General and Inorganic Chemistry

Experimental determination of covalent radii of elements

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The results of direct experimental determination of covalent bond lengths in molecular structures are presented. This made it possible to establish the values of normal covalent radii. The recommended values of covalent radii for 56 elements are tabulated.

Key words: bond lengths, interatomic distances, molecular structures, metals, covalent radii.

The idea to present interatomic distances as a sum of atomic increments (radii) suggested by Bragg[1] has been developed and substantiated in later works.[2—4] Since the estimated atomic sizes depended on the type of chemical bond and on the coordination number (CN), the covalent radii for CN = 4 [5,6] and CN = 6 [7] have been determined. Later on, the analytic dependence of covalent radii on bond multiplicity has been established[8]:

$$r_1 - r_n = a\log n, \qquad (1)$$

where r_1 and r_n are the radii of the atoms taking part in single and n-multiple bonds, a is the constant, and n is the valence to CN ratio. Later,[9,10] Eq. (1) has been modified for metals and clusters.

The "sensitivity" of the atomic sizes to be determined to specific features of their electron structures also allowed one to solve inverse problems. For example, it has been shown that the heteronuclear bond length is less than the sum of covalent radii by a value proportional to its ionic character,[11,12] that the sizes of transition metals depend strongly on the properties of d-electrons,[13] and that real radii of IB subgroup elements are considerably underestimated compared to theoretical values for CN = 12 due to anomalously high valences of these atoms.[14,15]

The comparison of interatomic distances in the internal sphere of complex compounds with the sum of covalent radii made it possible to determine and characterize the strength of the trans-effect of the atoms and radicals.[16—18] It is necessary to know exactly the values of covalent radii for calculating pressures of phase transformations of molecular structures into monoatomic metals, when intra- and intermolecular distances become equal.[19—21] The anisotropy of atoms (the ratio of covalent and van der Waals radii) determines the packing density of molecules in crystals.

In several works, the correlations between quantum-mechanical orbital and empirical covalent radii have been established,[22,23] which allowed one to estimate the electron density distribution profile and the distance

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Table 1. Fragments of the systems of covalent radii

Atom	*r*/E				
	See Ref. 27	See Ref. 28	See Ref. 29	See Ref. 30	Exp.
Be	0.887	0.96	0.81	1.11	0.97
Mg	1.373	1.30	1.21	1.60	1.36
Ca	1.74	1.74	1.50	1.97	1.63
Sr	1.91	1.91	1.66	2.15	1.88
Ba	1.98	1.98	1.88		1.96
Zn	1.29		1.07		1.23
Cd	1.493		1.28		1.34
Hg	1.500		1.32		1.32
B	0.822	0.82	0.79	0.88	0.84
Al	1.258	1.25	1.13	1.43	1.32
Ga	1.256	1.26	1.14	1.22	1.26
In	1.455	1.50	1.34	1.62	1.39
Tl	1.490		1.62		1.48
C	0.772	0.77	0.78	0.77	0.77
Si	1.169	1.17	1.12	1.17	1.18
Ge	1.223	1.22	1.21	1.22	1.22
Sn	1.420	1.41	1.37	1.40	1.40
Pb	1.48	1.55	1.53		1.44

from its maximum for an orbital to the "boundary" of an atom. Finally, covalent radii of elements are of self-contained significance for the calculation of electronegativities of atoms.[24–26]

However, the existing systems of covalent radii differ noticeably for the majority of elements (Table 1), except for I group metals, halogens, and IVB subgroup elements for which radii are defined as halves of the bond lengths in the corresponding A_2 molecules or crystals. This divergence in the values of covalent radii makes difficult their efficient application for interpreting and predicting properties of chemical compounds. However, the experimental material has been obtained to date that makes it possible to determine reliably the majority of covalent radii and thus to eliminate the existing disparity in values suggested by various authors on the basis of limited structural data.

