# Molecule Matters
# van der Waals Molecules

## 2. Noble Gas Clusters are London Molecules!

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**In Part 2 of this series, we discuss homo- and hetero-nuclear noble gas dimers. Experimental and theoretical results for dimers containing He, Ne, Ar, Kr and Xe are reviewed. These dimers are bound by London dispersive forces, which is one component of the van der Waals or intermolecular forces. Though these are usually called van der Waals complexes or van der Waals molecules, these dimers may be more appropriately called London molecules. Helium dimer is a particularly interesting case with the equilibrium internuclear distance estimated to be about 50 Angstrom.**

## 1. Introduction to Rare/Inert/Noble Gases

'Rare gases', 'inert gases' and 'noble gases' are the names used to describe the elements from Group 18 in the periodic table of elements. The elements are helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). Radon is the biggest of them all and it is radioactive as well. We will limit our discussions in this article to rare gases He to Kr. It used to be Group 0 [1] when I was a student and one wonders why it was not Group 8. During my student days, the group number was equal to the number of electrons in the *s* and *p* orbitals in the outermost shell. Helium could have caused some confusion having only 2 electrons in the 1*s* orbital with no electrons in *p* orbital and all the others having 8 electrons in the outer most *s* and *p* orbitals. Mendeleev had elements for Groups 1–7 already and the new elements discovered by Lord Rayleigh and William Ramsey [2–4] (mainly He and Ar) had to be accommodated. Of course Mendeleev did not know the electronic orbital structure of atoms at that time. It turned out that the other elements of the group had

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(what we now understand as) valencies changing as 1,2,3,4,3,2,1 as one goes from Group 1 (H/Li) to group VII (F/Cl). It seems appropriate that the inert gases that did not combine with any other atoms were put as Group 0 by Mendeleev.

To be historically accurate, helium was detected earlier by Pierre Jensen and Joseph Norman Lockyer by observing its spectral lines in the solar chromosphere [2]. However, Ramsay was the first to isolate helium on earth by heating the mineral *clevite*. I cannot resist pointing out that the first Director of the Indian Institute of Science and the Chairman of the Department of General Chemistry (which has now become the Department of Inorganic and Physical Chemistry, my work place), Morris Travers, had worked with Ramsey in the discovery of the other noble gases, xenon, neon and krypton.

All these elements happen to be gases at ambient conditions (room temperature and pressure) and so the second part of the name is quite appropriate. They are also inert at ambient conditions and so the label 'inert' was appropriate. In fact, they are the only elements in the periodic table naturally occurring as monatomic gases. For this reason, they are also called noble gases in analogy with noble metals such as gold which are very inert as well. Argon happens to be the third most abundant gas in the atmosphere (~1 % by volume), behind $N_2$ and $O_2$ only, and one wonders why is it included in the 'rare' gases. Moreover, helium is the second most abundant element in the universe behind H. However, except Ar, the other gases are indeed rare in our atmosphere with Ne at 18 ppm, He at 5 ppm, Kr at 1 ppm and Xe at 0.1 ppm.

The term 'inert gases' is not accurate any more as several compounds of Xe and Kr such as $XeF_4$, $KrF_4$, $XeF_6$, and $XeO_4$ have all been synthesized [3]. These have now become a part of Inorganic Chemistry textbooks [1]. These molecules have 'covalent bonds' as opposed to van der Waals interactions which is the topic of this article. In this article, we will be focusing on rare gas clusters that are bound by van der Waals forces and more specifically by London dispersive forces alone.

## 2. Van Der Waals Equation, again!

In Part 1 of this series [5], we discussed the van der Waals equation shown below

$$\left( P + \frac{n^2 a}{V^2} \right)(V - nb) = nRT$$

and pointed out that the constant *a* depends on the intermolecular potential (which controls the intermolecular interaction) and *b* is the excluded volume that is not available for the gas molecules to occupy due to the finite size of the molecule. As mentioned above, the noble gas

