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van der Waals Radii of Noble Gases

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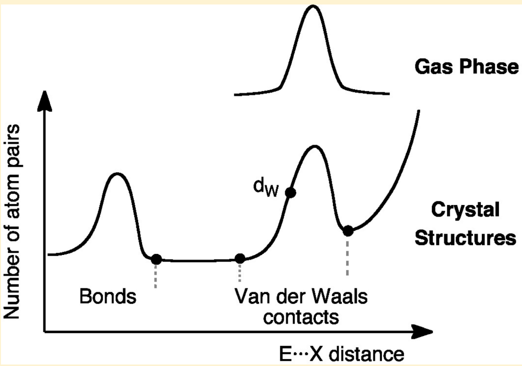
Ⓢ *Supporting Information*

ABSTRACT: Consistent van der Waals radii are deduced for Ne−Xe, based on the noble gas···oxygen intermolecular distances found in gas phase structures. The set of radii proposed is shown to provide van der Waals distances for a wide variety of noble gas···element atom pairs that represent properly the distribution of distances both in the gas phase and in the solid state. Moreover, these radii show a smooth periodic trend down the group which is parallel to that shown by the halogens.



■ INTRODUCTION

Despite the conceptual simplicity of the definition of a van der Waals radius for each element,[1] it has proven very useful to decide on the existence of a chemical bond or of a weak noncovalent interaction between two atoms in a crystal structure. The noble gases (represented from here on as G) constitute the paradigm of van der Waals interactions, given their little tendency to form chemical bonds. Yet, their commonly used van der Waals radii, proposed by Bondi in 1964,[2,3] may come from a rather limited set of structural data, since the first noble gas compounds had been reported only a couple of years earlier by Bartlett,[4] and practically only the elemental structures of those elements had been determined at that time. Even in the earlier books of Pauling[1] and Kitaigorodskii,[5] who discussed in detail van der Waals radii, values for the noble gases were missing.

Bondi stressed in his paper that its goal was to allow for the calculation of molecular van der Waals volumes. What he proposed was a list of "recommended" values of radii obtained by selecting "from the most reliable X-ray diffraction data those which could be reconciled with crystal density at 0 K, gas kinetic collision cross section, critical density, and liquid state properties". While he presented a detailed discussion on the origin and qualitites of the recommended radii for other groups of the p block, he did not mention the origin of the values proposed for the noble gases. It is out of the scope of this work to review the large number of proposals of van der Waals radii for the noble gases deduced from structural data, and we note only some leading reviews for the interested reader.[6,7]

An alternative approach used by several authors has consisted in deducing van der Waals radii from calculated nonbonded distances. In that respect, the values obtained by Pyykkö for the noble gases differ from those of Bondi by only one or two hundreths of an Ångstrom.[7] Truhlar and co-workers, on the other hand, fitted a linear combination of calculated radii for main group elements in such a way as to obtain a set of values consistent with those previously reported by Bondi while adding new radii for 16 main group elements.[8] The proposed radii for the noble gases therefore differ again from Bondi's values by at most two hundreths of an Ångstrom. For the missing noble gas in Bondi's table, radon, these two papers have proposed values of 2.24 and 2.20 Å, respectively.

In the preceding proposals, the van der Waals radii come from interatomic nonbonded distances in crystal structures or from computational studies. A radius for an element E is obtained as either half the E···E distance or as the E···X distance to another element X minus the previously determined radius of that element. Rowland and Taylor took a different approach.[9] For a selection of main group elements present in the set of Bondi radii (H, C, N, O, F, S, Cl, Br, and I), they analyzed the distribution of nonbonded distances in crystal structures, which has the general aspect shown schematically in Figure 1 (lower curve). The distribution of intermolecular E···X distances between atoms of two elements in crystal structures thus presents a peak at short distances coresponding to E···X bonds. At distances slightly longer than the bond length usually no E/X atom pairs are found, giving raise to a van der Waals gap, while at longer distances one finds a maximum of the distribution function that can be attributed to the existence of attractive van der Waals interactions, once hydrogen bonding has been ruled out. Finally, at still longer distances one finds a continuously increasing number of atom pairs that is due to a

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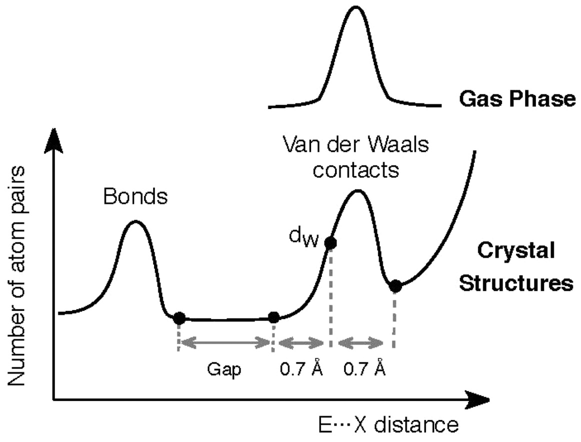

