

Table 4.2 Selected Atomic van der Waals Radii (in Å)

Element	r_{VDW}
Hydrogen	1.20
Carbon	1.70
Nitrogen	1.55
Oxygen	1.50
Fluorine	1.50
Phosphorus	1.85
Sulfur	1.80
Chlorine	1.70
Bromine	1.80

Values from A. Bondi, *J. Phys. Chem.* **68**,441 (1964).

tween two atoms is less than the sum of their van der Waals radii. Table 4.2 gives some typical radii for atoms commonly found in organic molecules.

23 Polarization Energy

When two molecules approach each other, there is charge redistribution within each molecule, leading to an additional attraction between the molecules. The energy associated with this charge redistribution is invariably attractive and is called the polarization energy. For example, if a molecule with polarizability α is placed in an electric field, E , the polarization energy is

$$E_{\text{pol}} = -\frac{1}{2} \alpha E^2$$

If the electric field is caused by an ion, then $E = qi/R^2$, where q is the ionic charge, \mathbf{i} is the unit vector along the ion-molecule direction, and R the ion-molecule distance, which is the $E_{\text{pol}} = -1/2\alpha q^2/R^4$ for this ion-induced dipole interaction. The corresponding formula for dipole-induced dipole interaction between two dipolar molecules is

$$E_{\text{pol}} = -\frac{1}{2} \frac{\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2}{R^6}$$

where the μ 's are the dipole moments of the molecules, the α 's are their polarizabilities, and R is the distance between molecules. The polarizability of a molecule can be broken down into atomic contributions [atomic polar-

izabilities are additive to a good approximation (8)], and it is roughly proportional to the number of valence electrons, as well as on how tightly these valence electrons are bound to the nuclei. Umeyama and Morokuma (9) have calculated the ion-induced dipole contribution to the proton affinities of the simple alkyl amines. They attributed the order of gas phase proton affinities in the alkyl amines [$\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$] to the greater polarizability of a methyl group than a hydrogen. A simple estimate using the above empirical equation for an ion-induced dipole interaction with $q = +1$, which is the difference in polarizabilities of a methyl and a hydrogen ($\Delta\alpha \approx 4 \text{ cm}^3$, a proton-methyl distance of 2.0 \AA , and a proton-proton distance of 1.6 \AA , leads to an expected increase of $\sim 20 \text{ kcal/mol}$ of proton affinity for every methyl group added to NH_3 . This very qualitative estimate is of the right magnitude but about two to three times too large (see below).

2.4 Charge Transfer Energy

When two molecules interact, there is often a small amount of electron flow from one to the other. For example, in the equilibrium geometry of the linear water dimer $\text{HO}-\text{H} \cdots \text{OH}_2$, the water molecule that is the proton acceptor has transferred about $0.05e^-$ to the proton donor water (9, 10). The attractive energy associated with this charge transfer is the charge transfer energy and can be thought of as a mixing of an ionic resonance structure $\text{H}-\text{O}^{(-)} \cdots \text{H}-\text{OH}_2^{(+)}$ into the overall wave function. Although the charge transfer energy is an important contributor to the interaction energy of most noncovalent complexes, the presence of a "charge transfer" electronic transition in the visible spectrum does not mean that the charge transfer energy is the predominant force holding the complex together in its ground state. For example, the complex between benzene and I_2 , earlier thought to be a prototype "charge transfer" complex, seems to be held together predominantly by electrostatic, polarization, and dispersion energies in its ground electronic state (11).