*Table 1. van der Waals constants, melting points and boiling points for the rare gases (data taken from [4,5]). *

| Element | $a$ ($L^2$bar/mol$^2$) | $b$ (L/mol) | Melting point (K) | Boiling point (K) |
|---|---|---|---|---|
| Helium | 0.03457 | 0.0237 | 0.95[*] | 4.4 |
| Neon | 0.2135 | 0.01709 | 24.7 | 27.3 |
| Argon | 1.363 | 0.03219 | 83.6 | 87.4 |
| Krypton | 2.349 | 0.03978 | 115.8 | 121.5 |
| Xenon | 4.250 | 0.05105 | 161.7 | 166.6 |

* Helium does not freeze under atmospheric pressure of 1 bar. The melting point given is for a pressure of 20 bar.

elements are inert and remain as monatomic gases at ambient conditions. From He to Kr, the size of the atom does increase as is typical of all the group elements. As the atoms become bigger, they become more polarizable and this can lead to inter-atomic attraction. Clearly, the boiling point and melting point of the noble gases increase as He < Ne < Ar < Kr < Xe. One thing unique to these noble gases is that the difference between the boiling point and freezing point is small for all of them. Hence, they remain liquids in a narrow range of temperature only (typically less than 10°). The attractive force between two He atoms is too weak and it does not freeze even at 0 K under atmospheric pressure. In fact, He is the only chemical system that would obey a modified van der Waals equation over a limited range of $T$ and $P$, $P(V–nb) = nRT$ i.e., $a$ is nearly zero in the van der Waals equation for He. *Table* I lists the $a$ and $b$ values for the rare gases. The $a$ constant for He is 0.034 $L^2$ bar mol$^{-2}$ and that for Kr is two orders of magnitude higher at 4.250 $L^2$ bar mol$^{-2}$. For comparison, the $a$ constant for $H_2O$ is 5.46 $L^2$ bar mol$^{-2}$ and that for $CH_3OH$ is 9.34 $L^2$ bar mol$^{-2}$. As the size of the atom/molecule becomes larger, it is more polarizable and one can see a good correlation between the values of $a$ and $b$ for these gases. As they become more polarizable, the inter-atomic attraction increases which results in increasing melting and boiling points.

## 3. London Dispersive Forces

Fritz Wolfgang London was the first to come up with an explanation for the attraction between 'inert gases'. He argued that the charge distribution in an atom at any instance could be asymmetric, though the time-average distribution is spherical, leading to instantaneous dipoles, quadrupoles, etc. Instantaneous dipoles in neighbouring atoms could have attractive interaction if they are correlated. This type of interaction is called 'induced dipole-induced dipole interaction' or 'London dispersive interaction'. Unlike the other forces discussed in Part 1 of this series [5] (such as dipole-dipole), dispersion leads to attractive interaction for all orientations. According to London, the dispersion interaction energy between two identical atoms is given by the following relation [7]:

$$E_{\text{dis}} = -\frac{3}{4}\frac{\alpha_0^2 I}{(4\pi\varepsilon_0)^2 r^6}.$$

Here, $\alpha_0$ is the polarizability, $I$ is the first ionization potential, $\varepsilon_0$ is the vacuum permittivity and $r$ is the distance between the two atoms. For two dissimilar atoms, the relation becomes:

$$E_{\text{dis}} = -\frac{3}{2}\frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0)^2 r^6}\frac{I_1 I_2}{I_1 + I_2}.$$

Here the subscripts 1 and 2 stand for the two different atoms. The crucial aspect of this equation is the inverse $r^6$ dependence for the energy compared to the $1/r$ dependence for the Coulombic interaction between ions. Fortunately or unfortunately, the $1/r^6$ dependence of interaction energy is found even for the average dipole-dipole interaction and for the dipole-induced dipole interactions [7], which will be discussed in detail in the forthcoming articles. Hence, experimental observation of such dependence cannot be used to confirm the nature of forces as dispersive, inductive or electrostatic (dipole-dipole). However, this fact has led to the Lennard–Jones potential popularly known as 6–12 potential with a $1/r^6$ term describing attraction and a $1/r^{12}$ term describing repulsion:

$$V(r) = \frac{c_{12}}{r^{12}} - \frac{c_6}{r^6}.$$

Here $V(r)$ is the intermolecular potential and the $c_6$ and $c_{12}$ are coefficients for the $r^{-6}$ and $r^{-12}$ terms, respectively. The interaction in rare gas clusters is only due to the London forces and they could well be characterized as London molecules, though this is yet to be adapted by the community of chemists and physicists.

