

GROUP THEORETICAL SELECTION RULES FOR ELECTRON-IMPACT SPECTROSCOPY *

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Received 9 August 1971

Revised manuscript received 13 September 1971

Simple group theoretical principles are applied to the consideration of electron scattering off atoms and diatomic and polyatomic molecules. For all scattering angles $S_g \leftrightarrow S_u$ is forbidden for atoms. For axial scattering (0° or 180° scattering angle), $\Sigma^+ \leftrightarrow \Sigma^-$ for linear polyatomic molecules and $S_g \leftrightarrow P_g \leftrightarrow D_g$, etc., for atoms. This approach is also used to estimate relative strengths of electron-impact-induced transitions of diatomic and polyatomic molecules.

1. Introduction

The use of a hierarchy of selection rules has played an important role in obtaining information about the symmetries of the states of atoms and molecules from photon absorption experiments [1]. However, a corresponding manifold of selection rules is not available for transitions induced by electron impact, except for high incident energies where the dipole selection rules of optical spectroscopy are applicable [2, 3]. Em-

pirically based rules have been developed and utilized [4] to distinguish the spin-exchange transitions from the "direct" excitation processes. However, more rigorous selection rules, valid at all incident energies, would be most helpful in determining the symmetries of the final states for electron-impact transitions in molecules.

Trajmar et al. [5] have noted for O_2 $1\Sigma_g^+ \rightarrow 3\Sigma_g^-$ an unusual decrease in the differential cross section (DCS) as the scattering angle approaches zero. Cartwright et al. [6], have derived a rigorous selection rule for this case using an expansion of the incoming plane wave in terms of partial waves with respect to the diatomic system, obtaining the result that $\Sigma^+ \leftrightarrow \Sigma^-$ is forbidden for zero (and 180°) scattering angle.

Herein we apply simple general group theoretical principles to the consideration of electron scattering off atoms, diatomic and polyatomic molecules. We find that for all angles $S_g \leftrightarrow S_u$ for atoms; and for

* Supported by a grant (PF-013) from the President's Fund of Caltech.

** Partially supported by a grant (GP-15423) from the NSF.

*** NSF Predoctoral Fellow.

‡ Contribution No. 4310.

†† Supported by USAF SAMSO Contract No. Fo4701-70-C-0059.

††† Supported by Contract NAS7-100, sponsored by NASA to JPL.

axial scattering (0° or 180° scattering angle) $\Sigma^+ \leftrightarrow \Sigma^-$ for linear polyatomic molecules and $S_g \leftrightarrow P_g \leftrightarrow D_g$ etc. for atoms. Besides these rigorous selection rules, we find that the relative intensities of various transitions of a system should exhibit certain trends with respect to the type of symmetry change involved.

We consider an $(N+1)$ -electron system with an initial state Ψ_i composed of a free electron with wave vector k_i and an N -electron molecule in a state Φ_i . The final state Ψ_f will be taken as a free electron with wave vector k_f (where $|k_f| \neq |k_i|$) and an N -electron molecule in a state Φ_f . The amplitude for such a transition will be zero whenever

$$\langle \Psi_f | \mathcal{T} | \Psi_i \rangle \quad (1)$$

is zero, where the \mathcal{T} operator is invariant under all operations of the molecular symmetry group. In examining (1), we consider the group \mathcal{G} of symmetry transitions leaving the $(N+1)$ -electron system invariant, and we determine if (1) can have a totally symmetric component (for \mathcal{G}). In the following, we consider only the electronic wavefunction, that is, we neglect any influence of the rotational and vibrational parts of the wavefunctions and any breakdown of the Born–Oppenheimer approximation. In addition, all relativistic effects (including spin–orbit coupling) are ignored.

2. Linear molecules

Consider first the case of forward or backward scattering, hereafter denoted as an *axial collision*.

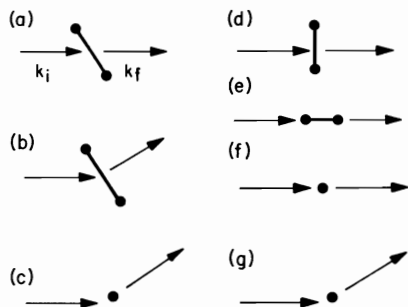


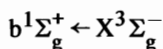
Fig. 1. Illustrations of the various scattering cases discussed in the text. Note that in (c) the axis of the molecule is perpendicular to the paper.