Figure 1. Ideal form of a distance distribution map between atoms of two elements E and X, in which regions of bonded atoms and intermolecular van der Waals contacts are separated by a gap. The van der Waals sum of the two elements (d_W) corresponds to the half height of the rising slope of the van der Waals peak. In comparison with the crystal structures, in the gas phase there are no noninteracting atoms at distances longer than the van der Waals peak (upper curve).

random distribution of atoms of X around an atom E, that depends roughly on the cube of the distance.

Rowland and Taylor defined the distance corresponding to the half-height of the contacts peak as the van der Waals distance from which the corresponding radii can be deduced. Although the values obtained by these authors are remarkably similar to the Bondi radii, it is clear that they have ascribed a somewhat different meaning to those radii, which are not just replicating a given nonbonded distance, but give the position of the statistical distribution of van der Waals distances, pointing to a value slightly below the maximum of the distribution function. This is the approach that we have used in our recent study of van der Waals territories[10] for all elements using crystal structure data and that will be revised in this paper for the noble gases by combining solid state and gas phase structural data. As a rule of thumb, it has been found[10] that the van der Waals peak roughly covers a range of distances 0.7 Å shorter or longer than the sum of the van der Waals radii of the two elements (hereafter referred to simply as the van der Waals sum and represented by d_W). For a more detailed discussion on the concept and applicability of van der Waals radii recent papers by Dance[11] and Taylor[9,12] are recommended.

The amount of crystal structural data nowadays available for noble gas derivatives[13] is much larger than that available to Bondi. Yet, our recent attempt[10] to revise their van der Waals radii based on solid state structural data was biased by the