## 4. Rare Gas Clusters

Even the rare gases can form dimers (homo or hetero), trimers, and small clusters under appropriate conditions. A homo-dimer is $Ar_2$ and a typical hetero-dimer is ArNe. Of course, these are called dimers rather than 'a diatomic molecule' because they are bound by only London dispersive forces and the binding energy is typically two orders of magnitude smaller than a typical covalent bond. To be precise, the H–H bond energy in $H_2$ is about 100 kcal mol$^{-1}$ and the Ar–Ar 'bond' energy is less than 1 kcal mol$^{-1}$. Under ambient conditions, these dimers cannot be formed and investigated and one typically cools the atoms down to a very low temperature in order to form them. One of the techniques that is quite popular for cooling the atoms/molecules is supersonic expansion of gases [8]. This technique is described next before we start our discussion of the noble gas dimers.

## 4.1 *Supersonic Molecular Beams*

Molecular beams are similar to a beam of light, such as a laser beam that is found in CD readers, laser pointers, scanners, etc. Like a laser beam that produces light traveling in the same direction for a very long distance, molecular beams produce molecules that travel in the same direction. If gaseous molecules/atoms are kept in a container at a finite temperature, they will be moving randomly in all directions with a distribution of speed which was explained by Maxwell and Boltzmann; see *Figure* 1 for a typical cartoon representation. Molecules also have rotational and vibrational energy levels in addition to translational energy levels. When there is complete equilibrium, the translational, rotational and vibrational temperatures will all be the same. When this sample is supersonically expanded into a vacuum, the random kinetic energy is converted to directional energy and all the molecules now travel in the same direction, as shown in *Figure* 2. A typical experimental setup is shown in *Figure* 3. After the expansion, a skimmer may be introduced to further control the direction of the flow. A sample kept in a reservoir on the left is expanded through a hole into a chamber on the right that is evacuated by pumps to a very low pressure. If the diameter of the hole is much smaller than the mean free path (the average distance traveled by an atom/molecule between successive collisions), typically a few microns, then there are no collisions and the temperature ($T$) will be the same in the reservoir and the chamber. This would produce what is called an 'effusive beam'. However, if the diameter of the hole is significantly larger than the mean free path (about 1 mm), then there will be numerous collisions. This results in cooling and all the random energy is converted to directional translational energy.

The molecules lose internal energy as well, such as vibrational and rotational energies, which

*Figure 1 (left). A cartoon showing random speed distributions for a collection of rare gas atoms and a $H_2O$ molecule. Blue circles represent a typical carrier gas, Ar atom.*
*Figure 2 (right). A cartoon showing the speed distributions after supersonic expansion of the gases in Figure 1. All atoms/molecules are traveling with very similar velocities.*
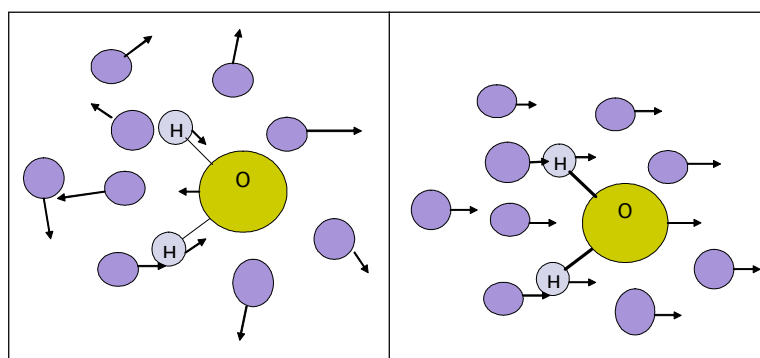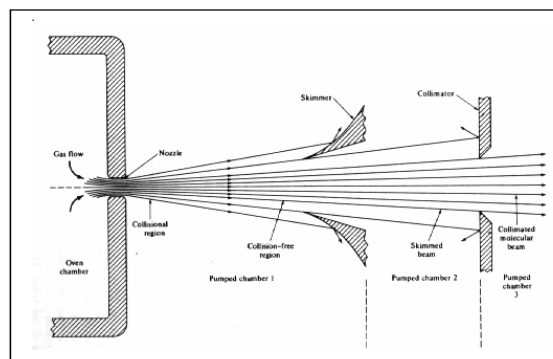
***Figure 3. Typical set-up for a supersonic beam experiment. On the left is a reservoir at ambient temperature and pressure which is connected to a vacuum chamber on the right through a nozzle hole. The gases expand into the chamber through this hole and during this expansion all the random kinetic energy (translational, rotational and vibrational) gets converted to directional energy. A skimmer and collimator may be added to reduce the divergence at larger distances from the nozzle***
(Figure taken with permission from R D Levine and R L Bernstein, Molecular Reaction Dynamics and Chemical Reactivity, Oxford University Press, New York, 1987).
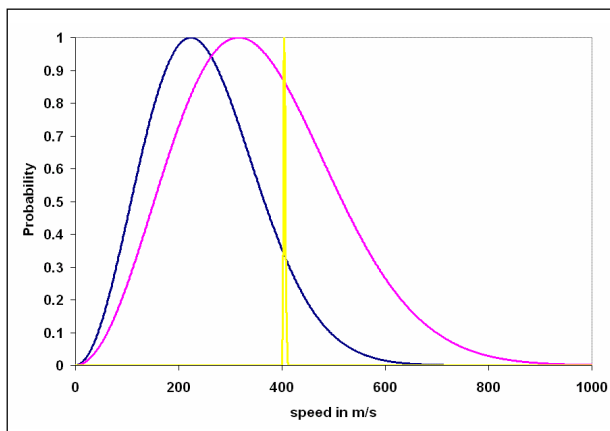


