.98	AlAr	3.5[27], 3.79[28]	1.65
CsAr	5.50	3.12	AlKr	3.7[27], 3.86[29]	1.70
CsKr	5.44	3.07	AlXe	3.6[27]	1.37
CsXe	5.47	3.03	InAr	3.6[30], 4.13[31]	1.91
AgAr	4.0[21]	2.03	InKr	3.9[30]	1.86
MgNe	4.40	2.46	InXe	3.55[30]	1.36
MgAr	4.49	2.46	SiAr	4.0[32]	2.04
MgXe	4.56	2.44			

Table 4. Van der Waals radii (Å) of metals

M	r_W	r_W^2	M	r_W	r_W^2
Li	2.7	1.82	Zn	2.2	1.39
Na	2.8	2.27	Cd	2.3	1.58
K	2.9	2.75	Hg	2.0	1.55
Rb	3.0	—	B	1.7	1.65
Cs	3.1	—	Al	1.7	—
Ag	2.0	1.72	In	1.9	1.93
Mg	2.5	1.73	Si	2.0	2.10

der Waals interactions of molecules in the gaseous state, i.e. under conditions analogous to our case.

The validity of the additivity principle for the calculation of interatomic distances in the heteroatomic molecules makes it possible to calculate the r_W of metals from the interatomic distances in molecules of MIg. Table 3 gives the experimental interatomic distances in these molecules[12,18–32] and the r_W(M) values obtained by Eq. (2) from the average values of r(MIg).

The average values of r_W(M) obtained in the present work are compared with the r_W(M) values of Bondi in Table 4.

Results and Discussion

Let us consider the meaning of the van der Waals radii of metals obtained in this work and their applicability to crystal chemistry.

First, note that the r_W of inert gases found from the interatomic distances in the molecules of Ig_2 are close to the respective values for the crystalline elements. Thus, according to Horton's[33] data, in the crystal structures of the inert gases with a Cu type structure, the atomic halfdistances are: Ne 1.578, Ar 1.874, Kr 1.996, Xe 2.167 Å, *i.e.*, on the average they differ by ±0.017 Å from the r_W of the same elements in the gaseous van der Waals molecules (see above). Hence the collective interaction of the atoms in the inert gas crystal (coordination number 12) does not markedly affect the r_W value, apparently because of the low energy of the interatomic interactions. One could therefore expect that the van der Waals radii of metals calculated by us could also be effectively used to describe the intermolecular contacts in the crystal structures.

In this connection it should be noted that the r_W of B and Si determined by Bondi from structural data are close to those calculated by us, while the r_W of alkali metals calculated by Bondi from the critical volumes approach our values as the boiling temperature of the metal decreases, *i.e.*, they depend on the ease of its transition to the gaseous state.

Table 5. Interatomic halfdistances $r_e/2$ (Å) and bond energies E_b(kJ/mol) in the molecules of M_2 compared, with r_W(M) (Å) and E_b(kJ/mol) for the molecules of MAr

M	M_2		MAr	
	$r_e/2$	E_b	r_W(M)	E_b
Mg	1.94[11]	5.2[34]	2.46	1.00
Ca	2.14[11]	13.1[34]	—	0.74
Sr	2.22[36]	15.2[34]	—	0.81
Zn	2.37[35]	3.3[35]	2.20	1.15
Cd	2.3±0.2[35]	3.9[35]	2.34	1.26
Hg	1.9±0.1[35, 37]	4.2[35]	2.04	1.70

The corrections to the r_W of metals[2] made by Mingos and Rohl[7] are also directed toward increasing r_W, thus approaching our values.

It is also interesting to compare the r_W of the metals found in this work with the measurements of the interatomic distances in the molecules of M_2, where M is a group II element of the Periodic System. These elements have in their outer orbit stable s^2-electron configurations that interfere with the formation of normal chemical bonds. The atomic interactions in these molecules are so weak that they are attributed to van der Waals interactions. Table 5 gives the values of the atomic halfdistances ($r_e/2$) and the bond energies E_b in the molecules of M_2 compared with the analogous characteristics (r_W(M) and E_b) for molecules of MAr.

As can be seen, for the M_2 molecules with the lowest bond energies, half the interatomic distance practically coincides with the additive r_W(M). And *vice versa* — the dissociation energy of Mg_2 is 5 times as large as the strength of the MgAr molecule. As a consequence, the Mg radius calculated from the interatomic distance in the latter molecule is markedly higher than $r_e(Mg_2)/2$. It should be noted that r_W(Mg) found by Bondi[2] (Table 4) is less than even this last undersized value. Since the dissociation energies of the molecules of Ca_2 and Sr_2 are even greater than that of Mg_2, it may be stated that the r_W of Ca and Sr should be markedly greater than 2.14 and 2.22 Å, respectively.

It should be expected that further progress in the spectroscopy of van der Waals molecules will allow us to refine the known data and to determine new van der Waals radii of elements.

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