

Chapter 12. Linear Molecules

Notes:

- *Most of the material presented in this chapter is taken from Bunker and Jensen (1998), Chap. 17.*

12.1 Rotational Degrees of Freedom

For a linear molecule, it is customary to align the molecule-fixed z -axis with that which joins the different nuclei composing the molecule. It follows that the orientation of the nuclei of the (rigid) molecule is completely specified with only two Euler angles, ϕ and θ , not three as was the case for non-linear molecules. As was discussed in previous chapters, a linear molecule made up of N nuclei will have $3N - 5$ vibration degrees of freedom, as opposed to $3N - 6$ for the general non-linear molecule.

Although it is perfectly feasible to write down a Hamiltonian using only two Euler angles, the absence of a third angle brings a fair amount of complications when the resulting Hamiltonian is compared to that for non-linear molecules, on which we have based everything we developed so far. For example, it is then found that

- The components of the molecule-fixed angular momentum do not obey the “anomalous” commutation relations given in equation (4.70).
- The rotational eigenfunctions are not the same as derived in Chapter 4 (i.e., the kets $|J, k, m\rangle$).
- The rotational Hamiltonian and the associated energies for a linear molecule are more complicated than for a non-linear molecule.

These reasons alone are sufficient to incite us to seek a treatment for linear molecules that would fit within the framework developed for non-linear molecules.

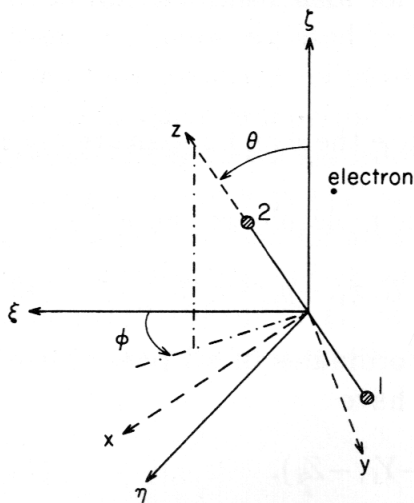


Figure 12-1 – Position of the molecule-fixed axes attached to a diatomic molecule in relation to the space-fixed axes using the two Euler angles ϕ and θ .

12.2 The Isomorphic Hamiltonian

It is found that re-introducing the Euler angle χ in the Hamiltonian and setting it to some arbitrary value resolves the aforementioned difficulties. This new Hamiltonian, called the **isomorphic Hamiltonian**, has one more degree of freedom and more eigenvalues and eigenfunctions. The correct number and set of eigenvalues and eigenfunctions (of the original Hamiltonian) are recovered by setting χ to a constant, which is equivalent to setting its conjugate angular momentum along the molecular axis to zero. Figure 12-2 shows the orientation of the new set of molecule-fixed axes (x' , y' , and z') relative to original set (x , y , and z). In this new coordinate system the components of the angular momentum are

$$\begin{aligned}(\hat{J}_x - \hat{p}_x - \hat{L}_x) &= (\hat{J}'_x - \hat{p}'_x - \hat{L}'_x) \cos(\chi) - (\hat{J}'_y - \hat{p}'_y - \hat{L}'_y) \sin(\chi) \\(\hat{J}_y - \hat{p}_y - \hat{L}_y) &= (\hat{J}'_y - \hat{p}'_y - \hat{L}'_y) \cos(\chi) + (\hat{J}'_x - \hat{p}'_x - \hat{L}'_x) \sin(\chi) \\(\hat{J}_z - \hat{p}_z - \hat{L}_z) &= (\hat{J}'_z - \hat{p}'_z - \hat{L}'_z) = 0,\end{aligned}\tag{12.1}$$

where \hat{J}_i , \hat{p}_i , and \hat{L}_i are the total, vibrational, and electronic orbital angular momenta.