Then, for an arbitrary orientation of a linear molecule, as in fig. 1a, the $(N+1)$ -electron system has a plane of symmetry. If (1) should change sign under the reflection (σ) in this plane, the transition amplitude must be zero and the transition is absolutely forbidden. Only Φ_i and Φ_f can be affected by the reflection and hence the transition is forbidden whenever

$$\sigma[\Phi_f \Phi_i] = -[\Phi_f \Phi_i] ; \quad (2)$$

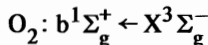
that is, *the reflection symmetry of a linear molecule cannot change in axial collisions*. For states with $\Lambda \neq 0$, there will always be one component for which (2) is not satisfied. However, (2) does lead to a rigorous selection rule for Σ states, namely that for axial collisions.

Indeed, Trajmar et al. [5] have recently found that the DCS for the

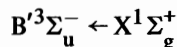
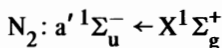


transition in O_2 goes to zero as the scattering angle goes to zero, in agreement with the above selection rule.

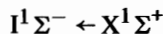
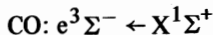
In addition, the results of Skerbele et al. [7] on



Lassette et al. [8], Skerbele et al. [9], Williams and Doering [10] on



and Skerbele and Lassette [11] on



are consistent with the above selection rule in that these transitions have *not* been observed in the above experiments (conducted at small scattering angles). Only in O_2 have these states been identified at large angles, although features have been observed in N_2 and CO at large angles (but not assigned).

In the more general case of non-axial scattering off a linear molecule, the $+ \leftrightarrow -$ selection rule applies only to the cases in which the molecule lies in the scattering plane (as indicated in fig. 1b) and consequently no rigorous selection rule is obtained for general scattering angles.

Consider next the case of a *non*-axial collision with a linear molecule of $D_{\infty h}$ symmetry (i.e., containing a center of inversion). If the molecule is oriented with the axis in the scattering plane as in fig. 1b, (1) must be invariant under the reflection (call it σ_v) in that plane, again leading to the condition that

$$+ \leftrightarrow - . \quad (4)$$

For the orientation of the molecular axis perpendicular to the scattering plane as in fig. 1c, (1) must be invariant under reflection (call it σ_h) in this plane (perpendicular to the molecule). Thus (2) is satisfied and hence the transition is prohibited for the following cases:

$$(\Sigma_g^{\pm}, \Pi_u, \Delta_g, \Phi_u, \text{etc.}) \leftrightarrow (\Sigma_u^{\pm}, \Pi_g, \Delta_u, \Phi_g, \text{etc.}) . \quad (5)$$

Putting conditions (4) and (5) together, we find that for linear $D_{\infty h}$ molecules in the orientations of figs. 1b and 1c, the DCS vanishes for *all scattering angles* for the transitions

$$\Sigma_g^+ \leftrightarrow \Sigma_u^- , \quad \Sigma_g^- \leftrightarrow \Sigma_u^+ . \quad (6)$$

However, figs. 1b and 1c represent just two special orientations of the molecule with respect to the scattering beam. For more general orientations, the extra symmetry elements of $D_{\infty h}$ (over those of $C_{\infty v}$) do not leave the scattering beam invariant, and hence we do not obtain any rigorous selection rules. Even so, the fact that the transition amplitude for (6) vanishes for both \parallel and \perp orientations suggests that the transition amplitude may then be small when averaged over all orientations of the molecular axis, and hence that transitions of type (6) may generally be weak for all scattering angles.

Next we consider the case of an axial collision with a $D_{\infty h}$ linear molecule. In this case there are two special orientations as shown in figs. 1d and 1e. Fig. 1e leads to allowed transitions only for $\Delta\Lambda = 0$ (but $\Sigma_{g,u}^+ \leftrightarrow \Sigma_{g,u}^-$), while fig. 1d leads to allowed transitions only for components that are symmetric for both σ_v and σ_h . Combining these conditions we see that for axial collisions

$$\begin{aligned} \Sigma_g^{\pm} &\leftrightarrow \Pi_g , & \Sigma_g^{\pm} &\leftrightarrow \Delta_u , & \Sigma_g^{\pm} &\leftrightarrow \Phi_g \\ \Sigma_u^{\pm} &\leftrightarrow \Pi_u , & \Sigma_u^{\pm} &\leftrightarrow \Delta_g , & \Sigma_u^{\pm} &\leftrightarrow \Phi_u \\ \Pi_g &\leftrightarrow \Delta_g , & \Pi_g &\leftrightarrow \Phi_u , & \Delta_g &\leftrightarrow \Phi_g \\ \Pi_u &\leftrightarrow \Delta_u , & \Pi_u &\leftrightarrow \Phi_g , & \Delta_u &\leftrightarrow \Phi_u \end{aligned} \quad (7)$$