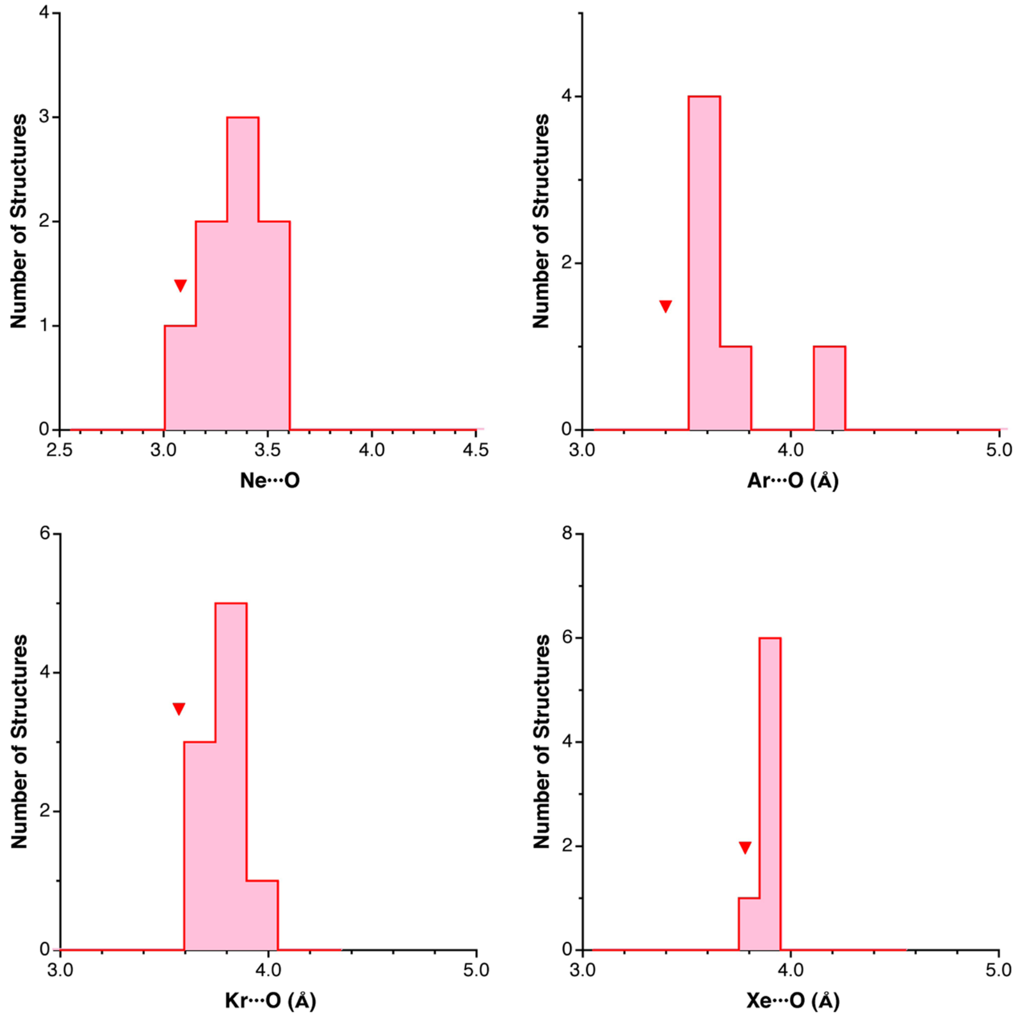

Figure 2. Distribution of the G···O non bonded distances in van der Waals complexes in the gas phase. The triangles indicate the van der Waals sum corresponding to the radii proposed here.

limited data sets and the nature of the characterized compounds. To give an idea of the small number of crystal structures available for noble gases and their compounds, the Cambridge Structural Database (CSD)[14] holds at the time of writing this paper some 700 000 entries, and only in about 0.01% of them (i.e., 57 structures) is a noble gas present. The situation is somewhat better in the Inorganic Crystal Structure Database (ICSD),[15] among whose approximately 160 000 current entries there is a 0.86% of noble gas-containing structures (1384 structures). Consequently, in our recent proposal of a consistent set of van der Waals radii for most elements of the periodic table,[10] deduced from E···O intermolecular distances (where E is any element), only tentative values were given for the noble gases down to Xe, and a warning was given about their uncertainty and the possible lack of representativity. Thus, the radius for He was deduced from 12 distances from just one crystal structure, that of the water−helium chlathrate, while for Ne only the solid state structure of elemental neon could be used. For Ar and Xe, on the other hand, the van der Waals radii were deduced from the more abundant contacts to carbon atoms, because of the scarcity of structures containing one of those noble gases and our standard probe atom, oxygen. Given the different probe elements used to deduce the radii and the limited structural data available, it comes as no surprise that they do not follow a smooth periodic trend down the group, neither do they seem to reasonably correlate with the radii of the halogens or with the trends in the corresponding covalent radii.[16]

On the other hand, the MOGADOC (Molecular Gasphase Documentation) database[17] comprises more than 8500 structural data sets, 484 of them containing noble gases (5.7%). Due to the existence of a variety of gas phase structural data for van der Waals complexes involving noble gases, duly available through the MOGADOC database,[17] we decided to analyze the distribution of the gas phase van der Waals contacts involving the noble gases and to try to define a consistent set of van der Waals radii that could be representative of the distribution of such contacts both in the gas and solid states. We therefore present here the result of our analysis of non bonded contacts involving noble gases as found in the Cambridge Structural Database (CSD),[14] the Inorganic Crystal Structure Database (ICSD),[15] and the gas phase structural database MOGADOC.[17] It must be noted that the limited number of gas phase structural data is in part compensated by the absence of nonbonded and noninteracting atom pairs at distances similar to the van der Waals distance or longer (Figure 1, upper curve).

■ METHODOLOGY

The histograms for the distribution of nonbonded G···O distances in the gas phase, obtained from the MOGADOC database,[17] have been analyzed as proposed by Rowland and Taylor[9] and van der Waals radii deduced for the noble gases, taking the radius of oxygen as 1.50 Å.[10] The resulting radii were then used to calculate the van der Waals sums for G···E contacts involving a noble gas and any other element E and compare them with the experimental values found in the gas phase and in the solid state.

■ NOBLE GAS VAN DER WAALS RADII FROM GAS PHASE CONTACTS TO OXYGEN

The histograms that show the distribution of G···O van der Waals contacts in the gas phase are presented in Figure 2, except for He and Rn, because the lack of gas phase structural data for those elements. In Figure 2 we can see that, in spite of the relatively small number of structural data available, sharp maxima allow us to estimate van der Waals radii for Ne through Xe (Table 1). We also note that the resulting radii are in good agreement with the general rule found earlier that the van der Waals and covalent radii of the same element differ roughly by 0.9 Å.[10] Next, we take advantage of a number of noble gas contacts to other elements E to check if the van der Waals sums $d_W(G\cdots E) = r_G + r_E$ yield reasonable estimates of the experimental distances in the gas phase, which is seen in Figure 3 to be the case.

