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Detailed symmetry selection rules for reactive collisions

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A simple general method for obtaining selection rules for the ro-vibronic states of reactant and product molecules connected in a reactive collision is discussed. Neglecting only the coupling with nuclear spin, rather stringent restrictions are found to occur in systems involving three and more identical nuclei. Several radical and ion molecule reactions of current interest are used to illustrate this finding. Even more restrictive selection rules are found when assuming weak coupling (' incomplete exchange of identical nuclei ') in the intermediate reaction complex. These include the well-known selection rules for inelastic collisions of molecules with several identical nuclei, but less trivial examples with chemical reaction are also presented. The symmetry corrections and nuclear spin statistics in statistical theories of scattering (including the prior distributions for the information–theoretic approach) are derived. Further applications are discussed briefly.

1. INTRODUCTION

Symmetry rules in chemical reactions have stimulated many discussions and applications since the advent of Shuler's rules [1–3] and the Woodward–Hoffmann rules [4, 5]. Both of these deal essentially with symmetry rules for the *electronic* states involved in chemical reactions. Although these rules are based on severe approximations, as has been pointed out by George and Ross [6], they have been shown to be useful for predicting and understanding the nature of the electronic states populated in many chemical reactions.

In recent molecular beam, chemiluminescence, and laser-induced fluorescence experiments, it has been possible to obtain detailed ro-vibronic product state distributions—sometimes as a function of the reactant internal states [7–13]. The question arises as to how to obtain detailed selection rules, if there are any, for such processes. Clearly, complete quantum-mechanical (e.g. close coupling) calculations for cross sections automatically exhibit these selection rules [14–17] and so would detailed semiclassical calculations [18, 19]. In this connection detailed symmetry selection rules for triatomic systems have been discussed previously [16, 17, 19]. However, an extension of these treatments to more complicated systems does not appear to be easy. Also the much simpler classical trajectory [20] and statistical calculations [12, 21–23] cannot, by themselves, predict such selection rules.

In molecular spectroscopy, for example, the selection rules tell us which states cannot combine in an optical transition. In a similar way we would

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like to obtain information about state-to-state transitions ‘ forbidden ’ in a chemical reaction without even doing any dynamical calculations for systems of any molecular complexity. The problem with which we are then faced may be seen from the following reaction :

$$H^+ + CH_4 \rightarrow CH_3^+ + H_2 \quad \Delta H_0^0 = -375 \text{ kJ mol}^{-1}. \tag{1}$$

This reaction might proceed by the strongly bound intermediate CH_5^+ with the possibility of complete scrambling of the protons. Are there any restrictions on the final internal states of CH_3^+ and H_2, the initial ro-vibronic state of CH_4 being specified ? The answer to this is yes. If, for example, the initial ro-vibronic state of CH_4 is totally symmetric (species A_1 in T_d), simultaneous production of H_2 in an even rotational state and of CH_3^+ in a state of ro-vibronic symmetry E' or E'' (in D_{3h}) will not be observed.

We shall show in the present paper how such a result may be obtained, which groups are to be used and which assumptions form the basis for the approximate (!) selection rules. We shall first illustrate the physical concept involved with the simplest example. We then give a simple general method for the classification of the channel states of a chemical reaction according to the irreducible representations of an appropriate group. This group involves essentially the permutations of the indices of identical nuclei (and electrons) of *all* reactant and product molecules in addition to the operations of the three-dimensional rotation-reflection group. In this connection it is necessary to discuss the relationship to the usual point group classification of molecular energy levels of the *individual* reactant and product molecules (see, e.g., references [3] and [23]). This discussion owes much to the work of Hougen [25], Longuet-Higgins [26] and Watson [27] on the symmetry groups of rigid and non-rigid molecules.

We then illustrate the resulting method for obtaining detailed selection rules with a number of pertinent examples, some of which may become experimentally accessible in the very near future. We finally point out, as another simple application, the symmetry corrections to the statistical dynamical theories of scattering [21–23] and similar corrections to be applied eventually [28] to the ‘ prior distributions ’ in the information–theoretic approach [29, 30].

2. Block diagonal form of the S-matrix

The asymptotic scattering wave function for a binary collision event may be written, with an incoming wave in channel i only [31] :

$$\psi_{(i)} = \psi_{\mathrm{I}i} - \sum_f S_{fi}\psi_{\mathrm{O}f} \tag{2}$$

with the incoming wave functions

$$\psi_{\mathrm{I}n} \propto \phi_n r^{-1} \exp\left[-(ikr - l\pi/2)\right]$$

and the outgoing wave functions

$$\psi_{\mathrm{O}n} \propto \phi_n r^{-1} \exp\left[+(ikr - l\pi/2)\right].$$

The channel wave functions ϕ_n depend only parametrically upon the inter-fragment separation r (l is the orbital angular momentum quantum number (partial wave) for the collision). The absolute squares of the S-matrix elements S_{fi} give the probability for the transition from a particular initial state $|i\rangle$ to some final state $|f\rangle$ during the collision. Cross sections are formally given by equation (3):

$$\sigma(f \leftarrow i) = \frac{\pi}{k_i^2} |\delta_{fi} - S_{fi}|^2 \tag{3}$$

with the channel wave number being given by $k_i^2 = 2\mu E_{ti}/\hbar^2$ (μ = reduced mass and E_{ti} = initial translational energy for the collision). Observable cross sections for elastic, inelastic, and reactive processes are actually given by appropriate sums and averages over expressions like equation (3). Selection rules for transitions arise from the S-matrix always being block diagonal in the *good quantum numbers*—corresponding to the constants of motion Λ which satisfy the relation (4):

$$\mathscr{H}\Lambda = \Lambda\mathscr{H}, \tag{4}$$

the S-matrix may, in addition, be diagonal in further *collision constants* [32]. Often these arise from the fact that the scattering problem may be treated (to a good approximation) with some approximate Hamiltonian $\mathscr{H}_0$ and the corresponding additional approximate constants of motion Λ_0. It is therefore convenient to write the states $|i\rangle$ and $|f\rangle$ of the collision problem in terms of all the good and approximately good quantum numbers.

The hamiltonian of a molecular system is invariant with respect to [33]

(i) any overall translation in space,
(ii) any translation in time and time reversal,
(iii) any rotation of all particle coordinates in space,
(iv) the reflection of all particle coordinates in the centre of mass,
(v) any permutation of the indices of identical particles (nuclei and electrons).

Invariances (i) and (ii) lead to the conservation of total momentum, total energy and to the symmetry of the S-matrix [31]. Otherwise they have no consequences for the internal states involved in reactions like equation (1).

Invariance (iii) leads to the conservation of total angular momentum, i.e. of the quantum numbers F for the absolute magnitude and M_F for the z-component of the total angular momentum. Invariance (iv) leads to parity conservation for molecular interactions (quantum number $\Pi = \pm 1$). In the partial wave expansion for the integral cross section states with different parity of the fragment internal states are coupled by the odd values of the orbital angular momentum quantum number l. Therefore, there will in general be no restriction on the parity of *internal* states of the fragments due to overall parity conservation, although there may be effects on the shape of the *angular distributions*.

The major effects to be considered in the present paper stem from (v). The corresponding group is the direct product of several symmetric groups S_{n_i}

$$S_{n_1,n_2\cdots} \equiv \sum_{i=1}^{N} S_{n_i}. \tag{5}$$

The product is taken over all species of particles, N. The scattering states $|i\rangle$ and $|f\rangle$ may be written in terms of functions which transform as the irreducible representations of this group. Transitions between states which differ in these labels cannot occur upon collision. However, according to the Pauli principle, only states of one particular irreducible representation occur, in which the characters under the group operations Q are given by equation (6):

$$\chi_Q = \prod_{i=1}^{N_F} (-1)^{P_{iQ}}. \tag{6}$$

P_{iQ} is the parity of the permutation of the ith kind of fermions (total number $= N_F$) in the group element Q. If Q permutes only bosons, we have $\chi = +1$. The general conservation law corresponding to (v) is then the rather obvious statement that before and after the collision only Pauli-allowed states occur. These can be easily evaluated for reactants and products using standard techniques [3, 24].

A more useful, though approximate, selection rule comes from the fact that the nuclear spin part of the total molecular wave function is only weakly coupled to the other degrees of freedom, i.e.

$$\psi \simeq \psi_0 = \psi_K \psi_m, \tag{7}$$

with an approximate hamiltonian for the collision process satisfying $\mathscr{H}_0\psi_0 = E_0\psi_0$. The additional approximate constants of motion Λ_0 (in the sense of equation (4)), may be expected to be collision constants. This leads to the additional approximate good quantum numbers I and M_I for the total internal nuclear (' spin ') angular momentum and J and M_J for the total ' motional ' (including electronic) angular momentum. Similarly, the nuclear spin species Γ_K and the motional species Γ_m (i.e. the irreducible representations of the group defined by equation (5)) are additional approximate collision constants. This is the fundamental physical assumption for the selection rules derived in the present paper. We may note that in deriving the general selection rule for ro-vibronic electric dipole transitions (excluding nuclear spin) in optical spectra one starts from this same assumption [3, 26]. For the sake of simplicity we shall hereafter consider the reactions to occur with well-defined electronic states which are properly antisymmetrized with respect to all the electrons. This is no restriction, since we may allow transitions between these states to occur, and in particular, electronic angular momentum including spin is *not* considered to be a collision constant.

