Symmetry and Spectroscopy

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1 Physical background

We are interested in electric transitions in molecules. Initially the molecule is in a state Ψ_i which is a solution to the Schrödinger equation with the Hamiltonian H_0. If we introduce a radiation field, there can be a transition to some final state Ψ_f. The radiation field can be treated as a perturbation to H_0 giving a new Hamiltonian

$$H = H_0 + H_1 \tag{1}$$

where

$$H_1 = \frac{e}{2m}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2}{2m}A^2 \tag{2}$$

$\frac{e^2}{2m}A^2$ corresponds to two-photon processes and can be neglected in the following. Since we are interested in electronic radiation, the $\mathbf{A}$ field can be written as a superposition of harmonic waves

$$\mathbf{A} = \mathbf{A}_0 e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})} + \mathbf{A}_0 e^{-i(\omega t - \mathbf{k}\cdot\mathbf{r})} \tag{3}$$

Using the coulomb gauge $\nabla\cdot\mathbf{A} = 0$ and equation 3, equation 2 can be written as

$$H_1 = \frac{e}{m}\mathbf{A}_0\cdot\mathbf{p}\left(e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})} + e^{-i(\omega t - \mathbf{k}\cdot\mathbf{r})}\right) \tag{4}$$

The wave function with this Hamiltonian can be written as a linear combination of the initial and final states

$$\Psi(\mathbf{r},t) = a(t)_i\Psi_i(\mathbf{r},t) + a(t)_f\Psi_f(\mathbf{r},t) \tag{5}$$

Using first order perturbation theory it can be shown that the probability to find the molecule in the final state is

$$|a_f(t)|^2 = \left(\frac{e}{m\hbar}\right)\left|\left\langle f\left|\mathbf{A}_0\cdot\mathbf{p}e^{i\mathbf{k}\cdot\mathbf{r}}\right|i\right\rangle\right|^2 \frac{\sin^2\frac{(\omega_{fi}-\omega)t}{2}}{\left[\frac{(\omega_{fi}-\omega)}{2}\right]^2} \tag{6}$$

where ω_{fi} is the difference in frequency between initial and final state. From a group theoretical point of view, the interesting part of this relation is the matrix element

$$\left\langle f \left| \mathbf{A}_0 \cdot \mathbf{p} e^{i\mathbf{k}\cdot\mathbf{r}} \right| i \right\rangle \tag{7}$$

since it is possible to make selection rules for allowed transitions from symmetry considerations. Performing a Taylor expansion of the exponential factor gives

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k}\cdot\mathbf{r} + \ldots$$

The first order approximation is to assume that $i\mathbf{k}\cdot\mathbf{r}$ is small and therefore $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$. This corresponds to the electronic dipole transition. With radiation incident in the x-direction, we get

$$\langle f \left| p_x \right| i \rangle = \frac{im}{\hbar} \left\langle f \left| H^0 x - x H^0 \right| i \right\rangle = \frac{im}{\hbar} \langle f \left| x(E_f - E_i) \right| i \rangle \tag{8}$$

For higher order transitions, more terms are included from the expansion. The next step is to include $i\mathbf{k}\cdot\mathbf{r}$. Again with radiation incident in the x-direction and polarised in y direction, this gives the squared matrix element

$$\left| \langle f \left| \mathbf{A}_0 \cdot \mathbf{p}(1 + i\mathbf{k}\cdot\mathbf{r}) \right| i \rangle \right|^2 = \left| \langle f \left| A_0 p_y \left(1 + ikx\right) \right| i \rangle \right|^2 \tag{9}$$

Using $\hbar l_z = x p_y - p_x y$, we can write

$$x p_y = \frac{\hbar}{2} l_z + \frac{1}{2}(x p_y + p_x y) \tag{10}$$

Neglecting the dipole contribution from eq. 9, and ignoring all constants, the matrix element looks like

$$\langle f \left| p_y x \right| i \rangle = \frac{1}{2} \left(\langle f \left| \hbar l_z \right| \rangle + \langle f \left| (x p_y + p_x y) \right| i \rangle \right) \tag{11}$$

The first term here corresponds to the magnetic dipole contribution. Using

$$x p_y = \frac{1}{2} m \frac{i}{\hbar} (H_0 x y - x y H_0) \tag{12}$$

the second term can be rewritten as to the form

$$\langle f \left| xy \right| i \rangle \tag{13}$$

The second term is called the electric quadrupole term.

2 Selection rules

From eq. 8, it can be seen that the electric dipole moment transforms like coordinates (x,y,z). (it transforms like a polar vector). For example, consider a rotation of angle φ around the z-axis

$$\Gamma^V(\varphi) = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{14}$$

This gives the character of the transformation

$$\chi^V(\varphi) = 1 + 2\cos\varphi \tag{15}$$

If this is combined with an inversion, there is a sign change

$$\Gamma^V(\varphi) = \begin{pmatrix} -\cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & -\cos\varphi & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{16}$$