Table 1. van der Waals Radii Proposed in This Work for the Noble Gases, Compared to Previously Proposed Values and with the Covalent Radii[a]

element	covalent + 0.9 Å	Bondi[2]	Alvarez[10]	this work
He	[1.18]	1.40	1.43	1.43
Ne	[1.48]	1.54	1.58	1.58
Ar	1.96	1.76	1.88	1.94
Kr	2.06	2.02	2.25	2.07
Xe	2.30	2.16	2.06	2.28
Rn	2.40			[2.40][b]

[a] Values given in square brackets are estimates obtained by extrapolation from those of neighboring elements in the periodic table. [b] A radius of 2.20 or 2.24 Å has been proposed for Rn in computational studies.[8,18]

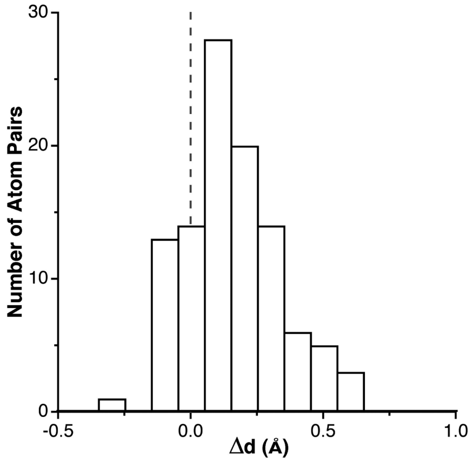

Figure 3. Distribution of the deviation of the G···E distances in the gas phase (data set of 104 distances) from the sum of the van der Waals radii (corresponding to a zero deviation and indicated by the dashed line). Data provided as Supporting Information.

■ A SURVEY OF NOBLE GAS-ELEMENT NONBONDING DISTANCES

In this section we analyze how the proposed set of van der Waals radii for the noble gases provide a sensible representation of the distribution of nonbonded close distances between noble gas atoms and other chemical elements both in the gas phase and in the solid state.

Helium. The van der Waals radius proposed by one of us[10] for He (1.43 Å) was deduced from the He···O distances in only one crystal structure, that of its water chlathrate. In the present revision we have found only three structural data sets for two van der Waals complexes in the gas phase whose nonbonded

He···E distances have been determined, He···CO_2 (3.56 Å)[19] and He···ClF (3.45 Å),[20] both slightly longer (0.4 and 0.2 Å, respectively) than the corresponding van der Waals sums and, therefore, well within the expected range of van der Waals distances. The deviation from the van der Waals sums of the He···E distances shorter than 4.5 Å in structures in the gas phase and in the solid state, obtained from the three databases, present the expected distribution within a range of ±0.7 Å of the van der Waals sum (Figure 4). It must be mentioned that the He···He distances in solid helium are centered at around 3.5 Å, i.e., 0.6 Å longer than twice the van der Waals radius proposed here, still within the expected range and in spite of the large coordination number (12) of He in its elemental close packed structure. Another remarkable case[21] is that of He@C_{60}, in which the radius of the cavity of the buckminsterfullerene (3.53 Å) is large enough to comfortably fit the helium atom (the He···C van der Waals radii sum is 3.20 Å), and the He···C distance may be determined by the size of the fullerene, rather than by the van der Waals interaction with individual carbon atoms. Omitting the data from this last structure, the radius deduced from the rest of the gas phase and inorganic structures coincides with that proposed earlier, 1.43 Å

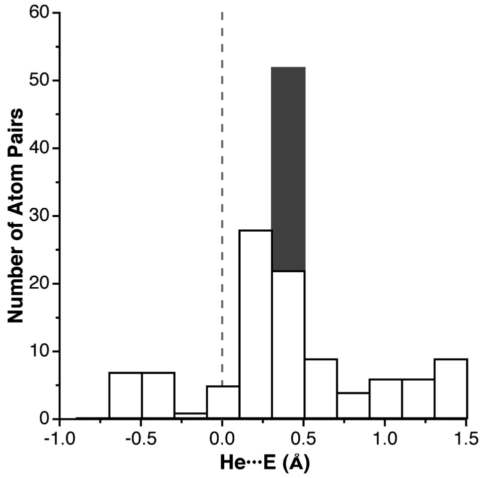

Figure 4. Distribution of the deviations of the He····E distances from the van der Waals sum (dashed line) for compounds in the gas phase (obtained from the MOGADOC database:[19,20] E = C, Cl) and in the solid state (ICSD data:[22,23] E = H, He, K, O), shown as white bins. The He···C distances in He@C_{60} are represented by the shaded bin.[21]

Neon. Since no structural data was available for Ne···O contacts in the CSD, the van der Waals radius proposed earlier by us (1.58 Å) was deduced from Ne···Ne contacts in solid neon. The same value is obtained from Ne···O contacts in the gas phase, using the methodology described earlier.[9,10] Application of this radius to a series of other Ne···E contacts indicates that the proposed value is representative of the variety of van der Waals distances determined in the gas phase (Figure 5), even if the number of structural data available is still scarce.