Let us consider, as a particularly simple example, the low energy scattering of protons off hydrogen molecules:

$$\mathrm{H}^+ + \mathrm{H}_2(v, j) \to \mathrm{H}^+ + \mathrm{H}_2(v', j'). \tag{8}$$

The scattering channels may be given by the quantum numbers J, M_J, I, M_I, j, l, v. Below 1·8 eV the electronic state ($^1A'$ in C_S) cannot change in this reaction. In figure 1 we show schematically one diagonal block $S(E \simeq 0{\cdot}07\ \mathrm{eV}, J=5)$ of the S-matrix. There are $2J+1$ equal diagonal blocks with different M_J. Each may be decomposed as shown into blocks of positive and negative motional parity depending on whether $(-1)^{j+l}$ is positive or negative. Assuming that the electronic wave function has been dealt with, we still have to discuss the transformation properties of the motional and nuclear spin wave functions with respect to the symmetric group of the permutations of the three protons (whose character table is shown in table 1). We can write the nuclear spin functions $|I, M_I\rangle$ in the basis of the products of spin functions $\alpha(m=\frac{1}{2})$ and $\beta(m=-\frac{1}{2})$.

Table 1. Character table for S_3 with the subduced representation $\Gamma(S_3)\downarrow S_2$ and the induced representation $\Gamma(S_3)\uparrow S_4$.

	E	(132) (123)	(12) (23) (13)	$\Gamma(S_3)\downarrow S_2$	$\Gamma(S_3)\uparrow S_4$
A_1	1	1	1	A	A_1+F_2
A_2	1	1	-1	B	A_2+F_1
E	2	-1	0	$A+B$	$E+F_1+F_2$

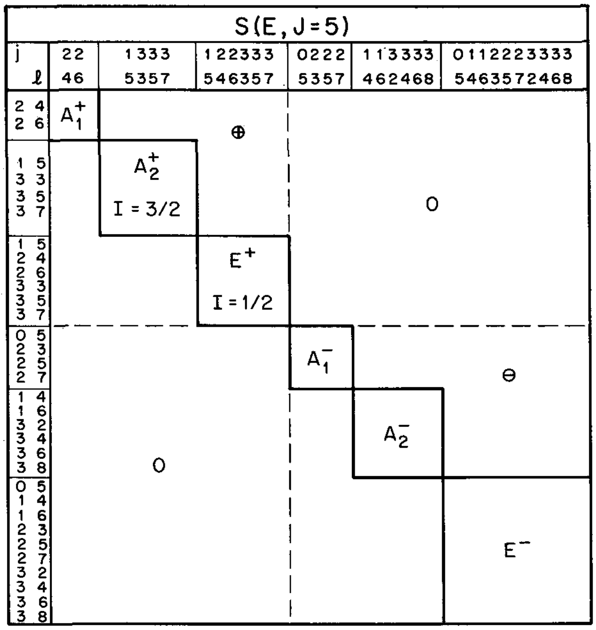

Figure 1. Decomposition of the S-matrix into block diagonal form for collisions of protons with H_2 at $E \simeq 0{\cdot}07$ eV. The rotational quantum number of H_2 is j, and l is the orbital quantum number. The total motional angular momentum is $J=5$. The nuclear spin angular momentum $I=\frac{3}{2}$ occurs with motional species A_2 and $I=\frac{1}{2}$ with E.

The 2^3 nuclear spin functions form the basis for a reducible representation of S_3 of the structure (compare table 1):

$$D_R = 4A_1 + 2E.$$

The four A_1 functions have $I=3/2$ $(-3/2 \leqslant M_I \leqslant 3/2)$ and the E functions have $I=\frac{1}{2}$ $(M_I = \pm\frac{1}{2})$.

The motional wave function may be written in the basis of the degenerate functions:

$$\left.\begin{array}{l} |\phi(1)\rangle \propto |k(1)\rangle |a(23)\rangle, \\ |\phi(2)\rangle \propto |k(2)\rangle |a(13)\rangle, \\ |\phi(3)\rangle \propto |k(3)\rangle |a(12)\rangle. \end{array}\right\} \qquad (9)$$

Here the symbolic notation $|k(m)\rangle\ |a(no)\rangle$ means that nuclei number n and o occupy the bound state in the diatomic molecule corresponding to the channel $|a\rangle = |J, M_J, v, j, l\rangle$, and nucleus m occupies the continuum state (wave number k). These functions generate a reducible representation of S_3 of the structure

$$D_R = A_2 + E \quad \text{if} \quad j_{H_2} \text{ is odd}$$

and

$$D_R = A_1 + E \quad \text{if} \quad j_{H_2} \text{ is even}$$

(see table 1, noting that the electronic state is totally symmetric). The total wave function for fermions must transform as A_2 in S_3 (cf. equation (6)), i.e. the nuclear spin functions with $I = 3/2$ combine with A_2 motional states (and odd j_{H_2}) to give Pauli-allowed wave functions, and each E-function with $I = \frac{1}{2}$ combines with one motional E-state to give *one* allowed wave function of species A_2. The motional wave functions of species A_1 do not occur for spin-$\frac{1}{2}$ particles. This leads to the block diagonal form of the S-matrix in figure 1. In reality there is no block of species A_1 and there are four identical blocks of species A_2 for the different values of $-3/2 \leqslant M_I \leqslant +3/2$, only one of which has been drawn. There are similarly *two* identical blocks of species E for $I = \frac{1}{2}$ and $M_I = \pm\frac{1}{2}$. This structure occurs similarly for positive and negative parity. To within our approximation of conservation of I and M_I no transitions between the different blocks are possible. In this particular case this does not lead to any simple selection rules for the *internal* states of H_2, since even and odd values of j are connected in the block of motional species E. In more complex situations, however, more interesting results are obtained.

3. EXCHANGE DEGENERACY, INDUCED REPRESENTATIONS AND MOLECULAR SYMMETRY GROUPS

The discussion of the elementary example H^+/H_2 in the previous section contains all of the basic physics (as did all of the detailed previous treatments of symmetry in triatomic systems, e.g., references [16, 17]). However, with more complex situations which are the subject of the present paper, it becomes impractical to write down the scattering wavefunctions according to equation (9) and to symmetrize them properly. Our task in the present section is to provide a simple direct way to obtain the reducible representations of the groups $S_{n_1,n_2}\ldots$ of equation (5) generated by the degenerate scattering wave functions of the generalized equation (9). For practical purposes it is also necessary to discuss the relationship to the seemingly unrelated point group classification of the fragment states which are two of the factors in the channel wave functions.

We consider two collision partners containing $k+m=n$ identical particles of *one* kind (the extension to several kinds of particles is obvious). The channel wave functions may be written as a product (compare equation (9)):

$$|a\rangle \propto |x(1, 2 \ldots k)\rangle |y(k+1, \ldots n)\rangle |Y_{ml}{}^{l}\rangle, \tag{10}$$

where $|x\rangle$ and $|y\rangle$ are classified according to the irreducible representations, Γ_k, of S_k and Γ_m of S_m and $|a\rangle$ according to the direct product representations $\Gamma_{k,m}$ of $S_{k,m} \equiv S_k \otimes S_m$. The exchange degeneracy [34] of the unsymmetrized channel states is equal to the number of configurations which are only distinguished by permutations of identical nuclei between the two collision partners :

$$g_{\mathrm{P}}=\frac{n!}{k!m!}. \tag{11}$$

The structure of the corresponding reducible representation of S_n is given by the *induced product representation* [34, 35] :

$$\Gamma_{k,m}\uparrow S_n\equiv(\Gamma_k\otimes\Gamma_m)\uparrow S_n=\sum_{\Gamma_n} f(\Gamma_k, \Gamma_m, \Gamma_n)\Gamma_n. \tag{12}$$

The frequency $f(\Gamma_k, \Gamma_m, \Gamma_n)$ of Γ_n is given by Frobenius' reciprocity theorem [36] ;

$$\Gamma_n\downarrow S_{k,m}=\sum_{k,\,m}^{g} f(\Gamma_k, \Gamma_m, \Gamma_n)\Gamma_{k,m}, \tag{13}$$

i.e. the frequency of Γ_n in the *induced representation* $\Gamma_{k,m}\uparrow S_n$ is the same as the frequency of $\Gamma_{k,m}$ in the *subduced representation* $\Gamma_n\downarrow S_{k,m}$. The latter is easily computed from the character tables of S_n and $S_{k,m}$, e.g., using the standard formula [36]

$$f_i^{D_R}=g^{-1}\sum_{j=1}^{g}(\chi_j^{\Gamma_i})^*(\chi_j^{D_R}). \tag{14}$$

$(\chi_j^{\Gamma_i})^*$ is the complex conjugate of the character of the irreducible representation Γ_i $(=\Gamma_{k,m})$ and $\chi_j^{D_R}$ is the character of the reducible representation D_{R} $(\triangleq\Gamma_n\downarrow S_{k,m})$ obtained by restricting the irreducible representations of S_n to the operations of the subgroup $S_{k,m}$. The order of the group is g. There are also more direct ways to obtain the $f(\Gamma_k, \Gamma_m, \Gamma_n)$, e.g., using the Young tableaux as shown in Chapters 7–12 of reference [37] or by using theorem 20 of reference [35 a]. We also note that

$$\left.\begin{array}{ll} & f(\Gamma_k, \Gamma_m, \Gamma_n)=f(\Gamma_m, \Gamma_k, \Gamma_n) \\ \text{or} & \\ & (\Gamma_k\otimes\Gamma_m)\uparrow S_n=(\Gamma_m\otimes\Gamma_k)\uparrow S_n. \end{array}\right\} \tag{15}$$

Equations (12)–(15) provide us with a simple way to obtain the transformation properties of the scattering wave functions in S_n if we know the transformation properties of the *ro-vibronic* wave functions of the separated collision partners under the operations of S_k and S_m. For diatomic and other simple molecules one might obtain these by elementary considerations (see, e.g., Chapter 7 of reference [38]).