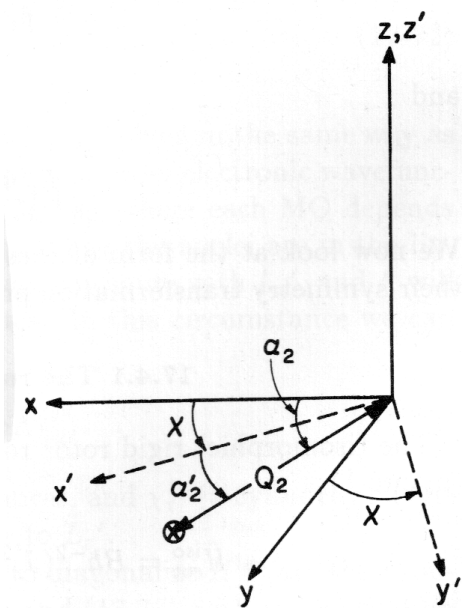


Figure 12-2 – The two sets of molecule-fixed axes. The Euler angle χ relating the two systems of coordinates is arbitrary. Also shown is a two-dimensional (i.e., twice degenerate) bending vibration mode of amplitude Q_2 and angle $\alpha_2 = \chi + \alpha'_2$ in the original Hamiltonian, and of amplitude Q_2 and angle α'_2 in the isomorphic Hamiltonian.

Evidently, the addition of the initially missing Euler angle does not affect the electronic and vibrational isomorphic Hamiltonians, while it transforms the rotational Hamiltonian (where the difficulties reside) into a form that closely resembles that of a prolate symmetric top (with the exception that $A_e = 0$, see equations (4.94) and (4.95)). Accordingly, it becomes possible to set up a general total wave function composed of a product of electronic, vibrational (harmonic oscillator), and rotational (rigid rotor) wave functions. We further have that

$$\begin{aligned}\hat{J}'_z |\Phi_{\text{rot}}\rangle &= k\hbar |\Phi_{\text{rot}}\rangle \\ \hat{p}'_z |\Phi_{\text{vib}}\rangle &= l\hbar |\Phi_{\text{vib}}\rangle \\ \hat{L}'_z |\Phi_{\text{elec}}\rangle &= \Lambda\hbar |\Phi_{\text{elec}}\rangle\end{aligned}\quad (12.2)$$

and in accordance with the last of equations (12.1) we set

$$k = \Lambda + l. \quad (12.3)$$

Focusing on the rotational component (since this is where the difficulties resided with the original Hamiltonian) we have for the isomorphic rigid rotor Hamiltonian (compare with equations (4.94) and (4.95))

$$\begin{aligned}\hat{H}_{\text{rot}}^{\text{iso}} &= B_e (\hat{J}'_x{}^2 + \hat{J}'_y{}^2) \\ &= B_e (\hat{J}'^2 - \hat{J}'_z{}^2),\end{aligned}\quad (12.4)$$

for which the eigenfunctions are those of symmetric tops (see equation (4.86))

$$\Phi_{\text{rot}}^{\text{iso}}(\theta, \phi, \chi) = \frac{1}{\sqrt{2\pi}} \Theta_{jkm}(\theta) e^{im\phi} e^{ik\chi}. \quad (12.5)$$

As was discussed in Chapter 4, linear molecules composed of N atoms (and therefore having $3N - 5$ vibrational degrees of freedom) have $N - 1$ one-dimensional stretching normal modes, and $N - 2$ two-dimensional bending normal modes. The resulting vibrational wave function can be written as (see equations (4.22) and (4.40))

$$\Phi_{\text{vib}}^{\text{iso}} = \Phi_{\nu_1, \dots, \nu_{2N-3}}(Q_1, \dots, Q_{2N-3}) e^{i l_1 \alpha'_1} \dots e^{i l_{N-2} \alpha'_{N-2}}, \quad (12.6)$$

where Q_1 to Q_{N-2} are the amplitudes of the two-dimensional bending modes and Q_{N-1} to Q_{2N-3} for the non-degenerate stretching modes. The $N - 2$ angles α'_j associated with the amplitude Q_j are of the type shown in Figure 12-2. Accordingly, for the second bending mode we have, for example,

$$\alpha'_2 = \alpha_2 - \chi, \quad (12.7)$$

where α_2 is the corresponding angle in the original Hamiltonian. The total vibrational angular momentum about the molecule axis from the second of equations (12.2) is

$$l\hbar = \sum_{j=1}^{N-2} l_j \hbar. \quad (12.8)$$

The last of equations (12.2) implies that \hat{L}'_z commutes with the electronic isomorphic Hamiltonian (i.e., they share the same wave functions), which also means that we can write for the electronic isomorphic wave functions