also get converted to translational energy. In a way, it is related to the familiar Joule–Thomson effect. In simple language, a gas at high pressure gets liquefied on expansion into a very low pressure. However, in a typical supersonic beam experiment, one expands the gas from atmospheric pressure (1 bar) to about $10^{-9}$ bar and the number densities are too low (about $10^{12}$ molecules $cm^{-3}$) to form a liquid drop. It is worth remembering that 18 ml of $H_2O$ has $6.022 \times 10^{23}$ molecules and it takes about 20 drops of water to make 1 ml. Clearly we need about $10^{21}$ molecules of water to make 1 drop! Though one does not make liquids in a supersonic expansion, the atoms/molecules expanded this way do become very cold. The temperature of the gases after expansion could be very low. Specifying the temperature of the beam is somewhat tricky and the details are discussed next.

After the expansion, the speed distribution would be very narrow and it fits a Maxwell–Boltzmann distribution with a very low $T$, typically 0.01 K which is called the translational temperature. This distribution for a given $T$ can be calculated with the expression shown below:

$$f(v) = 4\pi \left( \frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^2 \exp\left( -\frac{Mv^2}{2RT} \right).$$

Here, $M$ is the atomic/molecular weight, $v$ is the speed, $R$ is the universal gas constant, and $T$ is the temperature in K. However, the supersonic expansion is isenthalpic i.e., there is no loss or gain in the total energy for the molecular systems. All the random energy is converted to directional energy, mostly in one direction, and so the average speed/energy is higher now. The difference between the random speed distribution observed at an ambient $T$ of 300 K and that

*Figure 4. Maxwell–Boltzmann distribution of speeds at 300 K (blue), 600 K (pink) and 0.1 K (yellow) following a super-sonic expansion. See the text for complete description.*



following a supersonic expansion is clearly demonstrated in *Figure* 4. For comparison, the distribution expected for a higher *T*, 600 K is also shown in *Figure* 4. If the molecules are heated to higher *T*, the most probable speed (corresponding to the peak of the distribution) increases and the thermal energy of the molecules also increases. Moreover, the width of the distribution increases with *T* as is clear from *Figure* 4. However, after supersonic expansion the molecules get cold but they have not lost any energy. Hence, they end up traveling faster but with a very narrow distribution of speeds as shown in *Figure* 4.