In order to obtain a simpler general procedure for polyatomic molecules we use the relationship between the normal point group classification of molecular energy levels [3, 24], and a classification in a *permutation–inversion* group. This relationship has been pointed out by Hougen [25], Longuet-Higgins [26] and Watson [27]. We repeat here only briefly the general result and the reader is urged to consult the original papers for more details (see also references [39, 40]).

Hougen has shown how the ro-vibronic levels of any rigid molecule may be classified according to the species of the *full* molecular point group [25] (i.e. not only the subgroup of rotations). We shall use this result below without giving details here. He has also shown how a combination of *point*-group operations and operations on the rotational variables may be equivalent to some permutation, P, of the coordinates of identical nuclei and sometimes including an inversion E^* of the laboratory-fixed coordinate system in the origin. Longuet-Higgins [26] generalized these results by pointing out that the ro-vibronic energy levels of any molecule, including non-rigid molecules (linear molecules have been dealt with separately) [41] may be classified according to the irreducible representations of a molecular symmetry group M_{sg} of order g containing *feasible* permutations, P, of identical nuclei combined sometimes with an inversion E^* ($P^* \equiv E^*P = PE^*$). M_{sg} is a subgroup of the direct product group $S^*_{n_1,n_2} \ldots \equiv S^* \otimes S_{n_1,n_2} \ldots$ (compare equation (5) and $S^* \equiv \{E, E^*\}$). Any $P^{(*)}$ of M_{sg} for *rigid* molecules may be associated uniquely with a point-group operation which is a proper rotation for P and an improper rotation for P^*. Hence M_{sg} is isomorphous to the point group for rigid molecules, and we have the one-to-one mapping between the point-group species Γ_r' and the molecular symmetry group species Γ_r:

$$\Gamma_r \leftrightarrow \Gamma_r'. \tag{16}$$

For example, the group given by Longuet-Higgins for the symmetric H_3^+ molecule is the one we have used for the scattering problem H^+/H_2 multiplied by $S^* \equiv \{E, E^*\}$, i.e. $M_{S12} = S^* \otimes S_3 \equiv S_3^*$. It is isomorphous to the point group D_{3h} of H_3^+, with (123) replaced by C_3, (12) by C_2, E^* by σ_h, (123)* by S_3 and (12)* by σ_v. The reader may wish to verify that, indeed, the transformation properties of the ro-vibronic wave functions of the symmetric top H_3^+ may be obtained either directly with respect to the operations of S_3^* or with the method of Hougen [25] in the point group D_{3h}, leading to equivalent results as to $\Gamma_r' \leftrightarrow \Gamma_r$.

The important point made by Longuet-Higgins is that in general only a subgroup of *feasible* operations of the full group $S^*_{n_1,n_2} \ldots$ is useful for classifying molecular energy levels (and isomorphous to the point group for rigid molecules). If a spectroscopic state of a molecule transforms as Γ_r under the group of feasible P^* and P, which is a subgroup of $S^*_{n_1,n_2} \ldots$ it actually corresponds to a set of *degenerate states* which transform as

$$D_r = \Gamma_r \uparrow S^*_{n_1,n_2} \ldots \tag{17}$$

While equation (17) may be used to find (and define!) the subgroup of *feasible* P and P^*, there are also usually simple physical arguments to do so. These arguments have been investigated in detail by Watson [27] who first gave equation (17).

We shall consider only a simple example, the rigid ozone molecule whose point group is C_{2v}. The character table for C_{2v} and the associated feasible P and P^* are given in table 2. Each ro-vibronic level of ozone which is classified according to the non-degenerate species of C_{2v} is in reality three fold degenerate due to the three different 'frameworks' with nucleus 1, 2 or 3 in the middle, respectively (see figure 2). The interconversion between these three frameworks is physically prohibited by a very high energy barrier. Therefore, the corresponding permutations are *not feasible* in the sense of Longuet-Higgins. The species of these degenerate levels, according to equation (17), are given in the right-hand part of table 2.

Table 2. Character table for C_{2v} and S_2^* with the induced representation $\Gamma(S_2^*)\uparrow S_3^*$.

Class	C_{2v}	E	C_2	σ_{yz}	σ_{xz}		$\Gamma(S_2^*)\uparrow S_3^*$
Species	S_2^*	E	(12)	E^*	(12)*		
C_{2v}	S_2^*						
A_1	A^+	1	1	1	1	T_z	$A_1^+ + E^+$
A_2	A^-	1	1	-1	-1	R_z (u, v, w)	$A_1^- + E^-$
B_1	B^-	1	-1	-1	1	T_x, R_y	$A_2^- + E^-$
B_2	B^+	1	-1	1	-1	T_y, R_x	$A_2^+ + E^+$

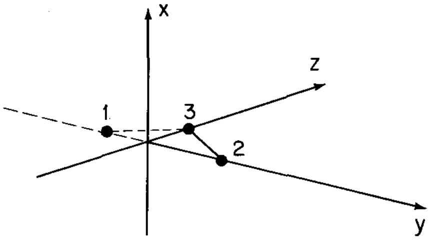

Figure 2. The C_{2v} structure of the ozone molecule (compare table 2). There are three equivalent frameworks with nucleus 1, 2 or 3 in the middle, respectively.

It is obvious, by the way, that the mathematical problem leading to equation (17) is the same as the one leading to equation (12). The permutations of nuclei between separated collision partners may be considered to be *not feasible* in the sense of Longuet-Higgins which makes equations (12) and (17) equivalent. We shall take here the position that feasibility is defined by the induced representation, but we shall come back to this point in § 5.

We stress by our notation the *parity* of the species by the index ± by definition

$$\Gamma_m(S_n)\uparrow S_n^* \equiv \Gamma_m^+ + \Gamma_m^-. \tag{18}$$

Note that the subgroup M_{sg} of feasible P and P^* *does not always contain* E^*, i.e. the feasible P do *not* always form a subgroup of S_{n_1,n_2} . . . with species of well-defined parity.

4. APPLICATIONS

We may summarize the discussion of the previous sections in a simple procedure for obtaining detailed selection rules for the ro-vibronic states in reactive collisions :

(i) Obtain a classification of ro-vibronic energy levels of reactants and products in the full point group, using standard techniques for rigid, non-linear molecules [3, 24, 25].

(ii) Obtain a classification in the molecular symmetry group M_{sg} of Longuet-Higgins according to equation (16).

(iii) Obtain a classification of the degenerate sublevels according to $\Gamma_r(M_{\mathrm{sg}})\uparrow S_k^*$ for each collision partner. As discussed by Watson [27] this is easily done by ‘ reading the correlation table backwards ’, i.e. by computing the subduced representations $\Gamma(S_k^*)\downarrow\Gamma(M_{\mathrm{sg}})$, and using Frobenius' reciprocity theorem [equation (13)]. In simple cases steps (i)–(iii) can be omitted, computing the transformation properties of reactant and product states under the operations of $S_{k,m}^*$ (etc.) directly.

(iv) Use equations (12)–(15) to compute the symmetrized scattering states for every combination of energy levels of the reactant and product molecules.

(v) Compute the species Γ_K and the angular momentum quantum numbers I, M_I for the nuclear spin states combining with the motional states of species Γ_m. This can be obtained from the character of the reducible representation generated by the basis of nuclear spin functions and using the Pauli principle, equation (6).

The S-matrix is approximately diagonal in the labels $\Gamma_m^{(\pm)}(S^*_{n_1,n_2}\ldots)$. If some combination of internal states $\{a, b\}$ of reactant and of product molecules $\{c, d\}$ is *not connected within any diagonal block*, then the product states $\{c, d\}$ cannot be reached from the reactant states $\{a, b\}$, even assuming very strong coupling of all but the nuclear spin degrees of freedom in the intermediate reaction complex. This is the simplest qualitative way of using the present symmetry rules. In the case of H^+/H_2 scattering there were no such complete exclusions. Let us consider now a few examples where such restrictions do occur. This will also demonstrate the ease of application of the present method.

4.1. *Three identical nuclei*

The reaction

$$H_2 + HeH^+ \rightleftarrows H_3^+ + He \tag{19}$$

has been observed experimentally [11, 42] and studied in an *ab initio* (SCF–CI) calculation [43]. A similar reaction occurs with KrH$^+$ [44]. As far as the protons are concerned, the reaction is similar to H^+/H_2, but here we have the possibility of H_3^+-formation. Let us ask which ro-vibronic states of H_2 and H_3^+ *do not couple* (if any). According to our rules (i)–(v), the reaction may be discussed with tables 1 and 2. The classification of H_3^+ ro-vibronic levels is easily obtained [3], and the results are summarized in table 3. From para H_2 (even j) there will be no production of H_3^+ in rotational states with the symmetric top quantum number $K=3n$ and in a totally symmetric vibronic state (the motional species A_1 does not occur with any nuclear spin function). Table 3 can, of course, also be used for the reaction $HeD^+ + D_2$, if one changes the column for the nuclear spin functions as follows : A_1 combines with $I=3$ and $I=1$ ($g_K=10$), A_2 with $I=0$ ($g_K=1$) and E with $I=1$ and 2 ($g_K=8$).

The two channels in the reaction (20)

$$HD^+ + H_2 \begin{array}{l} \nearrow H_3^+ + D \qquad (20\,a) \\ \searrow H_2D^+ + H \qquad (20\,b) \end{array}$$

basically obey the selection rules for reaction 19 (→20 *a*) and for H^+/H_2 (→20 *b*). Obviously, there are always many similar reactions following the same selection rules.