In this work, experimental covalent radii are determined for ordinary structures with single, double, and triple bonds. Bond lengths are taken from the works that make use of spectroscopic, X-ray, or electronographic methods, which give coincident or close results being applied to the same objects.

Spectroscopic determination of bond lengths

Spectroscopic methods make it possible to determine bond lengths in the simplest gaseous molecules with high accuracy. These data for interatomic distances in A_2 type molecules rounded off to the 3rd decimal point are presented in Table 2. For hydrogen, halogens, and I group metals 1/2 of the bond length in a molecule corresponds to the normal covalent radius, for oxygen and chalcogens it corresponds to the covalent radius in a double bond, and for nitrogen it corresponds to that in a triple bond. In all the other cases, special analysis is required to reveal the valent state and bond multiplicity in each particular molecule.

For example, it has been established on the basis of quantum chemical calculations that the B—B distance in the B_2 molecule presented in Table 2 corresponds to a single bond, while the bond lengths of 1.496 and 1.458 Å have been determined for double and triple bonds, respectively.[34] Single bond is realized in the $X^3\Pi_u$ ground state of Al_2 (see Table 2), while in the $B^3\Sigma_u^-$ state it is double bond (d = 2.560 Å). C_2 and Si_2 contain double bonds,[42] ground states of Sn_2 and Pb_2 contain single bonds,[36] and Ti_2 has a triple bond.[37]

By analogy with N_2, the bond multiplicity in P_2 and As_2 molecules is assumed to be equal to 3. For V_2 and Sb_2 the bond orders are formally equal to 5, however, their strengths are not too high, because the ns—ns and $(n-1)$d—$(n-1)$d optimum bond lengths differ substantially, and, therefore, these bonds cannot be simultaneously realized.[39] In Cr_2, Mo_2, and Pt_2, d-electrons participate[38,40] in the formation of multiple bonds, unlike those in Ni_2 (by analogy with Cu_2 [38]).

Despite the fact that the interpretation of chemical bonding is difficult in some cases, spectroscopic studies of gaseous molecules provide the most unprejudiced information about the lengths of covalent bonds that are not distorted by the disturbing effect of adjacent structural moieties, which takes place in condensed substances.

Table 2. Interatomic distances in gaseous molecules

A_2	d(A—A) /E	Ref.	A_2	d(A—A) /E	Ref.	A_2	d(A—A) /E	Ref.	A_2	d(A—A) /E	Ref.
Li_2	2.673	31	Al_2	2.701	35	Sb_2	2.342	31	Te_2	2.557	31
Na_2	3.079	31	C_2	1.242	31	Bi_2	2.660	31	H_2	0.7414	31
K_2	3.924	32	Si_2	2.246	31	V_2	1.766	38	F_2	1.412	31
Rb_2	4.170	32	Sn_2	2.746	36	Nb_2	2.078	39	Cl_2	1.988	31
Cs_2	4.648	32	Pb_2	2.927	36	Cr_2	1.679	40	Br_2	2.281	31
Cu_2	2.220	31	Ti_2	1.942	37	Mo_2	1.938	40	I_2	2.666	31
Ag_2	2.530	33	N_2	1.098	31	O_2	1.208	31	Fe_2	2.202	41
Au_2	2.472	31	P_2	1.893	31	S_2	1.889	31	Ni_2	2.154	42
B_2	1.679	34	As_2	2.103	31	Se_2	2.166	31	Pt_2	2.208	38

Table 3. Interatomic distances in solid simple substances

Substance	d(A—A) /Å	Ref.	Substance	d(A—A) /Å	Ref.
F_2	1.49	43	Se	2.374	43
Cl_2	1.979	44	Te	2.866	47
Br_2	2.286	44	N_2	1.064±0.03	43
	2.307	45	P	2.227	48
I_2	2.715	43	As	2.516	49
O_2	1.15	43	Sb	2.908	49
S	2.045	46	Bi	3.071	49
	2.060	43			