$$\Phi_{\text{elec}}^{\text{iso}} = \psi_{\text{elec}} e^{i\Lambda\chi'_e}, \quad (12.9)$$

where ψ_{elec} is some function of the electronic coordinates (similar to $\Theta_{jkm}(\theta)$ or $\Phi_{\nu_1, \dots, \nu_{2N-3}}(Q_1, \dots, Q_{2N-3})$, for example), and χ'_e is the conjugate angle for \hat{L}'_z (i.e., defining electronic rotation about the z' -axis). Just as was the case for the degenerate bending modes we have

$$\chi'_e = \chi_e - \chi, \quad (12.10)$$

where χ_e is the corresponding angle in the original Hamiltonian.

The important thing to note is that all three wave functions (i.e., equations (12.5), (12.6), and (12.9)) contain complex exponential that are functions of z' -axis angles. The full rovibronic wave function is, of course, the product of these functions and is subjected to equations (12.2) and (12.3).

12.3 The MS Groups of Linear Molecules

The only two possible MS groups for linear molecules are $D_{\infty h}(\text{M})$ for centrosymmetric molecules (e.g., H_2 , CO_2) and $C_{\infty v}(\text{M})$ for non-centrosymmetric molecules (e.g., CO , HCN). The $C_{\infty v}(\text{M})$ group contains only the E and E^* , while $D_{\infty h}(\text{M})$ contains the four elements $E, (p), E^*$, and $(p)^*$, where (p) is the permutation of all pairs of identical nuclei located symmetrically about the nuclear centre of mass. The corresponding character tables are given in Table 12-1 and Table 12-2 (for CO_2).

Table 12-1 – The character table for the $C_{\infty v}(\text{M})$ group.

$C_{\infty v}(\text{M})$:	E	E^*
$\Sigma^+, +$:	1	1
$\Sigma^-, -$:	1	-1

$:\Gamma(\mu_A)$

Table 12-2 – The character table for the $D_{\infty h}(\text{M})$ group of CO_2 , with the labels associated to the oxygen nuclei.

$D_{\infty h}(\text{M}):$	E	(12)	E^*	$(12)^*$	
$\Sigma_g^+, +s:$	1	1	1	1	
$\Sigma_u^+, +a:$	1	-1	1	-1	
$\Sigma_g^-, -a:$	1	-1	-1	1	
$\Sigma_u^-, -s:$	1	1	-1	-1	$:\Gamma(\mu_A)$

As can be inferred from Table 12-1 the two irreducible representations of $C_{\infty v}(\text{M})$ (i.e., Σ^\pm) are labeled according to their parity, i.e., their character under E^* . For the $D_{\infty h}(\text{M})$ group Table 12-2 shows that the four irreducible representations are labeled +s (or Σ_g^+), +a (or Σ_u^+), -s (or Σ_g^-), and -a (or Σ_u^-), where the ‘ \pm ’ sign is set by the parity (i.e., their character under E^*), the ‘s’ or ‘a’ by the character under (p) , and the ‘g’ or ‘u’ by the character under $(p)^*$.

12.3.1 The Symmetry Classification of the Wave Functions under the MS Groups

The isomorphic rovibronic wave functions are obtained by the product of equations (12.5), (12.6), and (12.9). If we focus on HCN or CO_2 as examples, we then have

$$\begin{aligned}\Phi_{\text{rve}}^{\text{iso}} &= \frac{1}{\sqrt{2\pi}} \Theta_{jkm}(\theta) \Phi_{v_1, v_2, v_3}(Q_1, Q_2, Q_3) \psi_{\text{elec}} e^{im\phi} e^{ik\chi} e^{i\alpha_2'} e^{i\Lambda\chi_e'} \\ &= \frac{1}{\sqrt{2\pi}} \Theta_{jkm}(\theta) \Phi_{v_1, v_2, v_3}(Q_1, Q_2, Q_3) \psi_{\text{elec}} e^{im\phi} e^{i\alpha_2} e^{i\Lambda\chi_e},\end{aligned}\tag{12.11}$$

