29 In D_{6h} for $(x_1, y_1, z_1 \ldots x_{12}, y_{12}, z_{12})$

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
$\chi(R)$	36	0	0	0	−4	0	0	0	0	12	0	4

getting the irreducible reps

$2A_{1g} = \frac{48}{48}$	36	−12	+12	+12
$2A_{2g} = \frac{48}{24}$	36	+12	+12	−12
$0B_{1g} = 0$	36	−12	−12	−12
$2B_{2g} = \frac{48}{24}$	36	12	−12	12
$2E_{1g} = \frac{48}{24}$	72	0	−24	6
$4E_{2g} = \frac{96}{24}$	72	0	24	0
$0A_{1u} : \frac{0}{0}$	36	−12	−12	−12
$2A_{2u} : \frac{48}{24}$	36	12	−12	12
$2B_{1u} = \frac{48}{24}$	36	−12	12	12
$2B_{2u}$ $\frac{48}{24}$	36	12	12	−12
$4E_{1u}$ $\frac{96}{24}$	72	0	24	0
$2E_{2u}$ $\frac{48}{24}$	72	0	−24	0

Total irred reps

$2A_{1g}$, $2A_{2g}$, $2B_{2g}$, $2E_{1g}$, $4E_{2g}$, $2A_{2u}$
$2B_{1u}$, $2B_{2u}$, $4E_{1u}$, $2E_{2u}$

Translational: E_{1u}, A_{2u}
Rotational: E_{1g}, A_{2g}

(b)

Vibrational modes = $2A_{1g}$, A_{2g}, $2B_{2g}$, E_{1g}, $4E_{2g}$, A_{2u}, $2B_{1u}$, $2B_{2u}$, $3E_{1u}$, $2E_{2u}$

activity: R N N R R IR N N IR N

(N = neither IR or RAMAN)

(c) in-plane vibrations have $\chi(\sigma_h) = +1, +2$

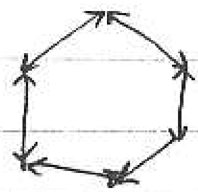
so that the inplane modes are

$2A_{1g}$, A_{2g}, $4E_{2g}$, $2B_{1u}$, $2B_{2u}$, $3E_{1u}$ = 21 modes

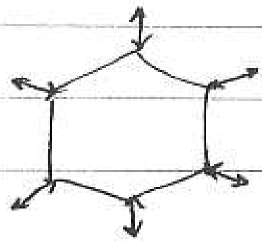
This corresponds to $24 = (12 \times \overset{(x,y)}{2})$ in plane coordinates minus three zero-frequency modes ((x, y) translation and R_z)

The best way to go for determining the in-plane modes is to evaluate the modes arising from C–C and C–H stretches. The in-plane angle bends would then correspond to those remaining in the above (part c) list.

C–C stretch



C–H stretch



D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	σ_h	$3\sigma_d$	3C
$\chi(R)_{C-C}$	6	0	0	0	0	2	0	0	6	2	0
$\chi(R)_{C-H}$	6	0	0	0	2	0	0	0	6	0	2

From C–C $A_{1g}, E_{2g}, B_{2u}, E_{1u}$

From C–H $A_{1g}, E_{2g}, B_{1u}, E_{1u}$

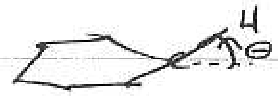
<u>Angular</u> (by looking at "unclaimed in plane")

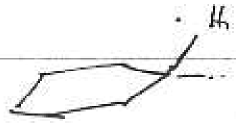
$A_{2g}, 2E_{2g}, B_{1u}, B_{2u}, E_{1u}$

The out-of-plane vibrational "wagging" modes have

$\chi(\sigma_h) = -1, -2$: $2B_{2g}, E_{1g}, A_{2u}, 2E_{2u}$

(these are the $\chi(\sigma_h) = -1, -2$ from list of <u>all</u> normal modes)

To isolate the C–H out-of-plane wagging modes from out-of-plane ring bends, consider the 6 <u>independent angles</u> C–H bonds make with the plane of the molecule 



	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	σ_h	$3\sigma_d$
$\chi(R)$	6	0	0	0	−2	0	0	0	−6	0

B_{2g}, E_{1g}, A_{2u}, E_{2u} result as waggings

[B_{2g}, E_{2u} are ring-bends out-of-plane]