Table 4. Homonuclear bond lengths in R_nAAR_n' compounds

A	d(A—A)	d(A=A)	d(A≡A)	Ref.
		/Å		
Cd	2.58			51
Hg	2.54			51,52
B	1.72	1.52	1.36	53,54
Al	2.66			55
Ga	2.46			55—59
In	2.78			55,60
Tl	2.91			61
C	1.54	1.34	1.20	55
Si	2.34	2.14	2.00	55
Ge	2.43	2.26	2.13	55,62—65
Sn	2.81	2.68		55,64
Pb	2.91			62,66
N	1.46	1.25	1.10	55
P	2.22	2.00	1.86	55
As	2.42	2.22		55
Sb	2.82	2.62		55
V			2.39	67
O	1.46	1.21		55
S	2.08	1.88	1.74	55
Se	2.34	2.14		55
Te	2.73	2.54		55,68,69
Cr			2.23	67,70
Mo			2.26	71—73
W	2.65	2.51	2.25	70,73
Cl	1.98	1.78		55
Br	2.28	2.08		55
I	2.66	2.46		55
Re		2.32		74
Ru	2.56	2.34		75,76

Table 5. Bond lengths in FeS_2 type structures

M	d(S—S) /Å	Ref.	d(Se—Se) /Å	Ref.	d(Te—Te) /Å	Ref.
Cu	2.030	77	2.33	79	2.746	81
Ba					2.772	82
Mn	2.091	77	2.332	80	2.750	81
Fe	2.177	77	2.53	79	2.626	81
Co	2.113	77	2.446	80		
Ni	2.072	77	2.42	80	2.650	81
Ru	2.171	78	2.453	78	2.790	81
	$\bar{d}$ = 2.09		$\bar{d}$ = 2.42		$\bar{d}$ = 2.71	

Structural analysis of crystalline elements

X-ray studies of some simple substances existing in the solid state under normal thermodynamic conditions provide direct information about normal covalent bond lengths. Interatomic distances for elements of subgroups V—VIIB are presented in Table 3, and data for conditions closest to the normal one are presented in the case of studies at various temperatures.

As can be seen from the comparison of the data in Tables 2 and 3, in A_2 type molecules, bond lengths depend slightly on the aggregate state. The differences in interatomic distances in gaseous and crystalline chalcogens and pnictides (phosphides, arsenides, and stibnides) are considerably greater and caused by the differences in bond multiplicities in these structures.

Interatomic distances in subgroup IVB crystalline elements with the diamond structure correspond to covalent single bonds, whence the following values of normal covalent radii can be obtained[50]: C 0.772, Si 1.176, Ge 1.225, and Sn 1.405 Å. Interatomic distances in metals in which valences are lower than the coordination numbers are attributed to the bonds with $n < 1$ and are not considered in this work.

Determination of covalent radii from structural parameters of compounds

The experimental covalent radii can be obtained from the interatomic A—A distances in $R_nA—AR'_n$ type structures, where R is an organic or inorganic radical. The A—A bond lengths averaged (to the 2nd decimal point) on the basis of the results of structural studies of the corresponding organometallic and inorganic compounds are presented in Table 4.

A useful information is also provided by X-ray study of MX_2 compounds with the pyrite structure in which single covalent bonds are realized between X atoms (S, Se, Te, P, As, and Sb); the corresponding experimental data are presented in Table 5. The Bi—Bi bond length in $PtBi_2$, which also has the pyrite structure but is absent in Table 5, is equal to 2.995 Å.[84] In carbonyl complexes containing Sb_2 and Bi_2 groups, the mean interatomic M—M values are 2.82 and 2.98 Å,[86] respectively.