Argon. The previously proposed van der Waals radius for Ar (1.83 Å) was deduced from Ar····C distances in the CSD, due to the scarcity of data on Ar···O contacts. Although 117 distances were used then, they came from only four compounds, since six other structures have disordered Ar atoms. The wider gas phase data set available allows us to deduce its radius from Ar···O distances, as done previously for most other elements. A resulting radius of 1.90 Å is not significantly different, but we propose to adopt it for consistency. We have also checked a variety of intermolecular distances with several other elements, in molecular crystals (CSD), in inorganic solids (ICSD), and in the gas phase (MOGADOC). The experimental distances show a distribution around the van der Waals sums that is in excellent agreement with the semiquantitative expectations discussed above (Figure 6). For instance, in a CSD structure,[24] the Ar···F contacts, the shortest contacts to Ar, are found at 3.196 and 3.402 Å, in good agreement with a radii sum of 3.36 Å

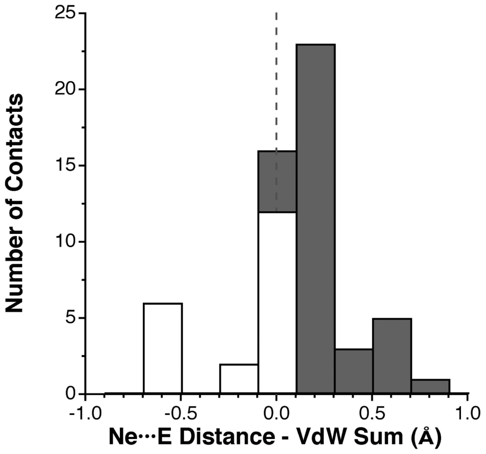

Figure 5. Distribution of the deviations of the Ne···E distances from the van der Waals sum (indicated by the dashed line) for compounds in the gas phase (white bins; E = Ar, C, Cl, Kr, Ne, S and Xe) and in $Ne_{0.24}@K_6[Sb_{12}O_{18}][SbSe_3]_2\cdot 7H_2O$ (gray bins; E = O, Ne).[23]

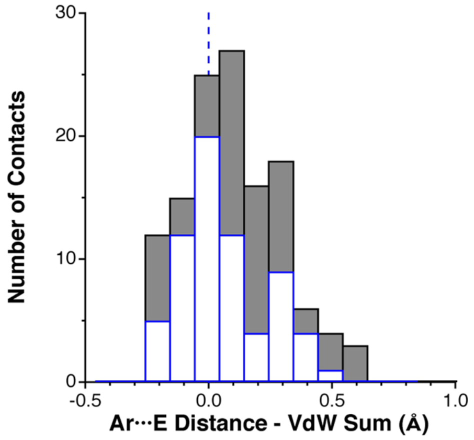

Figure 6. Distribution of the deviation of the Ar····E distances from the van der Waals sum (indicated by the dashed line) for compounds in the gas phase (white bins) and for all compounds in the gas and solid state (gray bins), obtained from the MOGADOC (E = Ar, Br, C, Cl, F, I, N, Ne, S, and Xe), CSD (E = C, F, O) and ICSD (E = O, Si) databases.

Krypton. The van der Waals radius reported earlier for Kr (2.25 Å) came from only four structures containing Kr···C contacts, whereas a wider set of intermolecular Kr···O distances from gas phase structures yields a smaller value, 2.07 Å. An analysis of the inorganic solids contaning Kr reveals also a distribution of contacts with other elements that is nicely distributed around the van der Waals sums (Figure 7), except for the Kr···C contacts in a fullerene clathrate[25] and for the contacts to fluorine in solid state compounds. In the fullerene

