

ROVIBRONIC CORRELATIONS AND SYMMETRY GROUPS OF NON-RIGID MOLECULES

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ABSTRACT

The symmetry groups of non-rigid molecules are employed in obtaining rovibronic correlation rules for general and simple reactions. The reaction system is considered as a supermolecule and the reaction itself is treated as a "transition" from reactants to products. The theory is applied to the general reactions: $(AC)_2 \rightarrow AC+AC$, $A_2+A \rightarrow A_2+A$ and $A_3(C_{2v})+A \rightarrow A_2+A_2$. The possibility of distinguishing between reaction paths is explored.

INTRODUCTION

Recent experimental advances in rovibronic state to state collisional cross section determinations (ref.1) have made desirable an extension of the electronic correlation schemes (ref.2) to include vibrational and rotational states. In doing the rovibronic correlations one tries to determine the symmetry allowed rovibronic states of the products given the rovibronic states of the reactants.

The general approach in such correlations is to consider the collision system as a supermolecule and the reaction itself as the transition from the initial state of the supermolecule (reactants) to its final state (products). The operator responsible for such a transition consists of one or more of the neglected terms of the exact hamiltonian of the collision system and therefore it must belong to the totally symmetric irreducible representation. In addition, the total angular momentum must be conserved and the nuclear spin statistics must be obeyed. Thus a correlation between the wavefunctions of the initial and final states may be achieved. This correlation becomes more or less unique when conservation of energy is also taken into consideration.

APPLICABLE GROUPS

The assumed transitions of the supermolecule may bring the system into two wildly different configurations, and this certainly qualifies it for a non-rigid molecule. The symmetry groups of such molecules are the well known permutation Inversion (PI) groups (ref.3, ref.4). The order of such groups depends on the feasibility or not of certain permutations. If all permutations are feasible the group is the so called Complete Nuclear Permutation Inversion (CNPI) group

(ref.4) and it has the highest possible order. Otherwise, its order is smaller and it is a subgroup of the CNPI group.

It is evident that the initial and final states of the supermolecule are essentially separate systems and may belong to different PI groups. If this is so, both groups must be subgroups of the PI group of the supermolecule. The PI group of the supermolecule is usually constructed by putting together in a set all feasible operations of the PI groups of both reactants and products and then checking to see if this set forms a group. This may lead to a group with order higher than the sum of the orders of the component groups since additional permutations may have to be included in the set to ensure closure. If the reaction may proceed through more than one paths a different PI group of the supermolecule may be involved in each path. This is so because each reaction path may be associated with different feasible permutations in the reactant and product groups.

METHOD OF CORRELATION

Once the appropriate PI group of the supermolecule has been determined, each of the irreducible representations (ir) of the reactant subgroup is correlated to an ir of the supermolecule group by comparing the characters of the common operations. Then each of the correlated ir of the supermolecule group is further correlated to an ir of the product subgroup in the same way. Next, the rovibronic wavefunctions of the reactants and products are classified according to the ir of their respective PI groups. Finally, the rovibronic wavefunctions of the reactants and products thusly classified are correlated to each other via the correlation of their respective ir.

The above correlation according to PI symmetry, eliminates many final states but many more are left which render such correlations far from unique. Thus, further narrowing down of possibilities may be persued by requiring conservation of total angular momentum, conservation of total energy as well as taking advantage of nuclear spin statistics. Here, however, we will consider correlations related only to PI symmetry conservation.

APPLICATIONS

First, let us examine the rovibronic correlations in complex formation and dissociation reactions of the type $C \rightarrow A+B$, where C is stable for a period of at least a few revolutions. In cases like this and if C is considered rigid, the PI group of the supermolecule is the same as the PI group of the separated A+B fragments and both are isomorphic to the point group corresponding to the assumed configuration of C. The assumption of rigidity is not essential as long as the PI group of a non-rigid C is the same (not just isomorphic) as that of the

A+B fragments. Of course, different wavefunctions (see below) will have to be used if the complex C is non-rigid.