and the transitions of (6) are forbidden for either orientation of fig. 1d and fig. 1e. For more general orientations of the molecule, the transitions of (7) are no longer forbidden, but even so since the transition amplitude is zero for both \parallel and \perp orientations, we might expect the DCS's of the transitions in (7) to be relatively weak (but non-zero) for scattering angles near zero (or 180°)*. This does not necessarily mean that the intensities of these transitions will decrease for small scattering angle, but they should decrease *relative* to the other transitions not prohibited by (6) or (7) but otherwise equivalent. For example [2], the N_2 $a^1\Pi_g \leftarrow X^1\Sigma_g$ transition leads to the same intensities at 0° and 12° whereas intensities of spin-allowed transitions usually increase markedly as $\theta \rightarrow 0$. (Ideally to test such predictions we should want two states with the same MO configuration and the same spin but different spatial symmetry.)

Summarizing these conditions on electron-impact transitions of linear molecules, we expect from the above group theoretical arguments:

(1) The DCS for

$$\Sigma_{g,u}^+ \leftrightarrow \Sigma_{g,u}^-$$

transitions should go exactly to zero for 0° (and 180°) scattering angle.

(2) The DCS for

$$\Sigma_g^+ \leftrightarrow \Sigma_u^- , \quad \Sigma_g^- \leftrightarrow \Sigma_u^+$$

transitions should be weak for all angles (compared to the intensity of transitions that are otherwise equivalent, e.g. involving the same configuration of orbitals).

(3) The DCS for the transitions of (7) should decrease (relative to otherwise equivalent transitions) as the scattering angle approaches 0° (and 180°).

3. Atoms

For an atom the case of an axial collision has $C_{\infty v}$ symmetry as illustrated in fig. 1f. Thus for (1) to be non-zero, $\Phi_f \Phi_i$ must have a component of Σ^+ sym-

* Actually such arguments indicate only that the transition becomes weaker relative to otherwise similar more-allowed transitions. For spin-exchange transitions of type (7), the DCS would be expected to decrease for small angle but spin-allowed transitions of type (7) might actually increase for small angle (but less than the more-allowed transitions).

metry. As an example, consider the $1S_g(1s)^2$ to $3P_g(2p)^2$ transition in He. In this case, Φ_i has Σ^+ symmetry and the states of Φ_f have Π and Σ^- symmetry. Thus the transition probability for the axial collision is zero, as was predicted theoretically by Becker and Dahler [12] and by Fano [13] and verified experimentally by Simpson et al. [14]. More generally, (1) is zero and hence the axial transition is forbidden whenever

$$L_i + p_i + L_f + p_f \text{ is odd,} \quad (8)$$

where L_i and L_f are the angular momenta and p_i and p_f are the parity numbers ($p = 0$ for an even state and $p = 1$ for an odd state) of the initial and final electronic states, respectively, of the N -electron atom. Examples of (8) are $S_g \leftrightarrow S_u$, $S_g \leftrightarrow P_g$, $S_u \leftrightarrow P_u$, $P_u \leftrightarrow P_g$, $P_u \leftrightarrow D_u$, and $P_g \leftrightarrow D_g$ (all for axial scattering).

For the more general case of *non-axial* scattering off an atom, only planar symmetry is retained, as in fig. 1g. Even so, we see that (2) applies to $S_g \leftrightarrow S_u$ and hence

$$S_g \leftrightarrow S_u \quad (9)$$

for all scattering angles (spin-orbit coupling and other such relativistic effects could make (9) *very* weakly allowed). There are several possible cases of (9), for example,

$$N: {}^2S_g[(2p)^2(3s)] \leftrightarrow {}^4S_u[(2p)^3]$$

is forbidden for all scattering angles (allowed only through relativistic and spin-coupling effects).

4. Polyatomic molecules

For non-linear polyatomic molecules, we do not obtain any general selection rules even for axial scattering, although the above type of analysis can also be applied to indicate that some types of transitions should be weaker than other *similar* transitions.

For example, for a system with C_{2v} symmetry such as the water molecule (with the coordinate system as shown in fig. 2), transitions

$$A_1 \leftrightarrow A_2 \quad \text{and} \quad B_1 \leftrightarrow B_2$$

are forbidden when the scattering plane coincides with the xz or yz symmetry planes,

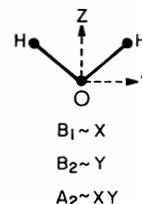


Fig. 2. The geometry of water and the symmetries of the irreducible representations of C_{2v} .

$$A_1 \leftrightarrow B_1 \quad \text{and} \quad B_2 \leftrightarrow A_2$$

are forbidden when the scattering plane coincides with the yz plane, and

$$A_1 \leftrightarrow B_2 \quad \text{and} \quad B_1 \leftrightarrow A_2$$

are forbidden when the scattering plane coincides with the xz plane.

