In this article, Debye’s contributions to understanding van der Waals attractive forces, specifically, dipole–induced dipole interaction, is discussed. The $Rg\cdots HF$ complex structure is influenced by this interaction. Hence, these types of van der Waals molecules can be more specifically called Debye molecules.

I. Introduction

Petrus Josephus Wilhelmus Debye (Peter Joseph Williams Debye) was born on March 24, 1884 in Maastricht, Netherlands, which is 167.5 km from Leiden, where van der Waals was born 37 years earlier [1,2]. Debye had his early education in maths and physics and got a degree in electrical engineering in 1905. Debye was a stellar figure in 20th century physics and is known for several significant contributions, some of which have been named after him. Debye model of heat capacity of solids and Debye–Hückel theory on conductivity of electrolytic solutions are featured in most of the physical chemistry textbooks. However, he won the Nobel Prize in Chemistry in the year 1936 ‘for his contributions to the study of molecular structure’, using dipole moment measurements and X-ray diffraction [1]. He applied the concept of dipole moment to the charge distribution in asymmetric molecules and developed equations relating dipole moments to temperature and dielectric constant. His contribution to understanding dipole moment of a molecule was so enormous that the unit of dipole moment was named Debye. In this article, we will be focusing on Debye’s contributions towards understanding van der Waals forces that bind the van der Waals molecules together.

Keywords
van der Waals forces, dipole-induced dipole interaction, Debye molecules.
2. Debye Interaction

We have discussed the van der Waals equation at length in Part 1 of this series [3].

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

The constant \(a\) was introduced to account for intermolecular attraction though van der Waals did not go into the origin of forces that lead to this attraction. Debye showed a lot of interest in unraveling the nature of intermolecular forces and he played a significant role towards this goal. Debye gave his second series of Baker Lectures on molecular forces at Cornell University in 1961. This series of lectures led to the book titled *Molecular Forces* written by Benjamin Chu [4], who had attended these lectures. In the foreword to this book, Debye points out that discussion on the nature of van der Waals forces started around 1920. While the Coulombic attraction between charges particles was well understood, the attraction between neutral molecules was a puzzle. It was realized that the electrical charge distribution in a molecule need not be spherical even for neutral molecules. Detailed analysis of average electrical field in a neutral molecule led to the determination of dipole, quadrupole and higher moments for neutral molecules [3]. Interestingly, Debye’s first series of Baker Lectures was on determination of molecular structures and he covered both the electrical and geometrical structures. It was realized that not only permanent charges (monopoles), but also dipole and other multipoles present in a neutral molecule could interact with dipole and other multipoles present in another neutral molecule. In any case, it was William Henrik Keesom who derived the expression for dipole-dipole interaction [6], which will be the topic of the next article in the current series. Debye realized that the attraction between two dipoles should vanish at a high enough temperature, in contradiction with experimental observation on many molecules. It was recognized
that the molecules are not rigid electrical structures but are deformable under the influence of an electric field, i.e., the molecules are polarizable. Debye pointed out that the combined influence of the electrical field carried by one molecule and the polarization induced in its partner leads to an additional potential energy proportional to the square of the field. Thus a polar molecule, such as HF, can induce a dipole moment on a non-polar atom such as a rare gas atom 'Rg' (He, Ne, Ar, Kr, and Xe). The interaction between the dipole and induced dipole leads to attraction, i.e., lowering of potential energy, leading to the formation of the Rg•••HF complex.

Debye derived the following expression [6] for the interaction energy due to induced dipole:

$$w(r) = -\frac{\mu_1^2 \alpha_{02} + \mu_2^2 \alpha_{01}}{(4\pi\varepsilon_0 \varepsilon)^2 r^6}.$$  

Here $\mu$ is the dipole moment, $\alpha_0$ is the polarizability, $\varepsilon_0$ is the permittivity in vacuum and $r$ is the distance between the two molecules and subscripts 1 and 2 stand for the first and second molecules. The dipole moment present in molecule 1 will induce a dipole moment in molecule 2 proportional to its polarizability and likewise the dipole moment present in molecule 2 will induce a dipole moment in molecule 1 proportional to its polarizability. If one of the two molecules has zero dipole moment, the numerator in this equation will have only one term. The dipole moment of one molecule could induce a dipole moment in the other molecule in two different ways as shown in Figure 1.