Consider the dissociation of a stable and rigid $(AC)_2$ complex in a C_{2v} configuration, into its AC fragments: $(AC)_2 \rightarrow AC+AC$. The atoms of one AC fragment are numbered 1 and 2 while the atoms of the other AC fragment are numbered 3 and 4 (1,3 for A and 2,4 for C). The numbering of the atoms is arbitrary but it must be consistent throughout the reaction. We assume separability of the rotational-vibrational-electronic degrees of freedom as well as conservation of the electronic symmetry and we concentrate on the rotational-vibrational (rovibrational) correlations. The rovibrational wavefunction of $(AC)_2$ is given by:

$$\Psi_{J+n,K,M}(\Gamma_{rv}) = N \cdot \chi(\Gamma_v) \cdot A_{J+n,K,M}(\Gamma_r) \quad (1a)$$

χ is the vibrational wavefunction of Γ_v symmetry; A is the asymmetric top rotational wavefunction of Γ_r symmetry, which depends on whether J+n and K are even or odd (ref.5); χ is given in terms of Hermite polynomials in the normal modes and A is in terms of the symmetric top wavefunctions as follows (ref.5):

$$A_{J+n,K,M} = \sum_K' a_{J+n,K,M} \cdot S_{J+n,K,M} \quad (1b)$$

$$S_{J+n,K,M} = (1/\sqrt{2}) \left[|J,K,M\rangle + (-1)^n |J,-K,M\rangle \right], \quad n = 0,1 \quad (1c)$$

The prime in the summation sign indicates that only even or only odd K values are to be included. The classification of the wavefunctions χ , A and their combination shown in eq. (1a) are done easily in a previously shown way (ref.6, ref.7) although if there are degeneracies the task becomes more complicated (ref.8). The Γ_{rv} 's are shown in table 1 in terms of the Γ_v 's, J+n's and K's.

After dissociation a part of the vibrational and rotational energy of $(AC)_2$ is transferred into the relative motion of the two AC fragments. This energy is associated with a translational (orbital) wavefunction which here is approximated by $\phi_L(kR) \cdot Y_L^M(\theta, \phi)$ where R is the distance between the centers of mass (c.m.) of the two fragments and θ, ϕ are the Euler angles that define the direction of R in a space fixed coordinate system with origin at the c.m. of the two fragments. $\phi_L(kR)$ approaches a spherical Bessel function as the interfragment potential tends to zero, and Y_L^M is a spherical harmonic. The rovibrational-translational (transrovibrational) wavefunctions of the two fragments are obtained in the zeroth order approximation by assuming a zero interfragment potential:

$$\Psi_{l_1'l_2m}(\Gamma_{rv}) = N \cdot (\psi_{l_1'}^a + (-1)^m \cdot \psi_{l_1'}^b) \cdot \phi_L(kR) \cdot Y_L^M(\theta, \phi), \quad m = 0,1 \quad (2a)$$

with

$$\Psi_{11}^a = \chi_v(r) \cdot \chi_{v'}(r') \cdot Y_1^m(\vartheta, \varphi) \cdot Y_1^{m'}(\vartheta', \varphi') \quad (2b)$$

$$\Psi_{11}^b = \chi_{v'}(r) \cdot \chi_v(r') \cdot Y_1^{m'}(\vartheta, \varphi) \cdot Y_1^m(\vartheta', \varphi') \quad (2c)$$

where χ_v are the vibrational wavefunctions of the AC diatoms while Y_1^m are their rotational wavefunctions; r, ϑ, φ , are the usual spherical coordinates of each diatomic fragment. The appropriate PI group of the fragments is the four element group $PI(4) = \{E, (13)(24), E^*, (13)(24)^*\}$ which is isomorphic to the C_{2v} point group. The classification of the transvibrational wavefunctions according to the ir of the $PI(4)$ group are easily done as it has been shown previously (ref. 6). The Γ_{rv} 's are shown in table 1 in terms of the $1+1'+m$'s and $L+m$'s. This table is the correlation table of the wavefunctions of the $(AC)_2$ complex to those of the two AC fragments. It is the main result of conservation of the permutation-inversion symmetry in the dissociation reaction we have studied.

TABLE 1

Correlation table for the reaction $(AC)_2 \rightarrow AC+AC$ (eqs. 1 and 2). e/o denote even/odd values of the indicated quantities.