where the label ‘2’ was chosen for the bending mode and equations (12.3), (12.7), and (12.10) were used to get the last equation. The last relation can easily be classified within the appropriate MS group since any dependency on the arbitrary Euler angle χ has disappeared. It is in fact the case that $\Phi_{\text{rve}}^{\text{iso}}$ is only a function of $\theta, \phi, \alpha_2, Q_1, Q_2, Q_3$, and the electronics coordinates. These all have very well defined transformation properties under the respective elements of the $C_{\infty v}(\text{M})$ and $D_{\infty h}(\text{M})$ groups. More precisely, we have for the angular transformations

$$\begin{aligned}E^*(\theta, \phi) &\rightarrow (\pi - \theta, \phi + \pi) \\ E^*\alpha_2 &\rightarrow \pi - \alpha_2 \\ E^*\chi_e &\rightarrow \pi - \chi_e.\end{aligned}\tag{12.12}$$

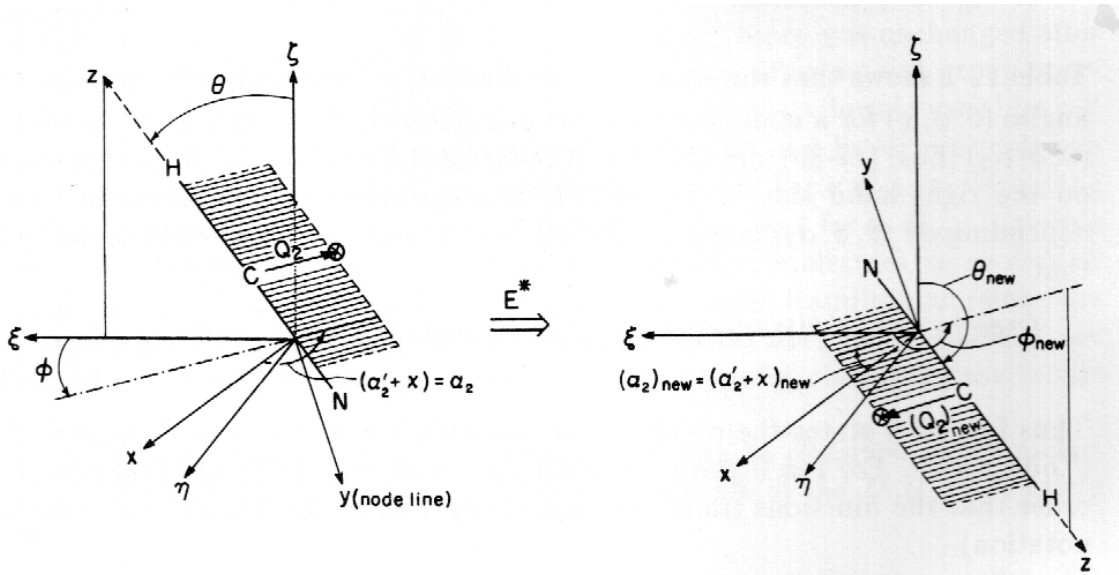


Figure 12-3 – Transformation of the Euler angles ϕ and θ and α_2 under the effect of E^* .

These transformations are determined in the same manner as was done in Chapter 9, and can be verified through Figure 12-3 (χ_e is similar in nature to α_2 and therefore transforms in the same manner). For the normal coordinates we find that

$$E^*(Q_1, Q_2, Q_3) \rightarrow (Q_1, Q_2, Q_3), \quad (12.13)$$

as Q_1 and Q_3 are stretching modes along the z -axis and are therefore unchanged, as is Q_2 since it is a vibration amplitude and therefore unsigned. The other electronic coordinates (beside χ_e) and orbitals will transform as shown in Chapter 9.