Thus, other factors being equal (e.g., similar configurations of orbitals), we would expect

$$A_1 \leftrightarrow A_1$$

transitions to be strongest

$$A_1 \leftrightarrow B_1, \quad B_2 \leftrightarrow A_2, \quad A_1 \leftrightarrow B_2, \quad \text{and} \quad B_1 \leftrightarrow A_2$$

transitions to be of comparable strength but weaker than $A_1 \leftrightarrow A_1$, and for

$$A_1 \leftrightarrow A_2 \quad \text{and} \quad B_1 \leftrightarrow B_2$$

to be even weaker.

In addition, for axial scattering along either of the x , y or z axes, condition (2) shows that

$$A_1 \leftrightarrow A_2 \quad \text{and} \quad B_1 \leftrightarrow B_2 \quad (10)$$

transitions are forbidden. Thus, although the DCS for zero (and 180°) angle need not be zero for the cases in (10), we would expect them to be weaker than otherwise similar transitions, and hence, (relative to an otherwise similar $A_1 \leftrightarrow A_1$ transition) the DCS should decrease significantly as the scattering angle approaches zero (this is analogous to the cases (5) and (7) discussed earlier).

5. Spin exchange

So far we have considered only the spatial symme-

try of the wavefunctions, despite the fact that the observation of strong spin-exchange transitions is the basis for some of the most useful applications of electron-impact spectroscopy. The reason is that the spin-exchange transitions observed in electron-impact spectroscopy do *not* result from spin-dependent terms in the hamiltonian (such as spin-orbit coupling) but rather arise from a spin-conserved transition of the $(N+1)$ -electron system (e.g.; for O_2 $1\Sigma_g^+ \leftarrow 3\Sigma_g^-$, the combination of $\Phi_i = 1\Sigma_g^-$ plus an electron leads to two components, one of which is a doublet; the transition is from one doublet to the other). In this case, the transitions are due to matrix elements involving the non-relativistic hamiltonian (transitions due to spin-orbit coupling should be six to ten orders of magnitude weaker). However, we have found that these matrix elements are rigorously zero in some cases, and it is relevant to examine to what extent these forbidden transitions may be allowed by the smaller spin-dependent interactions.

For example, consider the case of O_2 : $b\ 1\Sigma_g^+ \leftarrow X\ 3\Sigma_g^-$. Classifying the wavefunctions $\Phi_i = 3\Sigma_g^-$ and $\Phi_f = {}^2\Sigma_g^+$ according to the double point group, we obtain the symmetries [1]

$$\Phi_i: \Sigma_g^+ + \Pi_g, \quad \Phi_f: \Sigma_g^+.$$

Since $\Phi_i \Phi_f$ now contains Σ_g^+ , the transition is not forbidden. Thus to the extent that spin-orbit coupling occurs, the DCS for the $b\ 1\Sigma_g^+ \leftarrow X\ 3\Sigma_g^-$ transition will *not* approach exactly zero as the scattering angle goes to zero (or 180°)*.

6. Summary

Our objective here has been to indicate how simple group theoretical considerations may be used to obtain selection rules for electron-impact transitions. One rigorous selection rule for molecules was obtained:

* It is of interest to estimate the intensity at 0° expected for a forbidden transition such as O_2 : $b\ 1\Sigma_g^+ \leftarrow X\ 3\Sigma_g^-$. The intensity due to spin-orbit coupling would be expected to be about 10^{-6} to 10^{-10} that of allowed collinear excitations (e.g., O_2 : $B\ 3\Sigma_u^- \leftarrow X\ 3\Sigma_g^-$). Hence the DCS at 0° for O_2 : $b\ 1\Sigma_g^+ \leftarrow X\ 3\Sigma_g^-$ should be less than 10^{-23} cm²/ster [5].

namely, that the DCS for the $\Sigma^+ \leftrightarrow \Sigma^-$ transition goes to zero as the scattering angle goes to zero (or 180°). A similar selection rule was obtained for atoms and some qualitative predictions of relative intensities were obtained for linear and polyatomic molecules.

Similar symmetry considerations can be applied to dissociative attachment and ionization processes and a related approach has been applied by Dunn [15] † to predict the angular distribution of the dissociation products. We thank Dr. Ara Chutjian for a helpful discussion on this work.

† Dunn considers diatomic molecules \parallel and \perp to the axis of the *incoming* electron beam and classifies the symmetries with respect to the diatomic plus incoming electron system. He suggests that no symmetries exist for predicting excitation processes and suggests the use of the Born approximation for this case.

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