PI(4) Supermolecule	C_{2v} Complex $(AC)_2$			PI(4) Fragments AC+AC	
	Γ_v	J+n	K	1+1'+m	L+m
A_1	A_1	e	e	e	e
	A_2	o	e		
	B_1	o	o		
	B_2	e	o		
A_2	A_1	o	e	o	e
	A_2	e	e		
	B_1	e	o		
	B_2	o	o		
B_1	A_1	o	o	e	o
	A_2	e	o		
	B_2	e	e		
	B_1	o	e		
B_2	A_1	e	o	o	o
	A_2	o	o		
	B_2	o	e		
	B_1	e	e		

Now let us examine the rovibronic correlations in a reaction of the type $A+B \rightarrow [C] \rightarrow D+E$ where C represents an intermediate species not necessarily stable or rigid. The PI group of the supermolecule may either be the same as

that of the fragments on either side of C or it may contain the PI groups of these fragments as its subgroups depending on the path of the reaction.

Consider as the simplest meaningful reaction exhibiting this behavior the reaction $A_2+A \rightarrow [A_3] \rightarrow A_2+A$ where the atoms of the diatom are numbered 1 and 2 while the lone atom is numbered 3. Taking the reaction path $A_1-A_2+A_3 \rightarrow [A_1-A_2-A_3] \rightarrow A_1-A_2+A_3$ results simply in an energy transfer collision. The PI group of both the "reactants" and the "products" is $PI(4)_a = \{E, (12), E^*, (12)^*\}$ which therefore is also the PI group of the supermolecule. Taking the reaction path $A_1-A_2+A_3 \rightarrow [A_1-A_3-A_2] \rightarrow A_1-A_3+A_2$ results in an exchange reaction. The group of the reactants is the $PI(4)_a$ while the group of the products is $PI(4)_b = \{E, (13), E^*, (13)^*\}$. Clearly, the PI group of the supermolecule should contain $PI(4)_a$ and $PI(4)_b$ as subgroups and, as it turns out, it is the CNPI group of the $[A_1-A_3-A_2]$ species. This group has 12 elements and it is a cross product of S_3 and the inversion group: $PI(12) = S_3 \otimes \mathcal{E}$ with $\mathcal{E} = \{E, E^*\}$.

Because the groups of the two "products" contain different permutations - (12) for the energy transfer and (13) for the exchange reaction - one may pose the question of whether this fact could be used to distinguish between the two reaction paths. However, since the groups of the reactants and products in either path are $PI(4)$ groups, the correlations of their ir are the same even though in the exchange reaction one has to correlate via the $PI(12)$ group. Thus, in this case, no distinction is possible and the correlations are trivial since they involve essentially the same group. The zeroth order transrovibrational wavefunctions of the reactants and the products have the same form as follows:

$$\Psi_{1,L} = N \cdot \chi_V(r) \cdot Y_1^m(\theta, \phi) \cdot \phi_L(kR) \cdot Y_L^M(\theta, \phi) \quad (3)$$

Table 2 shows the symmetry of $\Psi_{1,L}$ in terms of the 1's and L's. This table serves also as a correlation table for this trivial case.

TABLE 2

Symmetries of the transrovibrational wavefunctions of the A_2+A system (eq. 3). e/o denote even/odd values of 1 and L.

$PI(4)_a, PI(4)_b$	A_1	A_2	B_1	B_2
1	e	e	o	o
L	e	o	e	o

Consider now the reaction $A_3(C_{2v})+A \rightarrow [A_4] \rightarrow A_2+A_2$ where the central atom in A_3 is numbered 1, the two side atoms are numbered 2 and 3 and the lone atom is numbered 4. The above reaction can take place either by A attacking the center atom of A_3 or by A attacking one of its side atoms. In the first case the

products will be $A_1-A_4+A_2-A_3$ while in the later case they will be $A_1-A_2+A_3-A_4$ (or equivalently $A_1-A_3+A_2-A_4$). The group of the reactants is $PI(4) = \{E, (23), E^*, (23)^*\}$. The group of the center attack products is $PI(16)_a = S'_{4a} \otimes \mathcal{E}$ where $S'_{4a} = \{E, (14), (23), (14)(23), (12)(43), (13)(42), (1243), (1342)\}$ while the group of the side attack products is $PI(16)_b = S'_{4b} \otimes \mathcal{E}$ where $S'_{4b} = \{E, (12), (34), (12)(34), (13)(24), (14)(23), (1324), (1423)\}$ or the equivalent $S''_{4b} = \{E, (13), (24), (13)(24), (12)(34), (14)(23), (1234), (1432)\}$. The $PI(4)$ group is a subgroup of the $PI(16)_a$, because of the common operations (23) and $(23)^*$, but it is not a subgroup of $PI(16)_b$. Therefore, the group of the supermolecule in the center attack mechanism is the $PI(16)_a$ group while in the side attack mechanism it must contain at least the $PI(4)$ and the $PI(16)_b$ groups. As it turns out, the supermolecule group in the side attack mechanism is the CNPI group of the $[A_4]$ species, which is the group $PI(48) = S_4 \otimes \mathcal{E}$.