For the $D_{\infty h}(M)$ group of centro-symmetric molecules we must then augment equations (12.12) with

$$\begin{aligned} (p)(\theta, \phi, \alpha_i) &\rightarrow (\pi - \theta, \phi + \pi, -\alpha_i) \\ (p)^*(\theta, \phi, \alpha_i) &\rightarrow (\theta, \phi, \alpha_i + \pi). \end{aligned} \quad (12.14)$$

As an example, let us we set $\Lambda = 0$ for the electronic ground state, then $k = l$ and the isomorphic rovibrational wave function is

$$\Phi_{rv}^{\text{iso}} = \frac{1}{\sqrt{2\pi}} \Theta_{jlm}(\theta) \Phi_{v_1, v_2, v_3}(Q_1, Q_2, Q_3) e^{im\phi} e^{il\alpha_2}. \quad (12.15)$$

This wave function (or associated ket) can then be symmetry-classified using equations (12.15), (12.12), and (12.14). If we define the ket corresponding to the Φ_{rv}^{iso} wave functions with $|J, l, m, v_1, v_2, v_3\rangle$ we then have

$$\begin{aligned}
 E|J, l, m, v_1, v_2, v_3\rangle &= |J, l, m, v_1, v_2, v_3\rangle \\
 E^*|J, l, m, v_1, v_2, v_3\rangle &= (-1)^{J+l} |J, -l, m, v_1, v_2, v_3\rangle \\
 (p)|J, l, m, v_1, v_2, v_3\rangle &= (-1)^J |J, -l, m, v_1, v_2, v_3\rangle \\
 (p)^*|J, l, m, v_1, v_2, v_3\rangle &= (-1)^l |J, l, m, v_1, v_2, v_3\rangle.
 \end{aligned} \tag{12.16}$$

[NB: These relations were determined using Table 9-3 and equations (9.66), with the realization that if we substitute in them $l \rightarrow k$ and $\alpha_2 \rightarrow \chi$ we find the following correspondences

$$\begin{aligned}
 E &\rightarrow R^0 \\
 E^* &\rightarrow R_{\pi/2}^\pi \\
 (p) &\rightarrow R_0^\pi \\
 (p)^* &\rightarrow R_z^\pi,
 \end{aligned} \tag{12.17}$$

using the definitions for R_α^π and R_z^β given in Chapter 9.]

It follows from equations (12.16) that for HCN (i.e., $C_{\infty v}(\mathbf{M})$)

$$\begin{aligned}
 |\Phi_{rv}^+\rangle &= \begin{cases} |J_{\text{even}}, 0, m, v_1, v_2, v_3\rangle, & l = 0 \\ \frac{1}{\sqrt{2}} [|J, |l|, m, v_1, v_2, v_3\rangle + |J, -|l|, m, v_1, v_2, v_3\rangle], & l \neq 0 \end{cases} \\
 |\Phi_{rv}^-\rangle &= \begin{cases} |J_{\text{odd}}, 0, m, v_1, v_2, v_3\rangle, & l = 0 \\ \frac{1}{\sqrt{2}} [|J, |l|, m, v_1, v_2, v_3\rangle - |J, -|l|, m, v_1, v_2, v_3\rangle], & l \neq 0. \end{cases}
 \end{aligned} \tag{12.18}$$

For CO_2 (i.e., $D_{\infty h}(\mathbf{M})$) we have for $l = 0$

$$\begin{aligned}
 |\Phi_{rv}^{+s}\rangle &= |J_{\text{even}}, 0, m, v_1, v_2, v_3\rangle \\
 |\Phi_{rv}^{-a}\rangle &= |J_{\text{odd}}, 0, m, v_1, v_2, v_3\rangle,
 \end{aligned} \tag{12.19}$$

while for $|l| \neq 0$

$$\begin{aligned}
|\Phi_{rv}^{+s}\rangle &= \frac{1}{\sqrt{2}} \left[|J_{\text{even}}, |l|_{\text{even}}, m, v_1, v_2, v_3\rangle + |J_{\text{even}}, -|l|_{\text{even}}, m, v_1, v_2, v_3\rangle \right] \\
|\Phi_{rv}^{+a}\rangle &= \frac{1}{\sqrt{2}} \left[|J_{\text{even}}, |l|_{\text{odd}}, m, v_1, v_2, v_3\rangle + |J_{\text{even}}, -|l|_{\text{odd}}, m, v_1, v_2, v_3\rangle \right] \\
|\Phi_{rv}^{-a}\rangle &= \frac{1}{\sqrt{2}} \left[|J_{\text{odd}}, |l|_{\text{even}}, m, v_1, v_2, v_3\rangle + |J_{\text{odd}}, -|l|_{\text{even}}, m, v_1, v_2, v_3\rangle \right] \\
|\Phi_{rv}^{-s}\rangle &= \frac{1}{\sqrt{2}} \left[|J_{\text{odd}}, |l|_{\text{odd}}, m, v_1, v_2, v_3\rangle + |J_{\text{odd}}, -|l|_{\text{odd}}, m, v_1, v_2, v_3\rangle \right].
\end{aligned} \tag{12.20}$$