Table 3. The selection rules for the reaction $H_2 + HeH^+ \rightleftarrows H_3^+ + He$ and similar reactions, assuming a totally symmetric *vibronic* state of H_3^+. $n = 1, 2, 3, \ldots$

j_{H_2}	$\Gamma(S_2)$	$\Gamma(S_2)\uparrow S_3$	$I(g_K)$	H_3^+
Even (g)	A	A_1	$-(0)$	$K=0$, $J=$ even $K=3n$, any J
		+		
		E	1/2(2)	$K=3n-1$ and $3n-2$
		+		
Odd (u)	B	A_2	3/2(4)	$K=0$, $J=$ odd $K=3n$, any J

In a reaction like (21), one the other hand :

$$HeH^+ + D_2 \rightarrow HD_2^+ + He \tag{21}$$

The D_2 group remains essentially unaffected. Therefore the even j of D_2 couple only with A_1 and A_2 states of HD_2^+ (in C_{2v}) and the odd j of D_2 only with B_1 and B_2 levels. For such simple systems these results can be obtained in an elementary manner.

The reaction

$$F + CH_3I \rightarrow CH_3 + IF \tag{22}$$

has recently been studied in molecular beam experiments, although with insufficient resolution to obtain any selection rules [35]. This reaction should be discussed with S_3^*, since the levels of ICH_3 do not have a well-defined parity. From table 4 we obtain the selection rules in equation (23) :

$$\left.\begin{array}{l} A_1 \quad \text{or} \quad A_2(C_{3v}) \leftrightarrow E^{\pm}(S_3^*) \\ \quad E(C_{3v}) \leftrightarrow (A_1^{\pm}) \quad \text{or} \quad A_2^{\pm}(S_3^*). \end{array}\right\} \tag{23}$$

Parity is not conserved for the CH_3 group individually and the species $A_1^{\pm}$ in S_3^* have zero proton spin statistical weight, as indicated by the parenthesis.

The selection rules for collisions of deuterium atoms with methyl radicals may be obtained for the reactive channel with the aid of tables 1 and 2 :

$$D + CH_3(A_2' \text{ or } A_2'' \text{ in } D_{3h}) \leftrightarrow CH_2D(A_1 \text{ or } A_2 \text{ in } C_{2v}) + H. \tag{24}$$

Table 4. Character table for C_{3v} and the isomorphous group M_{S6} with the induced representation $\Gamma(M_{S6})\uparrow S_3^*$.

C_{3v} M_{S6}	E E	$2C_3$ 2(123)	$3\sigma_v$ 3(12)*	$\Gamma_m\uparrow S_3^*$
A_1	1	1	1	$A_1^+ + A_2^-$
A_2	1	1	−1	$A_2^+ + A_1^-$
E	2	−1	0	$E^+ + E^-$

There are no further restrictions. On the other hand, one has ' no interconversion of nuclear spin isomers ', as is well known for the purely inelastic channel [3] :

$$\left.\begin{aligned} A_1 &\leftrightarrow A_1, \\ A_2 &\leftrightarrow A_2, \\ E &\leftrightarrow E. \end{aligned}\right\} \tag{25}$$

The species designations are for CH_3 in D_{3h} both with $'$ and $''$.

4.2. *Four identical nuclei*

The reaction (26)

$$H_2^+ + H_2 \rightarrow H_3^+ + H \quad \Delta H_0^0 \simeq -170 \text{ kJ mol}^{-1} \tag{26}$$

in the electronic ground state may be representative for the simplest reactions involving four identical nuclei [46]. Since all states of the reactant and product molecules have a well-defined parity, we may use S_2, S_3 and S_4 for obtaining selection rules. Table 5 shows the character table of S_4. On the right-hand side of table 5 we give some subduced representations (compare tables 1 and 2). The appropriate induced representations for reaction (26) are summarized in table 6. For H_2 and H_2^+ the species in S_2 is $A(B)$ if j is even (odd). Note that $(A \otimes B)\uparrow S_4 = (B \otimes A)\uparrow S_4$ as is given by equation (15). From table 6 we see, for instance, that there will be no production of H_3^+ in an A_2 level (A_2' and A_2'' in D_{3h}) if j and j' for H_2 and H_2^+ are both even. If both rotational quantum numbers are odd there will be no H_3^+ in A_1 states (A_1' and A_1''). The latter are Pauli-disallowed anyway for spin-$\frac{1}{2}$ particles, but not for deuterons, for example. The 2^4 nuclear spin functions (3^4 for deuterons) combine with the motional functions as indicated by table 7, to give allowed overall wave-functions. As usual, we have put the disallowed wavefunctions (for protons) in parenthesis in Table 6.

Table 6 and Table 7 apply to the chemical activation in reaction (27) as well,

$$CH_2(^1A_1) + H_2 \rightarrow (CH_4) \rightarrow CH_3 + H. \tag{27}$$

This insertion reaction has recently been the subject of *ab initio* studies [47]. The A_1 and A_2 levels (in C_{2v}) of CH_2 correspond to the totally symmetric

Table 5. Character table for the isomorphous groups S_4, T_d, and M_{S24}, with the induced representation $\Gamma(M_{S24})\uparrow S_4^*$ and the subduced representation $\Gamma(S_4)\downarrow S_3$. $P(S_4)$ is the partition for S_4.

	T_d M_{S24} S_4	E E E	$8C_3$ 8(123) 8(123)	$3C_2$ 3(12)(34) 3(12)(34)	$6S_4$ 6(1234)* 6(1234)	$6\sigma_d$ 6(12)* 6(12)	$\Gamma(S_4)\downarrow S_3$	$\Gamma(M_{S24})\uparrow S_4^*$
$P(S_4)$								
[4]	A_1	1	1	1	1	1	A_1	$A_1^+ + A_2^-$
[1^4]	A_2	1	1	1	-1	-1	A_2	$A_2^+ + A_1^-$
[2^2]	E	2	-1	2	0	0	E	$E^+ + E^-$
[2, 1^2]	F_1	3	0	-1	1	-1	$E + A_2$	$F_1^+ + F_2^-$
[3, 1]	F_2	3	0	-1	-1	1	$E + A_1$	$F_2^+ + F_1^-$

Table 6. The induced representations $\{\Gamma(S_2^{1,2})\otimes\Gamma(S_2^{3,4})\}\uparrow S_4$ and $\Gamma(S_3)\uparrow S_4$ which give the selection rules for reactions like

$$\mathrm{H_2}\{\Gamma(S_2^{1,2})\}+H_2^+\{\Gamma(S_2^{3,4})\}\rightleftharpoons\mathrm{H_3^+}\{\Gamma(S_3)\}+\mathrm{H}.$$

(Motional species with zero proton spin statistical weight in parentheses.)

$\Gamma(S_2^{1,2})$	$\Gamma(S_2^{3,4})$	$\Gamma(S_{2,2})$	$\Gamma(S_{2,2})\uparrow S_4$	$\Gamma(S_3)$	$\Gamma(S_3)\uparrow S_4$
A	A	A_1	$(A_1)+E+(F_2)$	(A_1)	(A_1+F_2)
A	B	A_2	$F_1+(F_2)$	A_2	A_2+F_1
B	A	B_1	$F_1+(F_2)$	E	$E+F_1+(F_2)$
B	B	B_2	A_2+E+F_1		

Table 7. Pauli-allowed combinations of motional species Γ_m with the 2^4 spin functions of four protons and the 3^4 spin functions of four deuterons.

Γ_m	${}^{(2I+1)}\Gamma_K$	
	Protons	Deuterons
A_1	—	${}^{9}A_1+{}^{5}A_1+{}^{1}A_1$
A_2	${}^{5}A_1$	—
E	${}^{1}E$	${}^{5}E+{}^{1}E$
F_1	${}^{3}F_2$	${}^{3}F_1$
F_2	—	${}^{7}F_2+{}^{5}F_2+{}^{3}F_2$

representation A in S_2, and B_1 and B_2 (in C_{2v}) correspond to B in S_2 (see table 2, we do not discuss in this paper the point-group classifications for the ro-vibronic levels, which are treated in standard references, e.g. [3, 24, 25]). Therefore with even j of $\mathrm{H_2}$ and $\mathrm{CH_2}$ ro-vibronic levels of A_1 and A_2 species, one does *not* produce any levels of the A_2 ro-vibronic species of $\mathrm{CH_3}$ (A_2' and A_2'' in D_{3h}. Note that the electronic ground state is ${}^2A_2''$ for $\mathrm{CH_3}$ [3]).

The inelastic scattering (including exchange) in reaction (28) can be investigated by computing $\Gamma_m(S_3)\uparrow S_4$:

$$\mathrm{H}+\mathrm{H_3^+}\rightarrow\mathrm{H_3^+}+\mathrm{H}. \tag{28}$$

This is easily obtained from $\Gamma_m(S_4)\downarrow S_3$ which is given in table 5. One then finds the selection rules for the internal states of $\mathrm{H_3^+}$ in S_3 (or D_{3h}) :

$$A_1\ ('\text{ or }'')\not\leftrightarrow A_2\ ('\text{ or }''). \tag{29}$$

This is a trivial restriction for the proton case since the A_1-levels do not occur in D_{3h} (or S_3). However, for the deuteron case the selection rule is meaningful since all species do occur with some spin function. The charge exchange reaction (30 *a*) follows the same selection rules

$$\mathrm{H^+}+\mathrm{CH_3}\begin{cases}\longrightarrow\mathrm{CH_3^+}+\mathrm{H} & \Delta H_0{}^0=-370\ \mathrm{kJ\ mol^{-1}} \quad (30\,a)\\ \longrightarrow\mathrm{CH_2^+}+\mathrm{H_2} & \Delta H_0{}^0=-280\ \mathrm{kJ\ mol^{-1}} \quad (30\,b)\end{cases}$$

The selection rules for (30 *b*) are the same as those for reaction (26). Whereas (30 *b*) probably proceeds via the bound intermediate $\mathrm{CH_4^+}$ (if at all), (30 *a*) may proceed in a direct way by simple charge exchange. Under these conditions there are more restrictive selection rules, as discussed in detail in § 5.

