A researcher in Germany named Driess recently reported a square planar arsonium cation, \([\text{AsR}_4]^+\). Assuming a point group of \(D_{4h}\), use group theory to determine what orbitals may be used for the sigma bonding. From your answer, what kind of hybrid orbitals would be used to make such a molecule according to VBT and how do these compare to the hybrids that you would expect for a normal arsonium cation.

The molecule has \(D_{4h}\) symmetry – note: the first \(C_2\) operation in the character table is the one derived from \(C_4^2\) (this is why there is only one in its class), the \(C_2'\) lies on the As-R bond axis, the \(C_2''\) lies between the As-R bond axes [when applicable, a single prime after a symmetry operation indicates that the symmetry element contains as many atoms as possible, the double prime means that the symmetry element contains fewer atoms].

Dihedral Group Table:

<table>
<thead>
<tr>
<th>(D_{4h})</th>
<th>E</th>
<th>2C_4</th>
<th>C_2</th>
<th>2C_2'</th>
<th>2C_2''</th>
<th>i</th>
<th>2S_4</th>
<th>(\sigma_h)</th>
<th>2(\sigma_v)</th>
<th>2(\sigma_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_{\sigma})</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

The reducible representation \(\Gamma_{\sigma}\) corresponds to the irreducible representation \((A_{1g} + B_{1g} + E_u)\) so the orbitals that may be used for \(\sigma\) bonding are: \(s\) \((A_{1g})\), \(d_{x^2-y^2}\) \((B_{1g})\), and the pair \([p_x, p_y]\) \((E_u)\). Since the central atom is As, these would be from the \(n = 4\) shell (i.e. \(4s\), \(4d_{x^2-y^2}\), \(4p_x\) and \(4p_y\)). This means that the hybridization of the As atom for this planar arsonium cation would be \(sp^3d\). This is obviously very different from all the other arsonium cations, which have tetrahedral structures and \(sp^3\) hybridization. The primary difference is that, because the atoms must all lie in the same plane, you can not mix in the \(4p_z\) orbital (this would make the hybrid orbitals point out of the xy plane) and you have to use an appropriate d orbital that is in the xy plane.

If you had aligned your molecule with the bonds pointing between the x and y axes (on the lines \(x = y\) and \(x = -y\)), you would have had the following reducible representation:

Dihedral Group Table:

<table>
<thead>
<tr>
<th>(D_{4h})</th>
<th>E</th>
<th>2C_4</th>
<th>C_2</th>
<th>2C_2'</th>
<th>2C_2''</th>
<th>i</th>
<th>2S_4</th>
<th>(\sigma_h)</th>
<th>2(\sigma_v)</th>
<th>2(\sigma_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_{\sigma})</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

The reducible representation \(\Gamma_{\sigma}\) corresponds to the irreducible representation \((A_{1g} + B_{2g} + E_u)\) so the orbitals that may be used for \(\sigma\) bonding are: \(s\) \((A_{1g})\), \(d_{xy}\) \((B_{2g})\), and the pair \([p_x, p_y]\) \((E_u)\). In this case, the appropriate d orbital is \(4d_{xy}\), which looks the same as a \(4d_{x^2-y^2}\) orbital that has been rotated by \(45^\circ\).
Question #2
More Bonding

Use group theory to determine what orbitals may be used for (i) the sigma bonding and (ii) the pi bonding in AsF$_5$ in its most stable geometry. Remember to split the pi bonding into axial, equatorial parallel, and equatorial perpendicular components.

(i)

\[
\begin{array}{ccccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\Gamma_\sigma & 5 & 2 & 1 & 3 & 0 & 3
\end{array}
\]

The reducible representation $\Gamma_\sigma$ corresponds to the irreducible representation $(2A_1' + E' + A_2'')$ so the orbitals that may be used for $\sigma$ bonding are: s ($A_1'$), d$_z^2$ ($A_1'$), the pair [p$_x$, p$_y$] (E') and p$_z$ ($A_2''$). Since the central atom is As, these would be from the $n = 4$ shell (i.e. 4s, 4d$_z^2$, 4p$_x$, 4p$_y$ and 4p$_z$). This means that the hybridization of the As atom in this molecule would be sp$^3$d, as you would predict using VBT.

(ii) For $\pi$ bonding, there are three different sets of vectors to consider. These are vectors for: (a) potential $\pi$ bonds perpendicular to the equatorial plane (this is considering one type of potential $\pi$ bonding for the equatorial As-F bonds) $\Gamma_{\text{eq\perp}}$; (b) potential $\pi$ bonds in the equatorial plane (this is considering the other type of potential $\pi$ bonding for the equatorial As-F bonds) $\Gamma_{\text{eq//}}$; and (c) potential $\pi$ bonds to the axial groups (this is considering both types of potential $\pi$ bonding for the axial As-F bonds) $\Gamma_{\text{ax}}$.

\[
\begin{array}{ccccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\Gamma_{\text{eq\perp}} & 3 & 0 & -1 & -3 & 0 & 1
\end{array}
\]

The reducible representation $\Gamma_{\text{eq\perp}}$ corresponds to the irreducible representation $(A_2'' + E'')$ so the orbitals that could be used for $\pi$ bonding perpendicular to the molecular plane are: p$_z$ ($A_2''$) and the pair [d$_{xz}$, d$_{yz}$]. Since the p$_z$ orbital has already been used for sigma bonding, the pair of d orbitals would be the best choice for use in pi bonding.