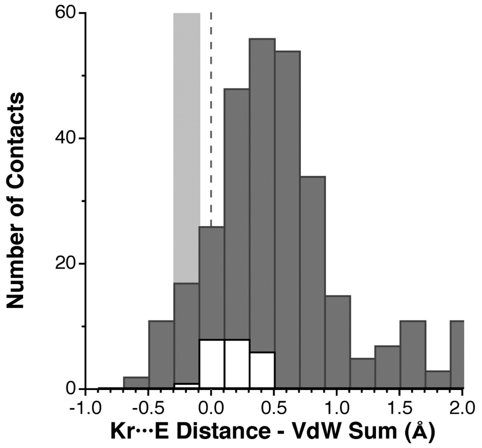

Figure 7. Left: Distribution of the deviation of the Kr····E distances from the van der Waals sums (dashed line) for compounds in the gas phase (white bins) and for all compounds in the gas and solid state (dark gray bins), obtained from the MOGADOC (E = Br, C, Cl, Cr, F, Kr, Mo, O, S, Si, W, and Xe), CSD (E = C, N, O, Cu, Rh), and ICSD (E = As, Bi, Br, Kr, Sb) databases. The light gray bin corresponds to the Kr···C contacts in Kr@C_{60}·[Ni(octaethylporphyrinato)]·benzene,[25] which are plotted separately. Right: Distribution of the distance difference for the Kr···F contacts in inorganic solids, which have been excluded from the general distribution histogram.

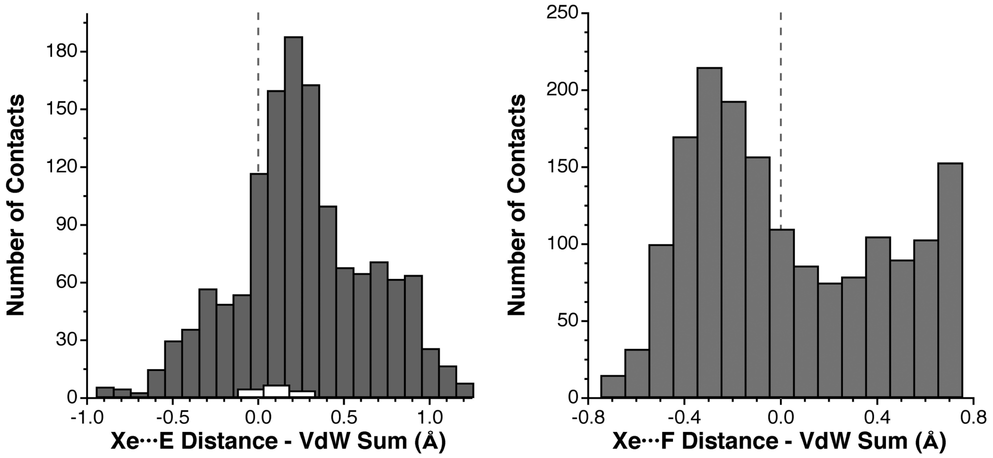

Figure 8. Left: Distribution of the deviation of the Xe···E distances from the van der Waals sum (indicated by a dashed line) for compounds in the gas phase, obtained from the MOGADOC database (white bins: E = Ar, Br, Cl, Cr, F, Kr, Mo, Ne, W, Xe), compared to the corresponding plot for the Xe···E contacts including solid state structures (gray bins) from the CSD (E = B, C, O, N, S, As, Xe) and the ICSD (E = Ag, As, B, Bi, Br, Cr, N, P, Pb, S, Sb, Tc, W, Xe). Right: Distribution of the Xe···F contacts in solid state compounds from the ICSD.

clathrate, the Kr···C distances are all within the range 3.53−3.55 Å, some 0.3 Å shorter than the van der Waals sum, still within the expected range for van der Waals interactions. The wealth of Kr···F contacts in the solid state show a distribution centered at shorter distances than expected from the van der Waals sum (Figure 7b), probably a reflection of the significant ionic contribution to those contacts that involve the KrF^+ and $Kr_2F_3^+$ cations. It must be emphasized that the analysis of Kr···F contacts has been carried out for distances longer than 2.5 Å, since this element shows a marked tendency to form hypervalent species such as KrF_2, with relatively long Kr−F bonds, similarly to what can be found in the structures of the isoelectronic triiodide ion. It must also be noted that the distribution of the Kr···E distances in the solid state presents a van der Waals peak followed by a characteristic random distribution at longer distances that increases with the cube of the distance, in contrast with the complexes studied in the gas phase, for which no long distance interactions can be characterized.

Xenon. The van der Waals radius previously proposed for Xe (2.06 Å) was derived from Xe···C contacts. The new value deduced from Xe···O contacts in the gas phase is significantly larger, 2.28 Å. The set of intermolecular Xe···E distances from gas phase structures are well represented by the van der Waals sums using this new value (Figure 8). As for Kr, the Ar···F contacts are shorter than expected from the van der Waals sum.