The reaction (31) occurring in the electronic ground state has been in the centre of some experimental work [48] :

$$\mathrm{Ar}^+(^2P_{3/2}) + \mathrm{CH}_4(^1A_1) \rightarrow \mathrm{ArH}^+(^1\Sigma^+) + \mathrm{CH}_3(^2A_2'') \quad \Delta H_0{}^0 = -160 \text{ kJ mol}^{-1} \tag{31}$$

(electronic point-group species in parentheses). Detailed selection rules are obtained from considering $S_4{}^*$ for this reaction. This group and the permutation inversion group M_{S24} for methane (isomorphous to T_d and S_4) have already been discussed by Hougen [49] in relation to the spectroscopy of the hypothetically inverting CH_4 molecule. The character tables of the three isomorphous groups of order 24 are contained in table 5.

The species designations in $S_4{}^*$ are the same as in S_4 with a positive or negative sign depending on whether the parity is positive or negative, as always in our notation. This is somewhat different from Hougen's notation [49] but saves us from giving the whole character table of $S_4{}^*$. In the right-hand side of table 5 we have given $\Gamma_m(M_{S24})\uparrow S_4{}^*$. This gives the species of the inversion doublets of methane. With $\Gamma_m(S_3)\uparrow S_4$ from table 1 we obtain the selection rules for reaction (31) :

$$\left.\begin{array}{c} A_1 \text{ or } A_2 \text{ (for CH}_4,\ T_d) \nleftrightarrow E' \text{ or } E'' \text{ (for CH}_3,\ D_{3h}) \\ E \nleftrightarrow A_1 \text{ or } A_2 \end{array}\right\} \tag{32}$$

the species of the ro-vibronic levels of CH_4 in T_d have been discussed by Hougen [49] and those for CH_3 (in D_{3h}) have been given in reference [3].

4.3. *Five identical nuclei*

We have already mentioned reaction (33) in the Introduction :

$$\mathrm{H}^+ + \mathrm{CH}_4 \rightarrow \mathrm{CH}_3{}^+ + \mathrm{H}_2 \quad \Delta H_0{}^0 = -375 \text{ kJ mol}^{-1}. \tag{33}$$

Although this reaction may proceed through a bound intermediate $CH_5{}^+$ with complete scrambling of the protons, there still remain some selection rules. In table 8 we give the part of the character table for the group $S_5{}^*$ which is sufficient for the present purpose and several useful reductions to subgroups. From this one easily obtains the induced representations shown in table 9. For convenience we have left out the parity designations, although M_{S24} is *not* a subgroup of S_5. Motional species which are Pauli disallowed for spin-$\frac{1}{2}$ particles have been put in parenthesis ($\Gamma_m = A_2$ occurs with $^6A_1$ proton spin functions, $\Gamma_m = G_2$ with $^4G_1$, and $\Gamma_m = \mathrm{H}_2$ with $^2H_1$. The others are missing). We find the general selection rule for nuclei of any spin (in related reactions, say with $D \equiv {}^2\mathrm{H}$, etc.) to be

$$E(\mathrm{CH}_4\ ;\ T_d) \nleftrightarrow A_2 \text{ or } B_1\ (H_2 + \mathrm{CH}_3{}^+\ ;\ S_{2,3}) \tag{34}$$

and the additional selection rule appropriate for spin-$\frac{1}{2}$ particles, taking only really occurring motional species into account, to be

$$A_1 \text{ or } A_2\ (\mathrm{CH}_4\ ;\ T_d) \nleftrightarrow E_1\ (\mathrm{H}_2 + \mathrm{CH}_3{}^+\ ;\ S_{2,3}) \tag{35}$$

there will, for example, be no creation of para-H_2 with $CH_3{}^+$ in a degenerate state if CH_4 were initially in a totally symmetric state (and so forth).

Table 8. Character table for S_5 (and essentially also S_5^*, noting that the Γ_m^- have the signs of the characters changed with all starred operations). For the subduced representations $\Gamma_m^{\pm}(S_5^*)\downarrow S_4^*$ and $\Gamma_m^{\pm}(S_5^*)\downarrow S_{2,3}^*$ one has $+\leftrightarrow+$ and $-\leftrightarrow-$. Furthermore one has the subduced representation $\Gamma_m^+\downarrow M_{S24}$ (with $\Gamma_m^-\downarrow M_{S24}$ in parentheses).

P	Γ_m	E	10 (12)	20 (123)	15 (12)(34)	30 (1234)	20 (123)(45)	24 (12345)	$\Gamma_m\downarrow S_4$	$\Gamma_m\downarrow S_{2,3}$	$\Gamma_m^+\downarrow M_{S24}$ ($\Gamma_m^-\downarrow M_{S24}$)
[5]	A_1	1	1	1	1	1	1	1	A_1	A_1	A_1 (A_2)
[1^5]	A_2	1	−1	1	1	−1	−1	1	A_2	B_2	A_2 (A_1)
[4, 1]	G_1	4	2	1	0	0	−1	−1	A_1+F_2	$A_1+B_1+E_1$	A_1+F_2 (A_2+F_1)
[2, 1^3]	G_2	4	−2	1	0	0	1	−1	A_2+F_1	$A_2+B_2+E_2$	A_2+F_1 (A_1+F_2)
[3, 2]	H_1	5	1	−1	1	−1	1	0	$E+F_2$	$A_1+E_1+E_2$	$E+F_2$ $(E+F_1)$
[2^2, 1]	H_2	5	−1	−1	1	1	−1	0	$E+F_1$	$B_2+E_1+E_2$	$E+F_1$ $(E+F_2)$
[3, 1^2]	I	6	0	0	−2	0	0	1	F_1+F_2	$A_2+B_1+E_1+E_2$	F_1+F_2 (F_1+F_2)

Table 9. The induced representations $\Gamma(M_{S24})\uparrow S_5^*$ and $\Gamma(S_{2,3}^*)\uparrow S_5^*$, omitting the parity designations. From this one obtains selection rules for reactions similar to (33), (motional species with zero statistical weight for spin-½ particles are put in parentheses).

$\Gamma(M_{S24})$	$\Gamma(M_{S24})\uparrow S_5^*$	$\Gamma(S_2)\otimes\Gamma(S_3)\equiv\Gamma(S_{2,3})$	$\Gamma(S_{2,3}^*)\uparrow S_5^*$
A_1	$(A_1+G_1)+A_2+G_2$	$A\otimes A_1\equiv A_1$	$(A_1+G_1+H_1)$
A_2		$A\otimes A_2\equiv A_2$	$G_2+(I)$
E	$(2H_1)+2H_2$	$A\otimes E\equiv E_1$	$(G_1+H_1+I)+H_2$
F_1	$(G_1+H_1)+G_2+H_2+(2I)$	$B\otimes A_1\equiv B_1$	(G_1+I)
F_2		$B\otimes A_2\equiv B_2$	$A_2+G_2+H_2$
		$B\otimes E\equiv E_2$	$G_2+H_2+(H_1+I)$

Let us consider as a second example involving five identical nuclei, the inelastic (and exchange) scattering

$$H_3^+ + H_2 \rightleftharpoons H_2 + H_3^+. \tag{36}$$

The selection rules are to be obtained from the induced representations in the right-hand part of table 9, namely in general ($\Gamma(S_{2,3})$) :

$$\left.\begin{array}{l} A_1 \not\leftrightarrow A_2 \text{ or } B_2, \\ B_1 \not\leftrightarrow B_2, \end{array}\right\} \tag{37}$$

and in addition for protons :

$$A_2 \not\leftrightarrow E_1. \tag{38}$$

Isotopic variants of reaction (36) have been studied in much detail by molecular beam techniques [11, 50] (so far at moderate COM translational energy resolution insufficient to detect selected ro-vibronic states). This leads us to an example containing two sets of identical nuclei :

$$D_3^+ + H_2 \rightarrow DH_2^+ + D_2 \tag{39 a}$$

$$\rightarrow D_2H^+ + HD. \tag{39 b}$$

The appropriate group is now $S_{2,3}$ (parity may be dealt with separately), and the subgroups for (39 *a*) and (39 *b*) are $S_{2,2}$ and S_2. The corresponding induced representations are given in table 10 (they can be obtained by combining tables 1 and 2 appropriately). The definitions for $\Gamma(S_{2,3})$ in terms of $\Gamma(S_2)\otimes\Gamma(S_3)$ are as shown in table 9. Thus we obtain rather restrictive selection rules for reaction (39 *a*). For example, para hydrogen colliding with D_3^+ molecules in a totally symmetric ro-vibronic state will give *only* even rotational states of D_2 with A_1 or A_2 states (in C_{2v}) for DH_2^+ (and so on). Similarly, in reaction (39 *b*) an A_1 (′ or ″ in D_{3h}) level of D_3^+ will give only A_1 or A_2 levels of D_2H^+ (in C_{2v}) colliding with either ortho or para-hydrogen.

Enough examples have been considered to show the ease of application and the many possible predictions of the present method. So far, we have assumed that the rearrangements during the collision are sufficiently profound that all identical nuclei *may* eventually be ‘ exchanged ’. For the examples treated this assumption appears to be realistic. Some additional selection rules arise if this is not the case.

Table 10. The induced representations $\Gamma(S_{2,2}^{(1,2)(4,5)})\uparrow S_{2,3}^{(4,5)(1,2,3)}$ and $\Gamma(S_2^{1,2})\uparrow S_{2,3}^{(4,5)(1,2,3)}$.
1, 2, and 3 refer to deuterons and 4 and 5 refer to protons in reaction (39).