\[
\begin{array}{ccccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\Gamma_{\text{eq//}} & 3 & 0 & -1 & 3 & 0 & -1
\end{array}
\]

The reducible representation $\Gamma_{\text{eq//}}$ corresponds to the irreducible representation $(A_2' + E')$ so the orbitals that could be used for $\pi$ bonding perpendicular to the molecular plane are the pair [d$_{xy}$, d$_{x^2-y^2}$] (E') because the A$_2'$ representation does not correspond to any orbitals and we have already used the [p$_x$, p$_y$] pair for sigma bonding. Notice that these results are exactly the same as those for the pi bonding in SO$_3$ in your notes.

\[
\begin{array}{ccccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\Gamma_{\text{ax}} & 4 & -2 & 0 & 0 & 0 & 0
\end{array}
\]

The reducible representation $\Gamma_{\text{ax}}$ corresponds to the irreducible representation $(E' + E'')$ so the orbitals that could be used for $\pi$ bonding for the axial bonds are: the pairs [p$_x$, p$_y$] (E' – note that the [d$_{xy}$, d$_{x^2-y^2}$] pair would not be suitable – make a drawing and you will see why) and [d$_{xz}$, d$_{yz}$] (E''). Because we have already used the [p$_x$, p$_y$] pair for sigma bonding, the E'' choice would be the most reasonable. Again, make a drawing of the orbitals and you will see why.

Please note: just because we don’t draw pi bonds in a Lewis structure does not mean that there isn’t pi bonding in a molecule! Symmetry tells us what orbitals we can use to make a pi bond and we have to use our chemical knowledge to determine the nature of the bonding in molecules.
Question #3
Character Tables and Vibrational Spectroscopy

Determine the number of vibrational modes that will be observed in (a) an Infrared experiment and (b) a Raman experiment for hydrazine (H₂N-NH₂) in each of the following conformations - each one has a different point group:

Since the number of atoms \( N = 6 \), you have to find \( 3(6) - 6 = 12 \) vibrational modes in each case.

(a) point group: \( C_{2h} \)

<table>
<thead>
<tr>
<th>( \Gamma_{tot} )</th>
<th>E</th>
<th>( C_2 )</th>
<th>( i )</th>
<th>( \sigma_h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂h</td>
<td>18</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

The reducible representation for all atomic motion \( \Gamma_{tot} \) yields the irreducible representation \( 5A_g + 4B_g + 4A_u + 5B_u \). In \( C_{2h} \), the translational modes have \( A_u \) (z) and \( B_u \) (x or y) symmetry and the rotational modes have \( A_g \) (\( R_z \)) and \( B_g \) (\( R_x \) or \( R_y \)) symmetry. Subtracting the 3 translational \( (A_u + 2B_u) \) and 3 rotational modes \( (A_g + 2B_g) \) leaves the irreducible representation for the vibrational modes \( (4A_g + 2B_g + 3A_u + 3B_u) \), which gives 6 IR active modes \( (3A_u + 3B_u) \) and 6 Raman active modes \( (4A_g + 2B_g) \), so we would expect to see 6 signals in either of the experiments.

(b) point group: \( C_{2v} \)

<table>
<thead>
<tr>
<th>( \Gamma_{tot} )</th>
<th>E</th>
<th>( C_2 )</th>
<th>( \sigma_v )</th>
<th>( \sigma'_v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂v</td>
<td>18</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

The reducible representation for all atomic motion \( \Gamma_{tot} \) yields the irreducible representation \( 5A_1 + 4A_2 + 5B_1 + 4B_2 \). In \( C_{2v} \), the translational modes have \( A_1 \) (z), \( B_1 \) (x) and \( B_2 \) (y) symmetry and the rotational modes have \( A_2 \) (\( R_z \)), \( B_1 \) (\( R_y \)) and \( B_2 \) (\( R_x \)) symmetry. Subtracting the 3 translational and 3 rotational modes leaves the irreducible representation for the vibrational modes \( (4A_1 + 3A_2 + 3B_1 + 2B_2) \), which gives 9 IR active modes \( (4A_1 + 3B_1 + 2B_2) \) and 8 Raman active modes \( (3A_2 + 3B_1 + 2B_2) \), so we would expect to see 9 signals in the IR spectrum and 8 signals in the Raman spectrum.

(c) point group: \( C_2 \)

<table>
<thead>
<tr>
<th>( \Gamma_{tot} )</th>
<th>E</th>
<th>( C_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂</td>
<td>18</td>
<td>0</td>
</tr>
</tbody>
</table>

The reducible representation for all atomic motion \( \Gamma_{tot} \) yields the irreducible representation \( 9A + 9B \). In \( C_2 \), the translational modes have \( A \) (z) and \( B \) (x or y) symmetry and the rotational modes have \( A \) (\( R_z \)) and \( B \) (\( R_x \) or \( R_y \)) symmetry. Subtracting the 3 translational and 3 rotational modes leaves the irreducible representation for the vibrational modes \( (7A + 5B) \), which gives 12 IR active modes \( (7A + 5B) \) and 12 Raman active modes \( (7A + 5B) \), so we would expect to see 12 signals in either of the experiments.

From these results, it is obvious that one can use the number of signals observed experimentally in the vibrational spectra to determine the conformation of \( \text{H}_2\text{N-NH}_2 \).