M	d(P—P) /Å	Ref.	d(As—As) /Å	Ref.	d(Sb—Sb) /Å	Ref.
Au					2.86	79
Cr					2.88	79
Mn					2.842	83
Fe	2.27	79	2.49	79	2.89	79
Ni			2.45	79	2.88	79
Pd			2.420	84	2.838	84
Pt	2.180	85	2.41	79	2.782	84
	$\bar{d}$ = 2.22		$\bar{d}$ = 2.44		$\bar{d}$ = 2.85	

Table 6. P—P and As—As bond lengths in M_3X_n clusters

Cluster	d_1(P—P)	d_2(P—P)	d_3(P—P)	Cluster	d_1(As—As)	d_2(As—As)	d_3(As—As)
	/Å				/Å		
Li_3P_7	2.249	2.147	2.176	Li_3As_7	2.495	2.401	2.424
Na_3P_7	2.262	2.105	2.195	Na_3As_7	2.493	2.361	2.411
Rb_3P_7	2.257	2.123	2.169	Pb_3As_7	2.499	2.352	2.401
Cs_3P_7	2.287	2.120	2.162	Cs_3As_7	2.510	2.355	2.401
Na_3P_{11}	2.247			Na_3As_{11}	2.469	2.395	2.456
K_3P_{11}	2.244			K_3As_{11}	2.459	2.375	2.444
	$\bar{d}$ = 2.20±0.05				$\bar{d}$ = 2.43±0.04		

Table 7. Bond lengths and covalent radii in MH molecules

M	d(M—H) /Å	Ref.	r(M) /Å	M	d(M—H) /Å	Ref.	r(M) /Å
Be	1.343	31	0.97	Ga	1.662	89	1.29
Mg	1.730	31	1.36	In	1.873	89	1.47
Ca	2.00	79	1.63	Tl	1.873	89	1.50
Sr	2.15	79	1.88	Hf	1.831	90	1.46
Ba	2.23	79	1.96	Bi	1.809	90	1.44
Zn	1.594	79	1.22	Cr	1.690	90	1.32
Cd	1.762	79	1.39	Mn	1.72	79	1.35
Hg	1.740	79	1.37	Co	1.542	93	1.17
Al	1.647	89	1.28	Ni	1.476	93	1.11

The P—P bond lengths in polyphosphides vary from 2.15 to 2.30 Å, depending on the phosphorus framework structure (chains, rings, polycycles, or spatial configurations) and the cation composition, and the mean value is equal[87] to 2.226±0.039 Å. In $(PPh)_n$, $(PCF_3)_n$, and $(PR)_n$ organic polycycles, where R = C_6F_5, hexyl, or butyl, and in P_nH_m, where $m < n$, and n varies from 4 to 22, the mean P—P bond length ≈ 2.222 Å with a mean deviation of ±0.010 Å.[88] The fact that the interatomic P—P distances are invariable and close to the bond length in phosphorus element is due the covalent character of bonding in organophosphorus compounds. In the case of salts of M_3X_7 and M_3X_{11} type, where X = P or As, X—X bond lengths vary considerably greater,[87] as can be seen from Table 6.

Additive covalent radii of metals

The experimental material presented above exhausts the literature data on the direct determination of covalent bond lengths in gaseous and crystalline structures containing homonuclear bonds. For several transition metals that do not form analogous compounds, the covalent radii can be determined by indirect methods, for example, by additive schemes from interatomic distances in molecules.

Since the bond polarity and multiplicity affect its length, it seems reasonable to use the data on interatomic distances in hydrides in which the most covalent single bonds are realized, because among monovalent nonmetals, hydrogen possesses the minimum electronegativity. The bond lengths (d_{MH}) in biatomic hydrides and covalent metal radii obtained by subtracting the covalent hydrogen radius (0.371 Å) from d_{MH} are presented in Table 7. However, these values should be considered as upper estimations of covalent metal radii, because bond lengths in MH moieties are always longer than in the corresponding MH_n molecules due to electron repulsion.[79]

The terminal M—H bond lengths in organometallic compounds and covalent metal radii obtained by the additive method are presented in Table 8. In our opinion, the accumulation of experimental data on M—H bond lengths in molecules and radicals will be the main source of new information about covalent radii of metals.