(a)

$\Gamma(S_2^{1,2})$	$\Gamma(S_2^{4,5})$	$\Gamma(S_{2,2}^{(1,2)(4,5)})$	$\Gamma(S_{2,2})\uparrow S_{2,3}^{(4,5)(1,2,3)}$
A	A	A_1	A_1+E_1
A	B	A_2	B_1+E_2
B	A	B_1	A_2+E_1
B	B	B_2	B_2+E_2

(b)

$\Gamma(S_2^{1,2})$	$\Gamma(S_2)\uparrow S_{2.3}^{(4,5)(1,2,3)}$
A	$A_1+B_1+E_1+E_2$
B	$A_2+B_2+E_1+E_2$

5. ADDITIONAL COLLISION CONSTANTS DUE TO INCOMPLETE EXCHANGE

We reconsider the collision of two molecules containing $n=k+m$ nuclei of one kind. The levels of the separated collision particles are now supposed to be classified according to the species of the molecular symmetry groups of feasible permutation-inversion elements in the sense of Longuet-Higgins, M_{sa} and M_{sb}. For the total system we use the direct product group $M_{\mathrm{s}(a\cdot b)}$ $(a\cdot b \leqslant 4k!m!)$. The scattering states occur in sets with a degeneracy $v=4n!/(a\cdot b)$. The collision dynamics may be such that transitions occur only between certain v/w-fold degenerate subsets which can be classified according to a group M_{sp} of order $p=w\cdot a\cdot b$. The irreducible representations of M_{sp} are then (approximate) collision constants, noting of course that only *overall* parity is conserved. We may consider the elements of M_{sp} to be feasible in the sense of Longuet-Higgins, extending the concept to the supermolecule in a collision. The validity of the approximate selection rules thus derived depends upon the validity of the dynamical assumptions made. This provides a means for obtaining information about the detailed reaction mechanisms just by looking at the product internal state distributions as a function of the initial state and without introducing perturbations by isotopic substitution. We shall illustrate this rather abstract concept with some examples.

The collisions of protons with H_2 discussed in § 2 again provide a particularly simple example. Indeed, from experiments with p-H_2 at a collision energy of 3·7 eV in the centre-of-mass system, it appears that transitions with odd Δj are negligible as compared to the very strong transitions with even Δj (up to $\Delta j=20$) [10]. This would indicate that ‘ exchange ’ between the incident proton and the protons of the hydrogen molecule is not feasible. The collision dynamics can be characterized by the species A and B of S_2 (or S_2^*). This is shown in figure 3, where we have repeated only the block of positive parity of figure 1. The important point is that the more rigorous decomposition into blocks labelled by the species of S_3 is still valid. But now we have a further decomposition of the block for the doubly degenerate species E into two blocks of species E_A and E_B depending on whether E has been induced in S_3 by a representation A or B in S_2. For practical purposes it would be sufficient to obtain just the decomposition according to the species A and B in S_2. However, in reality, the apparent lowering of the symmetry (from S_3 to S_2) introduces additional collision constants without removing the previous ones. These additional collision constants stem from dynamical constraints in addition to nuclear spin symmetry conservation. In the case of the H^+/H_2-scattering, the experimental result would not necessarily have been expected because the strongly attractive potential favours exchange. The (rather obvious) interpretation of the experimental result is that the cross section for rotational excitation at 3·7 eV is not due to a compound mechanism.

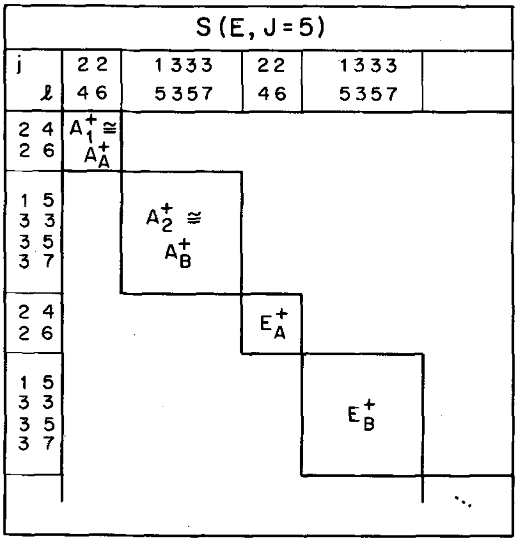

Figure 3. Block diagonal form for the positive parity channels in H^+/H_2 scattering, assuming no possibility of exchange between the incident proton and the protons of the hydrogen molecule (compare figure 1 and text).

In many situations we know in advance from physical arguments which nuclei may be ' exchanged ' in a collision and therefore we know M_{sp} and the appropriate collision constants. For example, in a low energy collision of H_2O and H_2S the protons will not be exchanged between the two molecules (we might treat them as distinguishable, due to their attachment or S or O, respectively). Therefore the species of the group $S_{2,2}$ are collision constants (A_1, A_2, B_1, B_2, compare table 10). This corresponds to the very well-known fact that the interconversion between ortho and para isomers, say in collisions of H_2O and H_2S, is a rare event. The more rigorous selection rules from S_4 (including all possibilities of exchange) which can be derived as shown in § 4 would then be much less restrictive.

Another example in which it is not obvious *a priori* whether the species of $S_{2,2}$ are collision constants is provided by reaction (40):

$$CH_2+H_2D^+\rightarrow CH_2D+H_2. \tag{40}$$

If the experimental selection rules corresponded to $S_{2,2}$, then we might assume a direct deuteron transfer. It is more probable, however, that only the weaker selection rules from S_4 apply, corresponding to a compound mechanism with the bound intermediate CH_4D^+.

Similarly, the selection rules for the reaction (30 *a*) already discussed in § 4 would be much more restrictive if the mechanism was that of a simple charge exchange. Then the only allowed transitions between species of S_3 (or of D_{3h} with superscripts $'$ and $''$) are

$$\left.\begin{array}{r} A_1\leftrightarrow A_1, \\ A_2\leftrightarrow A_2, \\ E\leftrightarrow E. \end{array}\right\} \tag{41}$$

For the simple examples given, the conclusions about internal state selection rules arising from incomplete exchange are intuitively obvious in any case. This is no longer true in more complex situations in which the group theoretical method is still straightforward. We conclude this section with one such example which has already been the subject of a molecular beam study [51]:

$$F+CH_3-C_6H_5\rightarrow C_6H_5F+CH_3. \tag{42}$$

Assuming only nuclear spin symmetry conservation we would have to use the procedure of § 4 with a group $S_{7,8}{}^*$, of order $2\cdot 7!\cdot 8!$. However, the energies in the reaction intermediate $(CH_3C_6H_5F)^*$ are probably too low to allow for any scrambling between ring protons (carbons) and substituent protons (carbon). We may then use a much smaller group, $M_{S24}{}'$, of order 24 (isomorphous to $S_{2,3}{}^*$) to obtain approximate selection rules for reaction (42). The molecular symmetry group of the reactant toluene is of order 12, as discussed by Longuet-Higgins for the similar case of CH_3BF_2 [26]. For convenience, we give its character table in table 11. We write (ab) for the simultaneous permutation of the appropriate nuclei 'facing' each other in the benzene ring (taking the C–CH_3 axis as the axis of the mirror perpendicular to the ring plane). Longuet-Higgins has discussed how the ro-vibronic levels of molecules like toluene may be classified according to the species of this group. Note that the levels do not possess a well-defined parity (we use $'$ and $''$ instead of $\pm$ in the species designation).

The induced representations, $\Gamma(M_{S12})\uparrow M_{S24}{}'$, in the right-hand part of table 1 contain the selection rules for reaction (42) if we omit the parity designations. The species designations in $M_{S24}{}'$ (isomorphous to $S_{2,3}{}^*$) are useful for the $C_6H_5F+CH_3$ product states. We may carry over the definitions for $\Gamma(S_{2,3})$ in table 9 if we replace S_2 by the group $\{E, (ab)\}$ for fluorobenzene (compare also table 2), and use S_3 for CH_3. Overall parity determines the $\pm$ sign in the $M_{S24}{}'$ species. We have then, for example, that an $A_1{}''$ or $A_2{}''$ level of toluene will *not couple* with either the A_1 and the A_2 levels of C_6H_5F (in C_{2v}) or with the E' or E'' levels of CH_3 (in D_{3h}).

Table 11. Character table of the group M_{S12} for toluene and the induced representation $\Gamma(M_{S12})\uparrow M_{S24}'$ useful for obtaining the selection rules for reaction (42).

		2	3		2		
$\Gamma(M_{S12})$	E	(123)	(12)*	(ab)	(123)(ab)	(12)(ab)*	$\Gamma(M_{S12})\uparrow M_{S24}'$
A_1'	1	1	1	1	1	1	$A_1^+ + A_2^-$
A_2'	1	1	−1	1	1	−1	$A_2^+ + A_1^-$
E'	2	−1	0	2	−1	0	$E_1^+ + E_1^-$
A_1''	1	1	1	−1	−1	−1	$B_1^+ + B_2^-$
A_2''	1	1	−1	−1	−1	1	$B_2^+ + B_1^-$
E''	2	−1	0	−2	1	0	$E_2^+ + E_2^-$

We shall give no more examples, since the evaluation of approximate selection rules is straightforward in most cases. The concept of these additional collision constants may be based upon the concept of the constants of motion of an approximate Hamiltonian (in the sense of equation (4)), valid to within reasonable accuracy under certain conditions for the *collision problem.* A change in the conditions may change the selection rules. The very low energy scattering of protons off hydrogen molecules may follow quite different selection rules than those valid at 3·7 eV. Furthermore, the same collision constants are valid (to within a given approximation) for a reaction and its reverse. This imposes restrictions upon the groups of *feasible* permutations, M_{sp}, which one might introduce by some physical argument. Even in cases in which intuitively one might have suspected restrictions due to ' incomplete exchange ', a group M_{sp} smaller than the complete permutation group cannot always be found.

