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Fundamentals of Molecular Symmetry ***Exercises***

Week 9/11

9.1 Consider the group $\boldsymbol{D}_{3h}(M)$ with the irreducible representations:

$\boldsymbol{D}_{3h}(M)$	E	(123) (132)	(12) (23) (13)	E^*	$(123)^*$ $(132)^*$	$(12)^*$ $(23)^*$ $(13)^*$
A_1'	1	1	1	1	1	1
A_1''	1	1	1	−1	−1	−1
A_2'	1	1	−1	1	1	−1
A_2''	1	1	−1	−1	−1	1
E'	2	−1	0	2	−1	0
E''	2	−1	0	−2	1	0

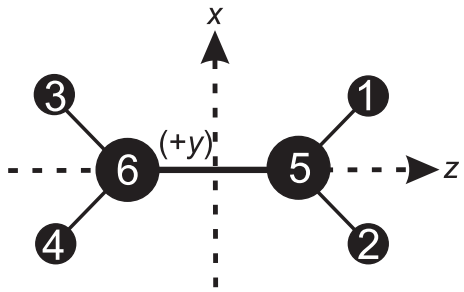
Construct all possible products of the irreducible representations and express the resulting products in terms of the irreducible representations.

9.2 The H_3^+ ion has $\boldsymbol{D}_{3h}(M)$ symmetry (see Problem 9.1 above). Determine, for H_3^+, the selection rules for electric dipole transitions.

9.3 We return to the ethylene molecule C_2H_4 from Problem 7.1. In the absence of tunneling through potential energy barriers its molecular symmetry group is $\boldsymbol{D}_{2h}(M)$ with the character table

$R:$	E	$(12)(34)$	$(13)(24)(56)$	$(14)(23)(56)$	E^*	$(12)(34)^*$	$(13)(24)(56)^*$	$(14)(23)(56)^*$
$A_\mathrm{g}:$	1	1	1	1	1	1	1	1
$A_\mathrm{u}:$	1	1	1	1	−1	−1	−1	−1
$B_{1\mathrm{g}}:$	1	1	−1	−1	−1	−1	1	1
$B_{1\mathrm{u}}:$	1	1	−1	−1	1	1	−1	−1
$B_{2\mathrm{g}}:$	1	−1	1	−1	−1	1	−1	1
$B_{2\mathrm{u}}:$	1	−1	1	−1	1	−1	1	−1
$B_{3\mathrm{g}}:$	1	−1	−1	1	1	−1	−1	1
$B_{3\mathrm{u}}:$	1	−1	−1	1	−1	1	1	−1

The numbering of the nuclei is chosen as shown in the diagram:

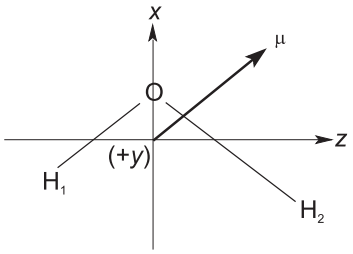


We have introduced a Cartesian, right-handed molecule-fixed axis system xyz for C_2H_4. When the molecule is in its equilibrium configuration, the z axis lies along the C–C bond and points from C_6 towards C_5. The x axis lies in the molecular plane and points towards the protons 1 and 3. Finally, the y axis is perpendicular to the molecular plane and points such that the xyz axis system is right-handed.

When the symmetry operations in the group $\boldsymbol{D}_{2\mathrm{h}}(\mathrm{M})$ are applied to the molecule, the xyz axis system is changed by each of them. Determine, on this background, the transformation properties of the xyz components of the dipole moment $\vec{\mu}$ under the symmetry operations in $\boldsymbol{D}_{2\mathrm{h}}(\mathrm{M})$.

Hint: After you have applied a symmetry operation to the nuclei, determine the new orientations of the axes.

9.4 We showed in the lecture that for the H_2O molecule, the non-vanishing dipole moment components μ_x and μ_z along the molecule-fixed axes have symmetries A_1 and B_2, respectively, in $\boldsymbol{C}_{2v}(M)$. We consider the vibrational wavefunctions Ψ_{vib} from Problem 5.1. Which selection rules result for the quantum numbers v_1, v_2, and v_3 in order that the vibrational matrix element $\langle \Psi''_{vib} | \mu_\alpha | \Psi'_{vib} \rangle \neq 0$, $\alpha = x$ or z?



$\boldsymbol{C}_{2v}(M)$	E	(12)	E^*	$(12)^*$
	1	1	1	1
$\boldsymbol{C}_{2v}$	E	C_2	σ_{ab}	σ_{bc}
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	−1	1
B_2	1	−1	1	−1