* * *

As can be seen from Tables presented in this work, in the majority of cases, covalent radii determined by various methods agree, on average, within several hundredths Å, and the scatter of values is higher for inorganic compounds. However, covalent bond lengths in organic molecules also vary in the 2nd decimal point, depending on structures, especially on the size, and

Table 8. Bond lengths and covalent radii in R_nMH_m molecules

M	d(M—H)/Å	Ref.	r(M)/Å	M	d(M—H)/Å	Ref.	r(M)/Å
Zn	1.617	94	1.25	Co	1.50	101	1.14
B	1.187	79	0.82		1.476	102	
Nb	1.70	95	1.33		1.556	96	
Ta	1.773	94	1.40	Ru	1.752	99	1.26
Mo	1.684	94	1.31		1.52	103	
W	1.732	94	1.36	Rh	1.580	94	1.21
Mn	1.576	96	1.21	Os	1.659	94	1.28
Re	1.684	94	1.31		1.649	104	
	1.665	97			1.64	105	
	1.685	98,100			1.655	100	
Fe	1.609	94	1.20	Ir	1.603	94	1.22
	1.58	99			1.61	106	
	1.527	100			1.587	107	
					1.58	100	
				Pt	1.610	94	1.24

Table 9. Recommended values of covalent radii

A	r/Å	A	r/Å	A	r/Å	A	r/Å
			Single bonds				
Li	1.34	Cd	1.34	P	1.11	F	0.71
Na	1.54	Hg	1.32	As	1.23	Cl	0.99
K	1.96	B	0.84	Sb	1.43	Br	1.14
Rb	2.08	Al	1.32	Bi	1.50	I	1.33
Cs	2.32	Ga	1.26	Nb	1.33	Mn	1.28
Cu	1.11	In	1.39	Ta	1.40	Re	1.31
Ag	1.26	Tl	1.48	O	0.73	Fe	1.20
Au	1.24	C	0.77	S	1.03	Co	1.15
Be	0.97	Si	1.18	Se	1.19	Ni	1.11
Mg	1.36	Ge	1.22	Te	1.40	Ru	1.26
Ca	1.63	Sn	1.40	Cr	1.32	Rh	1.21
Sr	1.88	Pb	1.44	Mo	1.31	Os	1.28
Ba	1.96	Hf	1.46	W	1.34	Ir	1.22
Zn	1.23	N	0.73	H	0.37	Pt	1.24
			Double bonds				
B	0.76	N	0.625	O	0.605	Cl	0.89
Al	1.28	P	1.00	S	0.94	Br	1.04
C	0.67	As	1.11	Se	1.08	I	1.23
Si	1.07	Sb	1.31	Te	1.28	Re	1.16
Ge	1.13			W	1.26	Pt	1.10
Sn	1.32						
			Triple bonds				
B	0.68	C	0.60	N	0.55	S	0.87
		Si	1.00	P	0.93	Cr	1.11
		Ge	1.06	As	1.05	Mo	1.13
		Ti	0.97	Sb	1.17	W	1.12
				V	1.19		

electronegativities of substituents. This means that covalent radii should be determined with the same accuracy.

The experimental data presented allow one to recommend the covalent radii of elements involving in single, double, and triple bonds (Table 9). It is seen that these radii change regularly as the number of the group or period changes. However, there are exceptions: an atomic size does not increase, but decreases on going from Al to Ga and from Cd to Hg. It is not clear yet whether this is caused by random superposition of experimental or calculation errors or determined by specific features of electronic states of elements in the objects studied.

Returning to Table 1, it should be emphasized that the system of covalent radii suggested in this work does not coincide exactly with either of recent compendia, but it is closest to the data of Sanderson[27] and Luo and Benson,[28] who have performed correlations between covalent radii and electronegativities.

It is also noteworthy that this system is not designed for exact calculation of interatomic distances but rather for their estimation. Moreover, the deviation of the real chemical bond length from the sum of covalent radii is an indication and measure of the deviation of the character of a given bond from a pure covalent one, which is significant for understanding and description of particular structures.

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