6. SYMMETRY CORRECTIONS IN STATISTICAL THEORIES OF SCATTERING

The selection rules derived so far simply tell us whether or not some transitions may occur. As a second simple application we shall discuss here the symmetry corrections for cross sections obtained from statistical theories of scattering such as phase space theory [21], the RRKM-models [22], and the statistical adiabatic channel model [23] (for a review see reference [12]).

Statistical theories in general are equivalent to parametrizing the $|S_{fi}|^2$-matrix such that all elements outside the diagonal are either zero or equal to some constant, usually, W^{-1}, the inverse of the number of dynamically accessible channels at energy E. For realistic statistical theories W is smaller than the number of asymptotically open channels, N, but for one of the possible statistical reference distributions in the information theoretic approach it is equal to N [28]. Obviously, one should apply such a parametrization to each diagonal block of the $|S_{fi}|^2$-matrix separately since it does not make sense to statistically allow transitions which are quite strongly forbidden by some selection rule. W (or N) should, therefore, be computed for each set of good quantum numbers $\{E, J, M, \Pi, \Gamma_1, \Gamma_2 \ldots\}$, where the Γ_i are the motional species in some permutation group as discussed above. The cross sections must be obtained by correctly summing with the proper weight over all diagonal blocks.

In general we have no experimental control of the nuclear spin state I, M_I. Thus, we may compute the cross section averaged over all nuclear spin functions consistent with the initial internal state combination, a, and summed over the nuclear spin functions consistent with the final state, b :

$$\sigma(b \leftarrow a) = \frac{\sum_m f_a(\Gamma_m) f_b(\Gamma_m) g_K(\Gamma_m) \sigma(\Gamma_m | b \leftarrow a)}{\sum_m f_a(\Gamma_m) g_K(\Gamma_m)}. \tag{43}$$

We imply that the probability for a transition between states of different nuclear spin species (and therefore motional species Γ_m) is zero. The frequencies of the motional species Γ_m in the initial state, a, and final state, b, are $f_a(\Gamma_m)$ and $f_b(\Gamma_m)$ respectively, and $g_K(\Gamma_m)$ is the nuclear spin statistical weight for the motional species Γ_m (in the appropriate permutation group).

As an example we may write out the inelastic cross section $\sigma(\Gamma_m | v', j' \leftarrow v, j)$, for collisions of an atom or ion with a diatomic molecule, summed and averaged over magnetic quantum numbers :

$$\sigma(\Gamma_m|v', j' \leftarrow v, j) = \frac{\pi}{2j+1)k_{vj}^2} \sum_{J=0}^{\infty} (2J+1) \sum_{\Pi=\pm 1} \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} |S_{v,j,l}{}^{v',j',l'}(E, J, \Pi, \Gamma_m)|^2. \tag{44}$$

We assume that $(v, j) \neq (v', j')$ and that the values of l and l' must satisfy the requirement for positive or negative overall parity, Π, respectively. In the case of collisions of protons with H_2 we have $f_a(\Gamma_m) = f_b(\Gamma_m) = 1 \neq 0$ only for $\Gamma_m = E$ if we require j to be even and j' to be odd (compare figure 1). For j and j' both being odd the species A_2 and E are possible (and so on). Formula (44) is easily extended to collisions of two polyatomic species. In statistical theories one would quite generally assume

$$|S_{fi}(E, J, \Pi, \Gamma_m)|^2 = W(E, J, \Pi, \Gamma_m)^{-1} \tag{45}$$

for the statistical range of the S-matrix and $|S_{fi}|^2 = \delta_{fi}$ otherwise. Since W is usually a large number, it would be quite cumbersome indeed to evaluate exactly all the dynamically accessible channels for all the possible combinations of the good quantum numbers, J, Π, Γ_m. The usual procedure is to neglect all symmetries but total angular momentum and to use, instead of equations (43)–(45), the simpler equation (46). For our example :

$$\sigma_t(v', j' \leftarrow v, j) = \frac{\pi}{(2j+1)k_{vj}^2} \sum_{J=0}^{\infty} (2J+1) \frac{W_t(E, J, v, j) W_t(E, J, v', j')}{W_t(E, J)}. \tag{46}$$

Here $W_t(E, J, v, j)$ replaces the sum over l. This sum is restricted by the same dynamical criterion as the one for $W_t(E, J)$ (depending on the particular model) [12]. In the adiabatic channel model we have, for example :

$$W_t(E, J) = \sum_{v,j} W_t(E, J, v, j) = \sum_{v,j} \sum_{l=|J-j|}^{J+j} h(E - V^J{}_{vjl_{\max}}). \tag{47}$$

Here we have the unit step function $h(x) = 0(1)$ for $x < 0$ (> 0) and the maximum of the adiabatic channel potential equal to $V^J{}_{vjl_{\max}}$.

It would be desirable to obtain a formula as simple as equation (46) but with some correction factors for symmetry and nuclear spin statistics in collisions of molecules with several identical nuclei. Parity is conveniently dealt with first. Equation (46) is then to be replaced by equation (47) (compare equation (44)) :

$$\sigma(v', j' \leftarrow v, j) = \frac{\pi}{(2j+1)k_{vj}^2} \sum_{J=0}^{\infty} (2J+1) \left\{ \frac{W^+(E, J, v, j) W^+(E, J, v', j')}{W^+(E, J)} + \frac{W^-(E, J, v, j) W^-(E, J, v', j')}{W^-(E, J)} \right\}. \tag{48}$$

The superscripts + or − indicate channels of positive or negative parity. In molecular collisions at moderate energies large values of J (and l) make dominant contributions. For large $j \gg 0$ we usually have then

$$W^+(E, J, v, j) \simeq W^-(E, J, v, j) \tag{49}$$

and we certainly have $W^+(E, J) \simeq W^-(E, J) \approx W_t(E, J)/2$. Equation (46) is then a good approximation to equation (48) unless j or j' are close to zero or unless

$W_t(E, J)$ is small. We shall consider hereafter that corrections due to parity conservation have been dealt with or may be neglected in this sense.

In order to deal with permutation symmetry, we assume that the channel numbers $W_{tr}(E, J)$ for the particular rearrangement channel r have been classified in some direct product group of the molecular symmetry groups of the two fragments for the arrangement r. We have to account for the degeneracy, g_{pr}, of the scattering channels thus evaluated. If we have only degeneracy for exchange *between* the two fragments, then :

$$g_{pr} = \prod_i \frac{n_i!}{k_{ir}!m_{ir}!}, \tag{50}$$

where the product is over all species i of nuclei (compare equation (11)). In the more general case, including inversion degeneracies, with groups M_{sa} for fragment a, M_{sb} for fragment b and only one kind of nuclei, we have :

$$g_{pr} = \frac{4n!}{ab}. \tag{51}$$

The total number of open channels summed over all rearrangement channels r is then

$$W(E, J) = \sum_r g_{pr} W_{tr}(E, J). \tag{52}$$

The number of channels for one particular species, Γ_m (of dimension $[\Gamma_m]$), of the full permutation group of order g ($=n!$ for one kind of particles) is given by equation (53) :

$$W(E, J, \Gamma_m) = [\Gamma_m] W(E, J)/g. \tag{53}$$

Note that each channel of species Γ_m is $[\Gamma_m]$-fold degenerate. Equation (53) states that the scattering channels (total number $W(E, J)$) may be reduced to give a multiple of the *regular representation*, R, of the full permutation group G of order g. In order to show under which conditions this is approximately true, we use the following lemmata :

$$R(G)\downarrow H = \frac{g}{h} R(H), \tag{54}$$

$$R(H)\uparrow G = R(G), \tag{55}$$

$$R \times \Gamma_m = [\Gamma_m] R. \tag{56}$$

Equations (54)–(56) follow directly from the properties of the regular representation (whose character is zero under all but the identity element, for which it is equal to the order of the group [36]). H is a subgroup of G, or order h. Equations (54)–(56) imply that equation (53) is true if the total number of *states* of the individual fragment molecules below the energy E ($W_1(E)$, $W_2(E)$ . . .) form a basis for the multiple of the regular representation of the molecules 1, 2, . . . in their molecular symmetry groups or in their point groups. For $E \to \infty$ this is a general property of the decomposition of the Hilbert space [33], whereas for $E \to 0$ it is certainly untrue. How well equation (53) is fulfilled at some finite energy can only be shown by explicit computation for each particular system. We have found that even for quite symmetrical systems equation (53) is reasonably valid as long as the necessary condition $W(E, J) \gg g$ is adequately fulfilled. Hereafter, we shall assume the validity of equation (53).