In this article, we will focus on Rg•••HX molecules (Rg = He, Ne, Ar, Kr, and Xe and X = F, Cl, Br, and I), where the HX induces a dipole moment in the Rg atom as shown in Figure 1a. However, the total interaction energy between an Rg atom and an HX molecule will have contributions from this Debye interaction and also London dispersion interaction [7], both of which are attractive. Moreover, as the Rg and HX get closer, there will be repulsion between the electrons in Rg and HX. At some optimum

![Figure 1. Two possibilities for a dipole moment in one molecule to induce a dipole moment in another atom/molecule with a zero dipole moment.](a) (b)
distance between Rg and HX, the attractive and repulsive forces balance leading to a minimum in the potential energy. The interplay between all these forces determine the structure of Rg•••HX complexes, as we shall see in the next section.

3. Rg•••HX Complexes

A complex formed between a rare gas atom and a hydrogen halide molecule offers an ideal example of Debye interaction. The rare gas atoms are neutral with a time-average electric charge distribution that is spherical. All the hydrogen halide molecules do have a dipole moment decreasing in the order HF (1.83 D) > HCl (1.11 D) > HBr (0.83 D) > HI (0.45 D) [8]. Hence, these molecules can and do induce a dipole moment in the rare gas atoms when the two interact. The induced dipole moment is proportional to the inducing field \( E \) and the proportionality constant is the polarizability, i.e., \( \mu_i = \alpha E \). However, as mentioned above, dispersion plays a role in all intermolecular interactions and depending on whether Debye or London interaction dominates, the structure of Rg•••HX would have a global minimum having a Rg•••HX or Rg•••XH geometry. Supersonic beam technique, discussed in detail in the previous article in this series [7] has helped in obtaining information on all these complexes for rare gases He to Xe and for all the hydrogen halides. These complexes have attracted significant attention from chemists and physicists, experimentalists and theoreticians. It is not our intention here to summarize all the work that has been published on these complexes as the literature is vast. Instead, we will focus on a recent article which compares all the Rg•••HX complexes [9].

Without looking at any experimental or theoretical results on these complexes, but based on the dipole moments of HX and the sizes and polarizabilities of Rg atoms [7], we can come to the following conclusions: 1) As the X changes from F to I, the induced dipole moment will reduce, as the dipole moment of HX decreases in this order. 2) As the X changes from F to I, the HX is more polarizable as the size of X increases in this order. 3) As the Rg atom changes from He to Xe, the Rg is more polarizable,
Table 1. Static electrical properties of the rare gas atoms and the hydrogen halides. $\alpha$ is the polarizability, $\mu$ is the dipole moment in units of 'Debye', $D$ (both taken from [8]) and $\Theta$ is the quadrupole moment given in units of $ea_o^2$, where $e$ is the charge of an electron and $a_o$ is the atomic unit for distance approximately equal to 0.529 Å (from [10]). $\Delta\alpha$ refers to the anisotropy in polarizability (from [9]) explained in the text.

<table>
<thead>
<tr>
<th>Rg</th>
<th>$\alpha(\text{Å}^3)$</th>
<th>HX</th>
<th>$\alpha(\text{Å}^3)$</th>
<th>$\Delta\alpha(\text{Å}^3)$</th>
<th>$\mu(D)$</th>
<th>$\Theta(ea_o^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.205</td>
<td>HF</td>
<td>0.80</td>
<td>0.95*</td>
<td>1.83</td>
<td>1.83</td>
</tr>
<tr>
<td>Ne</td>
<td>0.395</td>
<td>HCl</td>
<td>2.70</td>
<td>24.7</td>
<td>1.11</td>
<td>2.73</td>
</tr>
<tr>
<td>Ar</td>
<td>1.641</td>
<td>HBr</td>
<td>3.61</td>
<td>83.6</td>
<td>0.83</td>
<td>3.02</td>
</tr>
<tr>
<td>Kr</td>
<td>2.484</td>
<td>HI</td>
<td>5.40</td>
<td>115.8</td>
<td>0.45</td>
<td>3.30</td>
</tr>
<tr>
<td>Xe</td>
<td>4.044</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 gives the location of the global minimum, whether on H or X side, and the difference in energy between the two minima. As pointed out earlier, both experimental and theoretical works...
Table 2. Depths and locations of minima for Rg•••HX complexes. Each entry lists the location of the global minimum (on H or X side of HX) and the difference in depths (in cm$^{-1}$) between the minima. Two entries for the HBr complexes clearly indicate the difficulty involved in locating the global minimum of these weakly bound complexes. Some scientists determine the Rg•••HBr geometry to be the global minimum while others find Rg•••BrH geometry to be the global minimum. As evident from the numbers, the well depths for these complexes are very small. It may be remembered that 1 kcal mol$^{-1}$ is about 350 cm$^{-1}$. Reproduced from [9] with permission, Copyright [2004], American Institute of Physics.