Although this symmetry classification procedure works well for the rovibronic and rovibrational wave functions, it fails, however, when we consider the rotational and vibrational wave functions separately. This is because both equations (12.5) and (12.6) are dependent on the arbitrary Euler angle χ (remember equation (12.7)). The problem resides in the fact that there is no unique way to determine how this arbitrary angle transforms under the elements of the MS groups of linear molecules. Accordingly, it follows that we cannot specify the transformation of these wave functions and, therefore, their symmetry classifications within these MS groups.

12.4 The Extended MS Groups of Linear Molecules

Although we just saw that the MS group cannot be used to determine the symmetry of rotational or vibrational wave functions, it has been known for a long time that the point groups of linear molecules ($C_{\infty v}$ and $D_{\infty h}$) can be used for the vibrational problem. Returning to our isomorphic formulation of the problem, we will now see that these groups will also work well for the vibronic portion.

Considering once again HCN and CO_2 as examples we have

$$\begin{aligned}
\Phi_{ve}^{\text{iso}} &= \Phi_{v_1, v_2, v_3}(Q_1, Q_2, Q_3) \psi_{\text{elec}} e^{i l_1 \alpha'_2} e^{i \Lambda \chi'_c} \\
&= \Phi_{v_1, v_2, v_3}(Q_1, Q_2, Q_3) \psi_{\text{elec}} e^{-i k \chi} e^{i l \alpha_2} e^{i \Lambda \chi_c},
\end{aligned} \tag{12.21}$$

where the dependency on χ is made explicit. But since we know from our discussion in Chapter 6 that dealt with the relationship between the MS and point groups that the latter leaves the molecule-fixed axes (and the Euler angles) unchanged, it follows that the α'_2 and χ'_c vibronic angles have very well defined transformation properties within the point groups (see equations (12.24) below). As a result vibrational and electronic, as well as vibronic, wave functions are readily classified with the point groups.

The different elements that can compose these point groups are as follows:

- C_{∞}^{ε} , a right-handed rotation of the vibronic variables about the z' -axis through an angle ε . There is an infinite number of such rotations, note that $E = C_{\infty}^0$.
- $C_2^{\varepsilon/2}$, a two-fold rotation of the vibronic variables about an axis that makes an angle (right-handed) of $\varepsilon/2$ relative to the x' -axis. There are two such rotations for each value of ε .

- $\sigma_v^{\varepsilon/2}$, a reflection about a plane containing the z' -axis and another that makes an angle (right-handed) of $\varepsilon/2$ relative to the x' -axis.
- S_∞^ε , an improper rotation that is the product of C_∞^ε and σ_h , the plane perpendicular to the molecular axis (i.e., the z' -axis). There is an infinite number of such improper rotations, note that $S_\infty^0 = \sigma_h$ and $S_\infty^\pi = i$.

All of these elements are present in $D_{\infty h}$, while $C_2^{\varepsilon/2}$ and S_∞^ε do not occur in $C_{\infty v}$.

Correspondingly, we introduce the so-called **extended MS groups** $C_{\infty v}(\text{EM})$ and $D_{\infty h}(\text{EM})$ for which the character tables are given in Table 12-3 and Table 12-4. Each element composing these groups is chosen as to correspond to one (and only one) point group element. More precisely, we have

$$\begin{aligned}
 E &\rightarrow E \\
 E_\varepsilon &\rightarrow C_\infty^\varepsilon \\
 (p)_\varepsilon &\rightarrow C_2^{\varepsilon/2} \\
 E_\varepsilon^* &\rightarrow \sigma_v^{\varepsilon/2} \\
 (p)_{\pi+\varepsilon}^* &\rightarrow S_\infty^{\pi+\varepsilon}.
 \end{aligned} \tag{12.22}$$

The elements $(p)_\varepsilon$ and $(p)_{\pi+\varepsilon}^*$ are not part of $C_{\infty v}(\text{EM})$. In equations (12.22), as well as in Table 12-3 and Table 12-4, we have $0 \leq \varepsilon \leq 2\pi$ but independently for each operator.