We are now in a position to give the symmetrized statistical $|S|^2$-matrix in equation (45) in terms of unsymmetrized (trivially counted) channel numbers W_t:

$$|S_{fi}(E, J, \Gamma_m)|^2 = g[\Gamma_m]^{-1}[\sum_r g_{pr} W_{tr}(E, J)]^{-1}. \tag{57}$$

Suppose that the initial internal state combination, a, in a collision is classified according to the Γ_a of the subgroup H_a of permutations excluding permutations between the collision partners. Similarly the final state b may be classified according to the Γ_b of the subgroup H_b, which may differ from H_a. Then we define the frequencies $f_a(\Gamma_m)$ by equation (58);

$$\Gamma_a \uparrow G = \sum_m f_a(\Gamma_m)\Gamma_m(G) \tag{58}$$

and similarly for $f_b(\Gamma_m)$. If we have classified a and b according to the species of some product of point groups or molecular symmetry groups, we may define the frequencies f_a in a similar way, as shown in § 3. With equations (43), (44), and (57) we obtain then the general statistical cross section averaged and summed over magnetic quantum numbers and nuclear spin states :

$$\sigma(b \leftarrow a) = \frac{\pi g}{g_a k_a^2} \left\{ \sum_{J=0}^{\infty} (2J+1) \frac{\bar{W}_t(E, J, a)\bar{W}_t(E, J, b)}{\sum_r g_{pr} W_{tr}(E, J)} \right\} \times \{ \sum_m g_K(\Gamma_m) f_a(\Gamma_m) f_b(\Gamma_m)/[\Gamma_m] \}. \tag{59}$$

The total degeneracy of the initial state, a, is given by

$$g_a = g_{Ka}(2j_{a1}+1)(2j_{a2}+1)$$

$$g_{Ka} = \sum_m f_a(\Gamma_m) g_K(\Gamma_m),$$

where j_{a1} and j_{a2} are the rotational quantum numbers of collision partners 1 and 2 in the overall reactant state a (whose nuclear spin statistical weight is just g_{Ka}). The order of the full permutation group is g ($n!$ for one kind of particles) and the g_{pr} are the various degeneracies of the scattering channels as discussed. The evaluation of the trivially counted $\bar{W}_t$ and W_t must be consistent with the choice of subgroups and the g_{pr}. We indicate by the bar over $\bar{W}_t(E, J, a)$ that channels with an intrinsic degeneracy $[\Gamma_a(H_a)] > 1$ are counted only *once* (compare equation (44)). Note that g_{pr} does *not* appear in connection with the numbers of channels leading to states a ($\bar{W}_t(E, J, a)$) and b.

The statistical cross section in equation (59) implies the selection rules discussed in § 4 through the second bracket. If a transition between states a and b is forbidden by symmetry, this bracket has the value zero.

If all the g_{pr} are equal to one g_p, which is always true for purely inelastic processes (including exchange), we can simplify equation (59) :

$$\sigma(b \leftarrow a) = \sigma_t(b \leftarrow a) F(b, a), \tag{59 a}$$

$$\sigma_t(b \leftarrow a) = \frac{\pi}{(2j_{a1}+1)(2j_{a2}+1)[\Gamma_a]k_a^2} \sum_{J=0}^{\infty} (2J+1) \frac{W_t(E, J, a) W_t(E, J, b),}{W_t(E, J)} \tag{60}$$

$$F(b, a) = \frac{g}{g_p[\Gamma_b] g_{Ka}} \sum_m g_K(\Gamma_m) f_a(\Gamma_m) f_b(\Gamma_m)/[\Gamma_m]. \tag{61}$$

The statistical cross section $\sigma_t(b \leftarrow a)$ is the one which one would normally compute, disregarding all symmetry and nuclear spin statistics effects (note that $W_t(E, J, a) = [\Gamma_a(H_a)]\bar{W}_t(E, J, a)]$). $F(b, a)$ is then an appropriate correction factor depending on the initial and final state species in H_a $(=H_b)$. It is only in this particular case with all the $g_{pr} = g_p$, however, that one can apply such a correction to $\sigma_t(b \leftarrow a)$. For instance, literature data which were obtained without symmetry considerations cannot always be simply corrected afterwards without having all the W_{tr} (which are, of course, never given). From the validity of equations (59)–(61) it follows also that

$$\sigma_a \equiv \sum_b \sigma(b \leftarrow a) = \sum_b \sigma_t(b \leftarrow a) = \sigma_{ta}.$$

If we average the correction factor $F(b, a)$ over a regular representation of final states b in the permutation group H_b, we obtain

$$\langle F(b, a) \rangle \equiv g(H_b)^{-1} \sum_{b=1}^{B} [\Gamma_b]^2 F(b, a) = 1. \qquad (62)$$

B is the number of species in H_b. If we have a situation with many final states b in a small energy range, forming a multiple of the regular representation of H_b, and all $\sigma_t(b \leftarrow a)$ being about equal, then equation (62) states that

$$\langle \sigma_t(b \leftarrow a) \rangle_b = \langle \sigma(b \leftarrow a) \rangle_b. \qquad (63)$$

The average is over the final states b. This means that for the computation of product translational energy distributions in molecular beam experiments at low resolution the calculation of $\sigma_t(b \leftarrow a)$ would be sufficient. Note, however, that we have required that all $g_{pr} = g_p$ and that $\sigma_t(b \leftarrow a) \neq f(b)$ for the considered range.

It has been shown [28] that the assumption $|S_{fi}(E, J)|^2 = N(E, J)^{-1}$ leads to one possible reference distribution in the information–theoretic approach, namely, disregarding permutation symmetry :

$$P_0(b) \propto g(b), \qquad (64)$$

where $g(b)$ is the statistical weight of b. The more common reference distribution is the microcanonical equilibrium distribution [29, 30] with an extra factor $\sqrt{[E_t(b)]}$. If all the g_{pr} are equal to one g_p, we can obtain with equation (61) a distribution including nuclear spin symmetry conservation :

$$P_0(b, a) \propto g(b) F(b, a). \qquad (65)$$

Equation (65) is a distribution with ' memory ' [28], i.e. the final state distributions depend on the initial state because of the selection rules implied in the factor $F(b, a)$.

We conclude this chapter with a few examples for $F(b, a)$ in some typical reactions. For proton-H_2 scattering (allowing for exchange by compound transitions, say, at low energies) we have :

$$\left.\begin{array}{l} F(g \leftarrow g) = 1 \quad (14/9), \\ F(u \leftarrow g) = 1 \quad (4/9), \\ F(g \leftarrow u) = 1/3\ (8/9), \\ F(u \leftarrow u) = 5/3\ (10/9). \end{array}\right\} \qquad (66)$$

The values in parentheses are for D^+/D_2 scattering.

Collisions of oxygen atoms with oxygen molecules in the electronic ground state may proceed statistically due to intermediate O_3 formation. We give the statistical symmetry corrections for ^{17}O ($I=5/2$) and ^{16}O ($I=0$, in parentheses), noting that the ground state of O_2 ($^3\Sigma_g^-$) is antisymmetric with respect to an exchange of the two nuclei :

$$\left.\begin{aligned} F(g\leftarrow g) &= 13/9\ (-), \\ F(u\leftarrow g) &= 5/9\ \ (-), \\ F(g\leftarrow u) &= 7/9\ \ (-), \\ F(u\leftarrow u) &= 11/9\ (2). \end{aligned}\right\} \tag{67}$$

In equations (66) and (67) we have indicated by g and u whether the rotational quantum number of the diatomic molecule is even or odd. Detailed statistical model calculations including symmetry corrections for collisions of O with O_2 have been given previously [23].

A more complex example is provided by reaction (36) in § 4.3 (and similarly by inelastic collisions of H_2 with CH_3^+). The corresponding matrix $F(\Gamma_b, \Gamma_a)$ is given in table 12, which is easily obtained with the aid of tables 8 and 9. In table 9 we have also included the definitions of Γ_a and Γ_b (in $H=S_{2,3}$) in terms of $\Gamma(S_2)\otimes\Gamma(S_3)$.

Table 12. The matrix $F(\Gamma_b, \Gamma_a)$ for the reaction $H_2+CH_3^+$ (or H_3^+).

Γ_a Γ_b	A_1	A_2	E_1	B_1	B_2	E_2
A_1	0	0	0	0	0	0
A_2	0	3	0	0	1	2
E_1	0	0	6/5	0	1/5	2/5
B_1	0	0	0	0	0	0
B_2	0	3	12/5	0	37/5	14/5
E_2	0	3/2	6/5	0	7/10	7/5

7. CONCLUSION

The symmetry considerations of the present paper lead to a number of selection rules for the internal ro-vibronic states of reactant and product molecules connected in a collision. These selection rules are probably quite strong, even for truly polyatomic systems with strong coupling of all but the nuclear spin degrees of freedom. Any deviations from the predicted behaviour could be due to the *coupling of the ro-vibronic and nuclear spin degrees of freedom*, which might occur particularly in systems with an overall electronic angular momentum. However, the strength of the *electronic spin–orbit coupling is unimportant* for the present considerations, and so is the validity of the Born–Oppenheimer approximation.

Although so far few experiments are available with sufficient detail to show these selection rules (the scattering of protons off hydrogen molecules is a case [10], but a rather trivial one as far as the selection rules are concerned) present day experimental techniques, in principle, are able to provide such data [7–13].

As in molecular spectroscopy, the selection rules for reactive scattering could then be used, for example, to infer the symmetry of electronic and vibronic states of unstable radical products in chemical reactions. From the more approximate selection rules of § 5 one can obtain conclusions about the detailed collision mechanisms without introducing perturbations by isotopic substitution.

Furthermore, we have shown that even in rather crude theoretical approaches, such as in statistical theories of scattering [12, 21–23], there are sizable, non-trivial symmetry corrections which may be easily computed with the present method. Detailed discussions of symmetry corrections in reactive collisions have previously been given only in connection with the quantum theory and semiclassical calculations for systems involving just *three* identical atoms [16–19].

We have not discussed, in the present communication, an application of some (potentially) practical importance which concerns differences in the selection rules for molecules differing only by isotopic substitution. The corresponding isotope effect does not depend on mass differences or ratios of the isotopes and would occur also for heavy atoms and nuclear isomers with negligible mass difference. Our treatment can also be used to discuss symmetry effects in angular distributions and in unimolecular reactions. These will be dealt with in detail separately.

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