The cooling of rotational and vibrational degrees of freedom is less effective and typically the rotational temperature is 2–3 K and the vibrational temperature is 50 K. The rotational and vibrational energy levels are under equilibrium and they follow Boltzmann distribution as well, which can be calculated using the expression:

$$\frac{P_J}{P_0} = \frac{g_J}{g_0}\exp\left(\frac{-E_J}{kT}\right).$$

Here $P_J$ is the number of molecules present in the rotational level *J*, $E_J$ is the energy of the rotational level, $g_J$ is the degeneracy of the rotational level *J*. Typical rotational distribution for 3 K and 300 K are shown in *Figure* 5. At 300 K, we have more energy levels populated and the difference in population between successive levels is small. At 3 K, only few levels are populated and the difference is comparatively more. These levels are quantized and so *Figure* 5 has distinct points corresponding to various quantum numbers for rotational energy levels. The translational energy is practically continuous and so *Figure* 4 shows a line function, i.e., all velocities/translational energies are possible for the molecule, without a break. Like the speed distribution, rotational energy level distribution also peaks at a value higher than 0 and decays for higher values of quantum number. This happens due to degeneracy of translational and
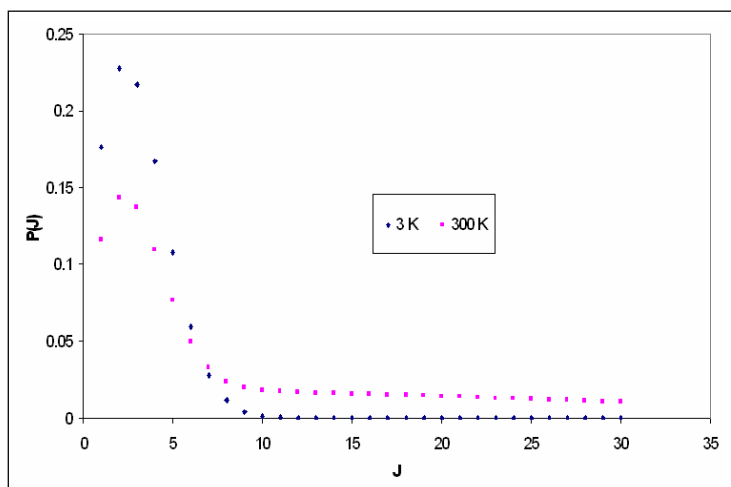
*Figure 5. Typical Maxwell–Boltzmann distribution of rotational energy levels at 300 K and at 3 K following supersonic expansion.*

rotational energy levels, i.e., several levels have identical energies. This degeneracy increases with energy and the population of energy levels decays exponentially with increasing energy. The distributions shown in *Figures* 4 and 5 are the products of these two factors. At the vibrational *T* of the beams, typically only the ground vibrational level is populated and there is no 'distribution'. In general, vibrational energy levels are non-degenerate as well and so if there is a distribution, one sees the population decreasing exponentially as the quantum number increases. Of course if we have an atomic beam, then there is no vibrational or rotational degree of freedom. Under these conditions when the molecules/atoms are internally cold, very weakly bound dimers/complexes such as the noble gas dimers discussed here, could be formed and studied.

Collisions between two atoms/molecules result in cooling. A three-body collision is required for forming a dimer in the beam. The requirement for the third body could be readily understood by a careful look at the potential energy curve for a typical dimer (*Figure* 6). When the two
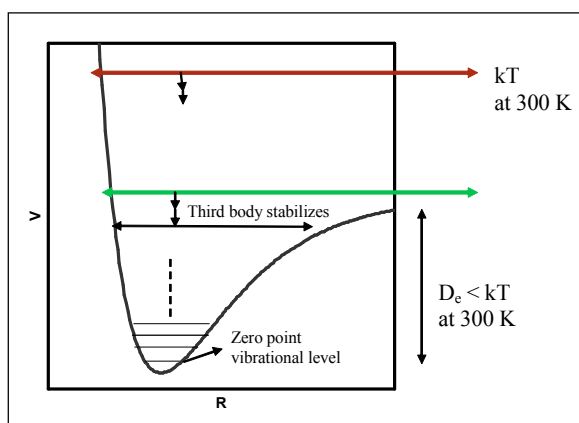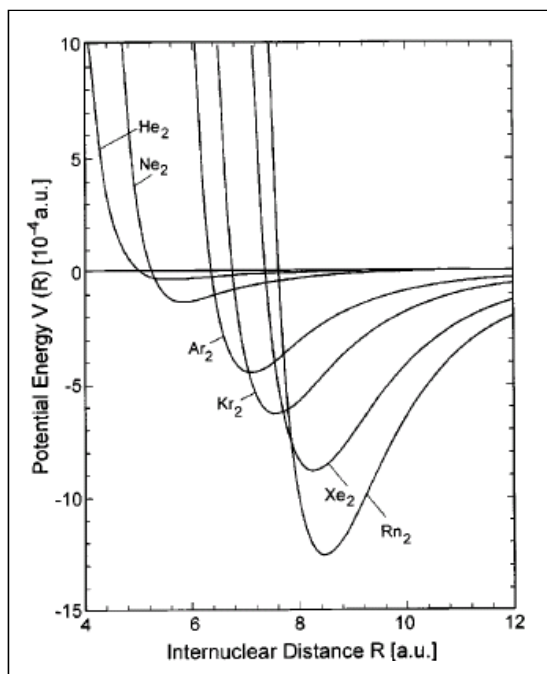