The main idea in introducing these groups is to combine the power of the MS groups for the classification of rovibronic wave functions with that of the point groups for the vibronic wave functions.

Table 12-3 – The character table for the $C_{\infty v}(\text{EM})$ group (e.g., HCN), with the z -axis along the molecular axis.

$C_{\infty v}(\text{EM})$:	E_0	E_ε	...	∞E_ε^*	
	1	2	...	∞	
$C_{\infty v}$:	E	$2C_\infty^\varepsilon$...	$\infty \sigma_v^{\varepsilon/2}$	
R_{tot} :	R^0	$R_z^{-\varepsilon}$...	$R_{(\pi+\varepsilon)/2}^\pi$	
$(+)\Sigma^+$:	1	1	...	1	$:T_z$
$(-)\Sigma^-$:	1	1	...	-1	$:\hat{J}_z, \Gamma(\mu_A)$
Π :	2	$2\cos(\varepsilon)$...	0	$:(T_x, T_y), (\hat{J}_x, \hat{J}_y)$
Δ :	2	$2\cos(2\varepsilon)$...	0	
\vdots	\vdots	\vdots	...	\vdots	

Table 12-4 – The character table for the $D_{\infty h}$ (EM) group for CO_2 , with the z -axis along the molecular axis.

$D_{\infty h}$ (EM):	E_0	E_ε	...	∞E_ε^*	$(12)_\pi^*$	$(12)_{\pi+\varepsilon}^*$...	$\infty(12)_\varepsilon$	
	1	2	...	∞	1	2	...	∞	
$D_{\infty h}$:	E	$2C_\infty^\varepsilon$...	$\infty\sigma_v^{\varepsilon/2}$	i	$2S_\infty^{\pi+\varepsilon}$...	$\infty C_2^{\varepsilon/2}$	
R_{rot} :	R^0	$R_z^{-\varepsilon}$...	$R_{(\pi+\varepsilon)/2}^\pi$	R^0	$R_z^{-\varepsilon}$...	$R_{\varepsilon/2}^\pi$	
$(+s)\Sigma_g^+$:	1	1	...	1	1	1	...	1	
$(+a)\Sigma_u^+$:	1	1	...	1	-1	-1	...	-1	$:T_z$
$(-a)\Sigma_g^-$:	1	1	...	-1	1	1	...	-1	$:\hat{J}_z$
$(-s)\Sigma_u^-$:	1	1	...	-1	-1	-1	...	1	$:\Gamma(\mu_A)$
Π_g :	2	$2\cos(\varepsilon)$...	0	2	$2\cos(\varepsilon)$...	0	$:(\hat{J}_x, \hat{J}_y)$
Π_u :	2	$2\cos(\varepsilon)$...	0	-2	$-2\cos(\varepsilon)$...	0	$:(T_x, T_y)$
Δ_g :	2	$2\cos(2\varepsilon)$...	0	2	$2\cos(2\varepsilon)$...	0	
Δ_u :	2	$2\cos(2\varepsilon)$...	0	-2	$-2\cos(2\varepsilon)$...	0	
\vdots	\vdots	\vdots	...	\vdots	\vdots	\vdots	...	\vdots	

Accordingly, the EM elements are defined such that a given operator O_ε has *i*) the same effect on the nuclear and electronic space-fixed coordinates and the θ and ϕ Euler angles as O in the MS group, and *ii*) transform the Euler angle χ as follows

$$\begin{aligned}
 E_\varepsilon \chi &= \chi - \varepsilon \\
 (p)_\varepsilon \chi &= 2\pi - \chi - \varepsilon \\
 E_\varepsilon^* \chi &= \pi - \chi - \varepsilon \\
 (p)_{\pi+\varepsilon}^* \chi &= \chi - \varepsilon,
 \end{aligned}
 \tag{12.23}$$