Because of the above differences there is the possibility that the center and side attack mechanisms may result in different correlations. This possibility is further explored below. The transrovibrational wavefunction of the reactants is similar to eq. (1a) with the addition of the orbital part:

$$\Psi_{J+n,K,L}(\Gamma_{rv}) = N \cdot \chi(\Gamma_v) \cdot A_{J+n,K,M}(\Gamma_r) \cdot \phi_L(kR') \cdot Y_L^M(\theta', \phi') \quad (4)$$

with A given by eq. (1b). The transrovibrational wavefunction of the products is identical to that given by eqs. (2). The classification of these wavefunctions (eqs. 2 and 4) according to the ir of the respective groups are done as previously shown (ref. 7, ref. 9). However, the correlations of the ir for the side attack mechanism must be done via the $PI(48)$ group while the correlations of the ir for the center attack mechanism must be done directly. The two correlations, shown in table 3, differ in that the side attack mechanism allows for fewer product states than the center attack mechanism. This is because the $PI(48)$ group has only four one dimensional ir while the $PI(16)$ group has eight such ir (ref.

TABLE 3

Correlations of the ir of the $PI(4)$ group to the ir of the $PI(16)_b$ (via $PI(48)$) and $PI(16)_a$ groups.

$PI(16)_b$	$PI(4)$	$PI(16)_a$
A_1^+	A_1	A_1^+, B_2^+
B_1^-	A_2	B_1^-, A_2^-
A_1^-	B_1	A_1^-, B_2^-
B_1^+	B_2	B_1^+, A_2^+

4). The correlations of the wavefunctions for both mechanisms are shown in table 4. Note that in both cases the same combination of even/odd values of the rotational quantum numbers is involved but in the center attack mechanism the additional + or - sign combinations in eqs. (2) is allowed.

TABLE 4

Correlation table for the reaction $A_3(C_{2v})+A \rightarrow A_2+A_2$ for both center and side attack mechanisms (eqs. 2 and 4). e/o indicate even/odd values of the shown quantities.

Center attack products PI(16) _a				Reactants PI(4)			Side attack products PI(16) _b			
l	l'	L	m	Γ_v	K	J+n+L'	l	l'	L	m
e	e	e	e	A ₁	e	e	e	e	e	e
e	e	e	o	A ₂	e	o				
				B ₁	o	o				
				B ₂	o	e				
e	e	o	o	A ₁	e	o	e	e	o	o
e	e	o	e	A ₂	e	e				
				B ₁	o	e				
				B ₂	o	o				
o	o	o	o	A ₁	o	o	o	o	o	o
o	o	o	e	A ₂	o	e				
				B ₁	e	e				
				B ₂	e	o				
o	o	e	e	A ₁	o	e	o	o	e	e
o	o	e	o	A ₂	o	o				
				B ₁	e	o				
				B ₂	e	e				

DISCUSSION

We have presented rovibronic correlation rules for certain types of reactions for cases where the electronic symmetry is conserved. The usefulness of such rules as shown in tables 1, 2 and 4 may be diminished by the entry into the picture of the orbital angular momenta. An exception to this are complex formation or dissociation reactions where there is only one orbital angular momentum, L, involved. Due to the conservation of the total angular momentum, L is related to the other angular momenta of the fragments via the addition theorem and the known rotational angular momentum of the complex.

An intermediate product of the derivation of the correlation rules is the determination of the symmetry of the transrovibrational wavefunctions. This could lead to the construction of accurate rovibrational wavefunctions for non-rigid molecules. They would consist of sums of the symmetry selected zeroth order

wavefunctions of the two fragments separated along the coordinate of non rigidity. It could also lead to block diagonalization of the secular equation matrix in rovibrational energy calculations of non-rigid molecules (ref.10).

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