*Figure 6. A typical interatomic potential between two inert gas atoms as a function of internuclear distance. The horizontal lines within the potential represent various vibrational levels. $D_e$ is the equilibrium dissociation energy. Red arrow shows a typical path of the two atoms at ambient T. Green arrow shows the path at a much lower T. Even at this low T, a third body is needed to remove some kinetic energy and push the two atoms into the well corresponding to the dimer.*

atoms/molecules are at infinite distance, there is no interaction between them and the potential energy is zero. As they approach each other, in general the potential energy drops, i.e., there is an attractive force between them. As the total energy needs to be conserved, the kinetic energy will increase, i.e., the two atoms/molecules would approach each other faster now. A very good analogy can illustrate this clearly. Assume you are walking on a plateau on a hill top and approach the point where it goes down-hill. If you do not reduce your speed, you would start running. As the atoms/molecules approach each other closer, the kinetic energy will continue to increase until they arrive at the equilibrium distance for the dimer. When they do arrive at this point, they cannot stop as they have the maximum kinetic energy now and will continue to move forward. As the potential energy increases beyond this point, they will slow down and finally loose all the kinetic energy when they come to the point where the total energy becomes potential energy, i.e., they hit 'the wall'. Here again, the atoms cannot stop as the potential is repulsive and the force acting on the atoms is equal to the negative derivative of the potential, i.e., $F = - (\partial V/\partial R)$, where $R$ is the inter-atomic distance. The atoms now start moving away from each other, virtually retracing their path and finally breaking apart.

Let us now consider the situation when the two atoms are within the 'bound region' of the potential, i.e., within the range of $R$ in which the potential energy is negative (see *Figure* 7 as well). When the two atoms are in this region, if a third body collides with them it could take away some of the kinetic energy of this system. The two atoms will then be pushed down into the potential well forming the dimer. The dimer would eventually lose all its kinetic energy, which now would be called vibrational energy as the two atoms bounce back and forth like two balls connected by a spring. Hence, the presence of a third body is essential for forming a dimer from two atoms.

### 4.2 *Rare Gas Homodimers*

Both experimental and theoretical results are now available on all rare gas homo-dimers



*Figure 7. Interatomic potentials for all six noble gas dimers (including radon). The potential energy and distance are given in atomic units: 1 a.u. of energy is 1 Hartree = 627.5 kcal mol$^{-1}$, 1 a.u. for distance is 1 Bohr = 0.529 Å.*
(Figure reproduced with permission from [9])

starting from $He_2$ to $Kr_2$. Investigations on these interesting systems are continuing and so the results presented here are likely to be refined further. However, the results presented here would be typical and one can see that both the inter-atomic distance and binding energy increase as we go from $He_2$ to $Kr_2$. Before the results are presented, it is important to define some parameters. Let us look again at the inter-atomic potential given in *Figure* 6. The distance at which the potential energy is minimum is denoted by $R_e$. This would be the equilibrium distance between the two atoms when the force acting on them is zero, i.e., the first derivative of the potential is zero: $-(\partial V/\partial R) = 0$. Typically, the inter-atomic distance measured in experiments is different from $R_e$. The main reason for this is that even when a dimer is hypothetically cooled to zero Kelvin, there will still be some vibrational energy left in the molecule. This is denoted as zero point vibration and it is shown in *Figure* 6. As mentioned above, vibrational energy is quantized and so one has several vibrational levels within the potential as shown by horizontal lines. As the vibrational energy increases, one can see that the amplitude of vibration increases. The average distance between the two atoms when the dimer is undergoing zero-point vibration is denoted as $R_0$. The two distances $R_0$ and $R_e$ are usually different as the potential is asymmetric, i.e., for a given energy, the two atoms could be stretched to a larger distance from $R_e$ than they could be compressed. In other words $(R_{max} - R_e)$ is usually larger than $(R_{min} - R_e)$, where $R_{max}$ and $R_{min}$ are the maximum and minimum inter-nuclear distance for a given vibrational level. If the dimer is strongly bound, the difference is small and if the dimer is weakly bound, this difference could be large. The second derivative of the potential at $R_e$ is related to the force constant and it is a measure of how strongly bound the dimer is. The second derivative tells us how the slope varies with $R$, i.e., how strongly the potential energy changes with $R$. If it is large, the well would be deep and if it is smaller the well would be shallow.