as can be verified from the equivalent rotations R_{rot} listed in Table 12-3 and Table 12-4 and Table 9-3. The transformations of the vibronic angles $\alpha'_i (= \alpha_i - \chi)$ and $\chi'_e (= \chi_e - \chi)$ follow from the effects of the point group elements with

$$\begin{aligned}
 E_\varepsilon \alpha'_i &= C_\infty^\varepsilon \alpha'_i = \alpha'_i + \varepsilon \\
 (p)_\varepsilon \alpha'_i &= C_2^{\varepsilon/2} \alpha'_i = -\alpha'_i + \varepsilon \\
 E_\varepsilon^* \alpha'_i &= \sigma_v^{\varepsilon/2} \alpha'_i = -\alpha'_i + \varepsilon \\
 (p)_{\pi+\varepsilon}^* \alpha'_i &= S_\infty^{\pi+\varepsilon} \alpha'_i = \pi + \alpha'_i + \varepsilon,
 \end{aligned}
 \tag{12.24}$$

as can be readily deduced from Figure 12-2 (χ'_e behaves the same way as α'_i). If we define the vibrational wave functions for the two-dimensional bending mode of HCN or CO₂ with $|v_2, l\rangle$ we have (using the relevant part of equation (12.21))

$$\begin{aligned}
 E_\varepsilon |v_2, l\rangle &= e^{il\varepsilon} |v_2, l\rangle \\
 (p)_\varepsilon |v_2, l\rangle &= e^{il\varepsilon} |v_2, -l\rangle \\
 E_\varepsilon^* |v_2, l\rangle &= e^{il\varepsilon} |v_2, -l\rangle \\
 (p)_{\pi+\varepsilon}^* |v_2, l\rangle &= (-1)^l e^{il\varepsilon} |v_2, l\rangle.
 \end{aligned}
 \tag{12.25}$$

It follows that a pair $(|v_2, l\rangle, |v_2, -l\rangle)$ transform into one another and the associated irreducible species for CO₂ are as given in Table 12-5. The one-dimensional stretching modes are totally symmetric for the reason stated when studying the MS groups.

The classification of the rotational wave functions is done in exactly the same way as was shown in Chapter 9 for non-linear molecules. That is, one simply has to use the equivalent rotations listed in the EM groups and use equations (9.66). We then have

$$\begin{aligned}
 E_\varepsilon |J, k, m\rangle &= R_z^{-\varepsilon} |J, k, m\rangle = e^{-ik\varepsilon} |J, k, m\rangle \\
 (p)_\varepsilon |J, k, m\rangle &= R_{\varepsilon/2}^\pi |J, k, m\rangle = (-1)^J e^{-ik\varepsilon} |J, -k, m\rangle \\
 E_\varepsilon^* |J, k, m\rangle &= R_{(\pi+\varepsilon)/2}^\pi |J, k, m\rangle = (-1)^{J+k} e^{-ik\varepsilon} |J, -k, m\rangle \\
 (p)_{\pi+\varepsilon}^* |J, k, m\rangle &= R_z^{-\varepsilon} |J, k, m\rangle = e^{-ik\varepsilon} |J, k, m\rangle.
 \end{aligned}
 \tag{12.26}$$

Similarly as for the bending mode, the pair $(|J, k, m\rangle, |J, -k, m\rangle)$ transform into one another and the associated irreducible species for CO₂ are as given in Table 12-6.

Table 12-5 – The irreducible species of associated to the two-dimensional bending mode of CO₂. The results for HCN in $C_{\infty v}$ (EM) are obtained by omitting the ‘g’ and ‘u’ subscripts.

l	$\Gamma(v_2, l\rangle)$
0	Σ_g^+
± 1	Π_u
± 2	Δ_g
± 3	Φ_u
\vdots	\vdots

Table 12-6 – The irreducible species of associated to the rotational wave functions of CO_2 . The results for HCN in $C_{\infty v}$ (EM) are obtained by omitting the ‘g’ subscripts.

k	$\Gamma(J, k, m\rangle)$
0	$\left\{ \begin{array}{ll} J_{\text{even}}, & \Sigma_g^+ \\ J_{\text{odd}}, & \Sigma_g^- \end{array} \right.$
± 1	Π_g
± 2	Δ_g
± 3	Φ_g
\vdots	\vdots