<table>
<thead>
<tr>
<th>Rg</th>
<th>HF</th>
<th>HCl</th>
<th>HBr</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>H: ~ 4</td>
<td>Cl: 2.0</td>
<td>Br: 6.9</td>
<td>-</td>
</tr>
<tr>
<td>Ne</td>
<td>H: 38</td>
<td>H: 7.4</td>
<td>Br: 13H: 3</td>
<td>I 15</td>
</tr>
<tr>
<td>Ar</td>
<td>H: 100</td>
<td>H: 35</td>
<td>Br: 21H: 5</td>
<td>I: 47</td>
</tr>
<tr>
<td>Kr</td>
<td>H: 160</td>
<td>H: 60</td>
<td>Br: 23H: 11</td>
<td>I: 34</td>
</tr>
<tr>
<td>Xe</td>
<td>H: 210</td>
<td>H: 1.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The contribution from the various forces, such as Debye interaction, London interaction and electron-electron repulsion can be calculated and there are various theoretical approaches available for doing the same [9]. However, as all these forces act simultaneously and they do act in a synergetic way, it is a difficult task to separate out the contribution from these forces. In any case, for the Rg•••HF complexes, it has been shown that the repulsion and dispersion contribute significantly to the overall interaction energy and they nearly cancel each other at all orientations. If these two are the only forces operating, there would be a shallow minimum favoring Rg•••FH geometry. The Debye interaction (induction) energy exhibits strongest anisotropy favoring the Rg•••HF geometry over Rg•••FH geometry. The Rg•••HF geometry is favoured as the H is smaller and the Rg atom can come much closer compared to Rg•••FH geometry as the relatively bigger F does not allow Rg to approach as closely. Hence, these Rg•••HF molecules may be classified as Debye molecules, a
The cover of this issue (reproduced here) shows the structure of two complexes, ethylene-$\text{H}_2\text{O}$ and ethylene-$\text{H}_2\text{S}$. The dipole moment of $\text{H}_2\text{O}/\text{H}_2\text{S}$ can induce a dipole moment in $\text{C}_2\text{H}_4$. The interaction between the dipole moment of $\text{H}_2\text{X}$ and the induced dipole moment in $\text{C}_2\text{H}_4$ leads to an attractive force between the two, contributing to the binding energy of these complexes. This interaction was first suggested by Debye as one component of the attractive forces implied by van der Waals equation. The numbers shown in the figure between the two molecules indicate the distance from the H atom to ethylene pi centre in Å.

As evident from Table 1, the quadrupole moment and polarizability both increase as we go from HF to HI. Quadrupole moment is important for induction as well. However, its contribution is significantly smaller than that from dipole moment. The authors of [9] point out that as we move from Xe•••HF to He•••HI (Table 2), the importance of induction energy decreases. In all $\text{Rg}•••\text{HX}$ complexes, induction would play some role. However, in the HF complexes, they do become structure determining and hence we choose to call the $\text{Rg}•••\text{HF}$ complexes as Debye molecules. Undoubtedly, all $\text{Rg}•••\text{HX}$ complexes are van der Waals molecules.

The Debye (dipole-induced dipole) interaction is also important in complexes formed between ethylene and $\text{H}_2\text{O} \text{HX}$ ($\text{X} = \text{F, Cl, Br, OH, SH}$) as well. The structures of $\text{C}_2\text{H}_4—\text{H}_2\text{O}$ [11] and $\text{C}_2\text{H}_4—\text{H}_2\text{S}$ [12] are explained in Box 1.

5. Conclusion

With his equation, van der Waals showed that there are forces operating between molecules, whether they are in the gas, liquid or solid state. Physicists of early 20th century, particularly
Keesom, Debye and London, showed that these forces originate due to interaction between permanent dipoles (and multipoles), interaction between a permanent dipole and induced dipole, and that between instantaneous dipole, and induced dipole. These forces – Keesom, Debye and London forces – when combined with the electron-electron repulsion account for the van der Waals forces between molecules. While it is simpler to classify a weakly bound complex as a van der Waals molecule, further classification as Debye molecule, Keesom molecule and London molecule is not straightforward. A complex formed from rare gases has inter-atomic forces due only to dispersion and repulsion and can be classified as London molecules [7]. The Rg•••HF complexes have Debye interaction as the structure influencing force, and we classify them as Debye molecules. The next article in this series will discuss molecules that can be classified as Keesom molecules.

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