The inter-nuclear distances and the well depth for all the five rare-gas homo-dimers have been experimentally and theoretically determined now and they are given in *Table* 2 [9]. Let us first consider the equilibrium inter-nuclear distances for the five dimers. It is hardly surprising that they increase from 3.0 Å for $He_2$ to 4.3 Å for $Xe_2$. As discussed earlier, the size of the atoms increases in this order and naturally the inter-nuclear distance increases. The increasing size makes the heavier rare gas atoms more polarizable and the well depth

| Atom | $R_e$ (in Å) | $R_0$ (in Å) | $D_e$ (in cm$^{-1}$) |
|------|------|------|------|
| He | 2.97 | **52±4** | 7.6 |
| Ne | 3.09 | 3.34 | 30 |
| Ar | 3.76 | 3.82 | 100 |
| Kr | 4.01 | 4.06 | 140 |
| Xe | 4.36 | 4.40$^*$ | 197 |

$^*$An estimate based on the difference between $R_e$ and $R_0$ for the other rare gas dimers.

*Table 2. Inter-nuclear distance and well depth of rare-gas homodimers [9].*

also increases from $He_2$ (7 cm$^{-1}$) to $Xe_2$ (197 cm$^{-1}$). The well depth is given in the unit cm$^{-1}$ for these weakly bound dimers and it is commonly known as wave number; 1 kcal mol$^{-1}$ is about 350 cm$^{-1}$. The observed trend in well depth for the noble gas dimers is not surprising either. The trend in $R_0$, however, could be surprising or even shocking at first sight. From $Xe_2$ to $Ne_2$, the trend is reasonable. The difference between $R_e$ and $R_0$ increases from $Xe_2$ (0.04 Å) to $Ne_2$ (0.25 Å). For comparison, the difference between $R_o$ and $R_e$ for the covalently bound molecule HF is much smaller at 0.008 Å [10]. This difference for $He_2$ is about 50 Å!

Clearly, the strongly bound $Xe_2$ has relatively smaller oscillations at the zero point level compared to $Ne_2$ or $He_2$. Remember that the second derivative of the potential is related to the force constant and it determines how strong the bond is and how deep the potential well for a dimer is. For the strongly bound $Xe_2$, the well is narrow and deep and $R_0$ and $R_e$ are close. The potential energies for the five homo-dimers as a function of distance between the two atoms are given in *Figure* 7. The potential given for $He_2$ is very floppy leading to a large difference between $R_e$ and $R_0$. The average distance at the zero point level, $R_0$, is determined to be very long, 52±4 Å [11]! Experimental determination of this distance is not trivial and attempts to form and detect helium dimer will continue. The value given here is from diffraction experiments from a transmission grating. Previous experiments had given an upper limit of 60 Å [12]! Clearly the inter-atomic potential for $He_2$ should be very floppy and the potential shown in *Figure* 4 does not show this clearly as it is plotted on a large scale.

The well depth determines how many vibrational levels could be supported. For a long time, it was believed that the helium dimer had too small a well depth and it would not even support the zero point energy level. However, recent experiments have shown that there is one and only one bound level for helium dimer. It turns out that neon dimer has two levels [13], and for argon dimer, up to five vibrational levels have been experimentally observed [14]. Again, for the covalently bound HF molecule, there are 19 bound vibrational levels. The difference between $Ar_2$ and HF is much more significant than the difference between 5 and 19. This is because the spacing between the vibrational energy levels is much higher for HF compared to $Ar_2$. The binding energy for HF is about 135 kcal mol$^{-1}$ (47250 cm$^{-1}$ compared to 100 cm$^{-1}$ for $Ar_2$). It may be noted that the spacing between the vibrational energy levels decreases as they get closer to the dissociation limit, where it becomes zero.