Radon. Since no structural data is available for Rn, and taking into account that the van der Waals radii are in average 0.9 Å larger than the corresponding covalent radii, we propose a tentative estimate of 2.40 Å for the van der Waals radius of Rn, 0.2 Å larger than the value deduced from computational studies,[8,18] and consistent with the much shorter Rn−H and Rn−X bond distances found computationally in H−Rn−X molecules (1.82 < Rn−H < 1.89 Å; Rn−X = 2.20, 2.69, 2.85, 2.48, 2.41, 2.42 for X = F, Cl, Br, I, CN, NC, CCH, respectively).[26]

■ DISCUSSION

We had observed recently that the van der Waals radii are on average 0.9 Å larger than the corresponding covalent radii.[10] The values proposed here for the noble gases follow the same trend (Figure 1), since they are larger than the covalent ones by

1.15 (He), 1.00 (Ne), 0.88 (Ar), 0.91 (Kr), and 0.88 Å (Xe). It must be said, though, that the differences for He and Ne must be taken with a grain of salt, because their covalent radii are tentative values only.[16] The new set of van der Waals radii proposed for He through Xe, on the other hand, is consistent in the sense that most of them have been deduced using as a probe the contacting oxygen atoms, as done previously for other elements. Moreover, the radii increase smoothly down the group, in contrast with the previous values, which showed an odd contraction on going from Kr to Xe (Figure 9). It can also be seen that the variation of the radii down the group is roughly parallel to that presented by the halogens.

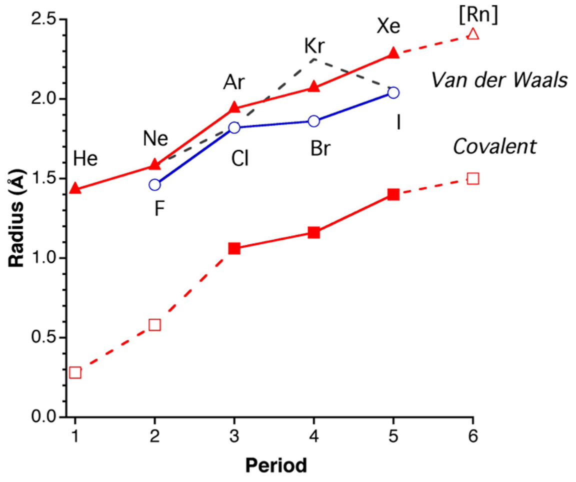

Figure 9. Revised set of van der Waals radii for noble gases proposed in this work (triangles), compared with previous values (dashed line), with those for the halogens (circles),[10] and with covalent radii (squares). The radii connected by dashed lines are extrapolated from those of neighboring elements in the periodic table (see text).

As a final check for the applicability of the new set of noble gas van der Waals radii, we have compared the experimental G$\cdots$M contact distances in the gas phase with the corresponding radii sums for a series of van der Waals complexes of composition G$\cdots$[M(CO)$_6$], where M = Cr, Mo, W. Figure 10 shows an excellent correlation between the two parameters, thus confirming an excellent representativity of the proposed radii for a wide variety of noble gas$\cdots$element van der Waals contacts. The G$\cdots$C distances in fullerene-enclathrated noble gases (G = He, Xe) have been disregarded for the deduction of the van der Waals radii because they are determined by the radius of the buckyball (3.5 Å) rather than by the optimal atom–atom nonbonded distance. However, it is interesting to observe that the G$\cdots$C distance in such clathrates falls within ±0.7 Å of the van der Waals radii sum for all noble gases, which makes them suitable for enclathration.

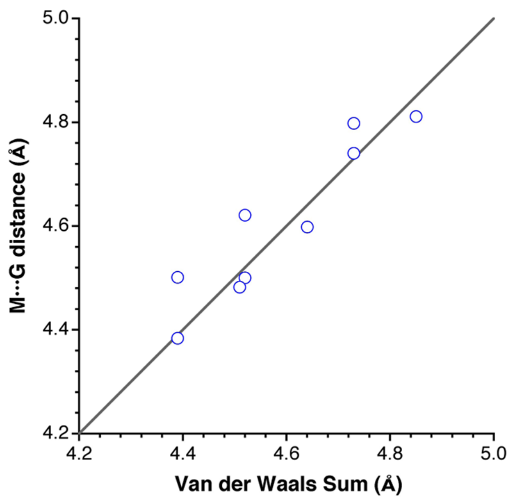

Figure 10. Comparison of gas phase G$\cdots$M distances in noble gas$\cdots$[M(CO)$_6$] complexes with the corresponding van der Waals sums (M = Cr, Mo, W).