This causes the character to change sign as well

$$\chi^V(\varphi, i) = -(1 + 2\cos\varphi) \tag{17}$$

For the magnetic dipole moment, it will instead transform like rotations (an axial vector). Since they are invariant under inversion the transformation matrix will look like eq. 14 for both proper and improper rotations. Hence the character of the magnetic dipole moment operator will always be

$$\chi^A(\varphi) = 1 + 2\cos\varphi \tag{18}$$

To to illustrate how the coordinates transform, let us use C_{3v} as an example. The character table of C_{3v} looks like

C$_{3v}$	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	R_z
E	2	-1	0	$(x,y),(R_x,R_y)$

let us first check how each operator changes the vector r

$$\begin{aligned} P_E \begin{pmatrix} x \\ y \\ z \end{pmatrix} &= \begin{pmatrix} x \\ y \\ z \end{pmatrix} \\ P_{C_3} \begin{pmatrix} x \\ y \\ z \end{pmatrix} &= \begin{pmatrix} -\frac{x}{2} + \frac{\sqrt{3}y}{2} \\ -\frac{\sqrt{3}x}{2} - \frac{y}{2} \\ z \end{pmatrix} \\ P_{\sigma_v} \begin{pmatrix} x \\ y \\ z \end{pmatrix} &= \begin{pmatrix} x \\ -y \\ z \end{pmatrix} \end{aligned} \tag{19}$$

First, to study how the z component transforms, we have that every operation performed on the group will leave the z component intact. Hence, the character of every transform on the z component is 1. If we look at the character table, the representation A_1 also has all characters equal to 1. This means that this the z component transforms as A_1. Since the x and y component are coupled to each other, we study them together. If we apply the unit operator on x and y, the character will be 2, since it is a 2x2 unit matrix. For C_3, we have that the character of x and y is -1, and for σ_v, the character is zero. If we match this with the character table, we find that x and y transforms in the same way as E.

We know that magnetic dipole transitions transforms as rotations. We also know that for electronic dipole transitions, the character changes sign when there is an inversion involved, but for magnetic dipole transitions, the character is the same. This leads to the conclusion that if the group contains no inversions, the electronic and the magnetic transitions will correspond to the same representation, however, when there are inversions involved, electronic and magnetic dipole transitions will be different. We also know that for elements that involve an inversion, the character for the magnetic dipole transition for this element will be opposite to that of the electronic dipole transition. To take C_{3v} as an example, we know that the electronic dipole transition in the z component has character 1 for all operations. We also know that the element σ_v involves an inversion. Hence, the character of the magnetic dipole transition is opposite that of the electronic one, i.e. -1. This leads to the conclusion that the magnetic dipole transition in z direction belongs to A_2 while electronic dipole moment transitions belongs to A_1. For the x and y components, the character for σ_v is 0, therefore, both belong to the same irreducible representation.

Looking again at eq. 7 the initial and final states must transform like irreducible representations of the group. As was just shown, the electric and magnet moments also transform like irreducible representations. Thus the orthogonality relations for irreducible representations can be used to see if the matrix element can be nonzero. This can only happen if the representation for the initial state can be found in the direct product of the representations of the operator and the final state

$$\langle \Gamma_i \, |\Gamma_T| \, \Gamma_f \rangle = \langle \Gamma_i | \Gamma_T \otimes \Gamma_f \rangle \neq 0 \tag{20}$$

The direct product can be decomposed into a sum of irreducible representations using the following relation

$$(\gamma\beta|\alpha) = \frac{1}{g} \sum_{classes} r_a \chi^{\beta}(K_a) \chi^{\gamma}(K_a) \chi^{\alpha}(K_a)^* \tag{21}$$

For example in C_{3v} the direct product table will look like this

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	$A_1 + A_2 + E$

Looking at electric dipole transitions, when the radiation is polarised in the z-direction the electric dipole moment will transform like A_1. This means that transitions can only occur between states with the same symmetry since the product of A_1 with another representation will just give back the representation. However when the radiation is polarised in the x or y direction the dipole moment will transform like E leading to the conclusion that if the initial state transform like A_1 or A_2 the final state must transform like E. But if the initial state is E the final state can be any of the irreducible representations. For the magnetic transitions, when the radiation is polarised in the x or y direction, the allowed transitions is the same, since both transforms like E. However, when the radiation is polarised in the z-direction, the magnetic dipole moment transforms like A_2. This will allow transitions between A_1 and A_2, or from E to E. However, there will be no magnetic dipole transitions between two states who both transforms like A_1 or A_2.

One other thing that needs to be investigated is which states that are allowed in the first place. Using the LCAO-MO model for NH_3 (ammonia) we can find the symmetry of the molecular orbitals. The orbitals participating in the bonding of the molecule is the $2s$ and $2p$ orbitals of the nitrogen and the $1s$ orbitals of the hydrogen. the $2p$ orbitals will transform like the coordinates. The $2p_z$ orbital like A_1 and $2p_{x,y}$ like E, 2_s will also transform like A_1. For the hydrogen atoms we can first make a reducible representation with the atomic orbitals as basis and then decompose this into irreducible representations.

C_{3v}	E	$2C_3$	$3\sigma_v$
χ	3	0	1

from this we can calculate $\Gamma_{reducible} = A_1 + E$ which is the same as for the nitrogen $2p$ orbitals. This means that for ammonia we can construct molecular orbitals of A_1 and E symmetry. Thus electric dipole transitions between electronic states can occur as we saw above.

3 References

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