### 4.3 *Rare Gas Hetero-Dimers*

As for the homo-dimers, experimental and/or theoretical results are available for all the hetero-dimers. The author of this article was involved in experimental determination of the inter-nuclear distance in ArNe [15]. $R_0$ of ArNe was measured to be 3.61 Å and $R_e$ was determined

**Table 3. Inter-nuclear distances $R_e$ and $R_o$ (in Å, first and second entries in every cell) and well depth (in cm$^{-1}$, third entry in every cell) for all rare-gas dimers [9].**

| Atom | He | Ne | Ar | Kr | Xe |
|------|------|------|------|------|------|
| He | 2.97<br>**52±4**<br>7.6 | 3.04<br>-<br>15 | 3.50<br>-<br>21 | 3.70<br>4.25<br>21 | 3.97<br>-<br>20 |
| Ne | | 3.09<br>3.34<br>30 | 3.46<br>3.61<br>46 | 3.65<br>3.76<br>48 | 3.88<br>3.99<br>49 |
| Ar | | | 3.76<br>3.82<br>100 | 3.89<br>3.95<br>117 | 4.09<br>4.14<br>130 |
| Kr | | | | 4.01<br>4.06<br>140 | 4.20<br>4.23<br>163 |
| Xe | | | | | 4.36<br>4.40<br>197 |

with the help of theoretical calculations to be 3.46 Å. Thus, the difference between $R_e$ and $R_0$ for ArNe is 0.15 Å. For the heavier KrXe dimer, this difference is only 0.03 Å and for the HeKr, this difference is 0.55 Å. One can see a very similar trend in well depth and inter-nuclear distance for the noble gas hetero-dimers as was discussed for the homo-dimers. The data for all the homo- and hetero-dimers are given in *Table* 3. One interesting observation is that, the size of Ne appears not much larger than that of He and one can see that RG-He (RG = Ar, Kr and Xe) complexes have R$_e$ larger than RG–Ne complexes. The difference in $R_0$ for KrNe and KrHe is much larger and it is again due to the very large amplitude zero-point vibration of He compared to Ne.

The well depth for the heterodimers follow similar trend as well. However, there are some interesting patterns that are worth pointing out. For RG-He and RG-Ne dimers, the increase in well depth as RG changes from He to Xe is modest. However, for Kr and Xe, as the partner changes from He to Xe, the well depth increases more dramatically. For example, the well-depth is about 20 cm$^{-1}$ for HeAr, HeKr and HeXe. However, for KrAr, Kr$_2$ and KrXe, the well-depths are 130, 163 and 197 cm$^{-1}$, respectively. This is the result of the polarizabilities of the noble gas atoms. Helium is the least polarizable and the binding partner does not make a big difference. Xenon is the most polarizable and for it the polarizability of the other atom affects the well-depth more significantly compared to He-RG dimers.

## 5. Conclusions

In this article, we have discussed all the homo- and hetero-dimers of the five noble-gas atoms He, Ne, Ar, Kr and Xe. All these dimers are bound only by dispersive forces first explained by

London. Though dispersion is an important part of van der Waals interaction, it is commonly assumed to be the only part of van der Waals interaction and these dimers have been usually called van der Waals molecules. In our view, these noble gas clusters should be rightfully called London molecules, a specific category of van der Waals molecules. Noble gas trimers and tetramers have also been investigated recently [16]. These studies provide important input about how the interatomic potentials shown in *Figure* 7 get affected by the presence of a third body. It is crucial to a fundamental understanding of condensed matter. Moreover, in the last decade, a new series of molecules involving rare gases such as HRGX (where RG = He, Ne, Ar, Kr, Xe and X = F, Cl, CN, OH) have been investigated. These molecules also have nearly covalent bonding involving the rare gas atoms and are outside the purview of this article.

## Acknowledgements

## Suggested Reading

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