The G$\cdots$M distances in the gas phase complexes of the type G$\cdots$M–X (M = Cu, Ag, Au; X = F, Cl, B) are much shorter than the van der Waals radii sum, clearly indicating that the noble gases should be considered as coordinatively bonded to the metal atoms in those complexes. As an example, the Cu$\cdots$Ar distance of 2.30 Å is much shorter than the van der Waals sum of 4.32 Å. In fact, the covalent radii for Ar and Kr[16] were deduced from those noble gas-noble metal bond distances in the gas phase reported by Gerry and co-workers.[27]

An intriguing family of van der Waals complexes are the 1:1 adducts with boron trifluoride, G$\cdots$BF$_3$. While one would expect the noble gases in those complexes to act as a Lewis acid, much like they behave in complexes with transition metals, the gas phase distances (Table 2) are much longer than the sum of covalent radii to be considered as bond distances but fall well within the expected width of the van der Waals peaks signaled by radii sums. This distance analysis suggests that boron trifluoride forms van der Waals rather than coordination complexes with some noble gases.[28−30] Also the G$\cdots$SiF$_4$ adducts appear to be van der Waals complexes based on a distance criterion. In contrast, the noble gas complexes with the methyl cation (Table 2), although isoelectronic with BF$_3$, present G$\cdots$CH$_3$ distances somewhat longer than the covalent radii sum, but clearly much shorter than the van der Waals sum, and should probably be considered donor–acceptor complexes.

Table 2. Comparison of Some G$\cdots$E Distances with the Covalent and van der Waals Radii Sums (all values in Å)

		radii sum		
complex	G$\cdots$E distance	covalent	van der Waals	ref
Ne$\cdots$BF$_3$	3.09	1.42	3.49	29
Ar$\cdots$BF$_3$	3.32	1.92	3.81	28
Kr$\cdots$BF$_3$	3.46	2.00	3.98	29
Ar$\cdots$SiF$_4$	3.80	2.17	4.13	31
Kr$\cdots$SiF$_4$	3.94	2.27	4.26	31
Ne$\cdots$CH$_3^+$	2.30	1.34	3.35	32
Ar$\cdots$CH$_3^+$	2.02	1.82	3.67	33

It should be taken into account that all Ar-, and Kr-containing solid state structures in the CSD correspond to van der Waals complexes, while a number of well-defined Ar–E and Kr–E bonds are characterized in the gas phase (E = Cu, Ag, Au, Na, N, F, H), with bond distances that are at most 0.2 Å longer than the sum of the covalent radii. In the case of Xe, one can find, both in the gas phase and in the solid state, bond distances that nicely match the covalent radii sum, and longer bond distances (some 0.3−0.7 Å in excess of the covalent radii sum, but considerably shorter than the van der Waals sum) that correspond to hypervalent compounds of the general formula X–Xe–Y$^+$. Noteworthy are the GH$^+$ ions

(G = He, Ar, Kr, Xe), whose interatomic distances exceed the sum of covalent radii by at most 0.18 Å, among which ArH^+ is the first noble gas molecule found in outer space recently.[34] A different situation appears in the Ar···H−X gas phase adducts, with Ar···H distances between 1.9 and 2.6 Å (data provided as Supporting Information), clearly intermediate between the expected bond length (1.4 Å) and the van der Waals sum (3.0 Å) that could be classified as hydrogen bonds. A similar situation appears in He···HCO^+,[35] Kr···HCO^+,[36] and in Ne···HNN^+ complexes.[37] Finally, several Ar···H−R (H−R = hydroxyl, formic acid, formamide, acetaldehyde, acrylonitrile, 2-butanol, and mercapto) gas phase adducts present Ar···H distances between 2.79 and 4.42 Å, well within the region expected for van der Waals contacts[10] (van der Waals radii sum = 3.14 Å) and clearly confirming how the covalent and van der Waals radii allow us to discriminate three different types of noble gas−hydrogen atom interactions: two-electron bonds, hydrogen bonds, and van der Waals contacts (see Supporting Information, Table S6).

■ CONCLUDING REMARKS

We have deduced van der Waals radii for the noble gases from the distances to oxygen atoms in gas phase complexes. The resulting values are seen to have consistent periodic trends, and the corresponding van der Waals radii sums for a wide variety of noble gas···element combinations represent well the distribution of nonbonded distances both in the gas phase and in the solid state. The radii proposed in this work are just slightly larger than those recommended by Bondi, from 0.03 Å for He to 0.12 Å for Xe.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

All the interatomic distances used for the present work are presented in Tables S1−S6 as Supporting Information, together with the corresponding van der Waals radii sums and references to the entries in the MOGADOC, CSD, and ICSD databases. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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