Symmetry selection rules in inelastic collisions of diatomic molecules in 3Π electronic states

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Recently, considerable attention has been devoted to collisions involving open-shell diatomics, [1-5] where the manifold of rotational levels is split by interactions with the electronic spin or orbital angular momenta. Some experimental work[5] has indicated that certain transitions between the various symmetry and parity doublets are more favored than others. In a series of papers we have shown[2-4] how this type of propensity rule can be derived starting from a rigorous quantum formulation of the collision dynamics. In the present note we extend this type of analysis to collisions of molecules in $^3\Pi$ electronic states, where several new selection rules can be derived, which do not apply to the systems examined previously.

In Hund's case (a) the wave function for a diatomic molecule is written as[6]

$$|JM\Omega v\Lambda S\Sigma\rangle = |JM\Omega\rangle\,|v\Lambda S\Sigma\rangle\,, \qquad (1)$$

where J denotes the total angular momentum and the other quantum numbers have their usual meaning. For a $^3\Pi$ electronic state, $S = 1$ and for simplicity will be suppressed. It is convenient to use the definite parity states

$$|JM\Omega, \epsilon = \pm 1, v\rangle = |JM\Omega^f_\epsilon v\rangle$$
$$= 2^{-1/2}[\,|JM\Omega\rangle\,|v\Omega\Sigma\rangle \pm |JM, -\Omega\rangle\,|v, -\Lambda, -\Sigma\rangle\,]\,, \qquad (2)$$

where Ω will be hereon assumed to be a positive number (or zero). For a $^3\Pi$ electronic state this index can be $0(\Lambda = \pm 1, \Sigma = \mp 1)$, $1(\Lambda = \pm 1, \Sigma = 0)$, or $2(\Lambda = \pm 1, \Sigma = \pm 1)$. The total parity of the $|JM\Omega\epsilon v\rangle$ functions is[7] $\epsilon(-1)^{J-1}$. In contemporary spectroscopic notation,[8] the $\epsilon = -1$ levels, with parity $(-1)^J$, are labeled e, and the $\epsilon = +1$ levels, with parity $-(-1)^J$, are labeled f.

In the case (a) limit[6,9] the spin-orbit splitting is much larger than BJ, where B is the rotational constant, so that the $\Omega = 0$, 1, and 2 rotational manifolds are widely separated, at least at low J. Transitions can be either elastic in Ω, corresponding to rotationally inelastic processes within a particular spin-orbit manifold, or inelastic in Ω, corresponding to transitions between two spin-orbit manifolds.

For both situations, in the general treatment of the collision with a structureless target, one expands[1,2] the overall wave function in eigenfunctions of the total angular momentum $\mathcal{J}$, which are designated $|JL\Omega\epsilon v\mathcal{J}\mathfrak{M}\rangle$, where L is the orbital angular momentum and $\mathfrak{M}$, the space-fixed projection of $\mathcal{J}$. The inelastic scattering amplitude can be expressed in terms of inelastic T-matrix elements, which are solutions to the so-called

close-coupled equations.[1,2,10] The coupling between the individual $|JL\Omega\epsilon v\mathcal{J}\mathfrak{M}\rangle$ channels is governed by a potential matrix, whose elements represent an effective electrostatic potential, obtained by integration over the electronic and vibrational coordinates. The symmetry properties of this potential have been discussed by several authors.[1,2] Without giving any details we present only the explicit expression, namely,[2]

$$V^{\mathcal{J}}_{J'L'\Omega'\epsilon'v', JL\Omega\epsilon v}(R) = (-1)^{J+J'+\mathcal{J}-\Omega}[(2J+1)(2J'+1)$$
$$\times (2L+1)(2L'+1)]^{1/2} \sum_l F^l_{J\epsilon, J'\epsilon'}\begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \begin{Bmatrix} J & L & \mathcal{J} \\ L' & J' & l \end{Bmatrix}\left[A^{v'\,v}_l(R)\begin{pmatrix} J' & l & J \\ -\Omega' & 0 & \Omega \end{pmatrix} + \epsilon I(\Omega, \Omega')\right.$$
$$\left. \times B^{v'\,v}_l(R)\begin{pmatrix} J' & l & J \\ -\Omega' & 2 & -\Omega \end{pmatrix}\right]\,, \qquad (3)$$

where $(:::)$ and $\{:::\}$ are $3j$ and $6j$ symbols, respectively,[11] and $A^{v'\,v}_l(R)$ and $B^{v'\,v}_l(R)$ are functions arising from the expansion of the atom molecule interaction potential. Here

$$F^l_{J\epsilon, J'\epsilon'} = \tfrac{1}{2}[1 + \epsilon\epsilon'(-1)^{J+J'+l}]\,, \qquad (4)$$

and

$$I(\Omega, \Omega') = 1\,, \quad \text{if } \Omega = \Omega' = 1\,; \quad \Omega = 0,\ \Omega' = 2\,;$$
$$\text{or } \Omega = 2,\ \Omega' = 0\,,$$
$$= 0\,, \quad \text{otherwise}\,. \qquad (5)$$

The $I(\Omega, \Omega')$ term reflects the fact that for purely electrostatic coupling the spin projection quantum number cannot change.

We observe that because of the sum rule for the denominators of the $3j$ symbols in Eq. (3),[11] the coupling will always vanish between the $\Omega = 1$ rotational levels and the $\Omega = 0$ or $\Omega = 2$ rotational levels. *Thus collision induced transitions between the $^3\Pi_1$ and $^3\Pi_0$ or $^3\Pi_2$ rotational manifolds will be rigorously forbidden.* On reflection this is not surprising, since a purely electrostatic interaction can not lead to changes in the spin projection quantum number, so that the $\Omega = 1$ manifold, with $\Sigma = 0$, will not be collisionally coupled to the $\Omega = 0$ and $\Omega = 2$ manifolds, with $\Sigma = \pm 1$.

In the case of transitions within the $^3\Pi_0$ manifold ($\Omega = \Omega' = 0$), the second term in square brackets in Eq. (3) will not contribute, and, due to the symmetry of the $3j$ symbol,[11] the first term will contribute only if $(J'$

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$+ l + J$) is even. This implies, from Eq. (4) that the coupling will vanish unless $\epsilon = \epsilon'$. Thus, if we ignore the coupling to the $\Omega = 2$ spin-orbit state, *collisional change of the e/f symmetry index will be rigorously forbidden in the* $^3\Pi_0$ *manifold*. If the separation between the $\Omega = 0$ and $\Omega = 2$ spin-orbit manifolds is large compared to the rotational spacings within the $\Omega = 0$ manifold, then transitions between levels of different e/f symmetry arising from $\Omega = 0 \to \Omega = 2 \to \Omega = 0$ coupling will be weak, so that even when this higher order coupling effect is taken into account a strong propensity towards conservation of e/f symmetry will still be apparent for transitions within the $\Omega = 0$ manifold.

We point out that the derivation of both selection rules in the preceding two paragraphs does not depend on a particular dynamical limit; and thus both rules are completely general. Furthermore, since the derivation depends only on the symmetry properties of the potential, the propensity rules will apply to the S-matrix itself, and, consequently, to both differential and integral cross sections, either M dependent or degeneracy averaged. In several previous articles[2,4] we have shown how a propensity toward e/f symmetry conservation will apply to all open-shell diatomics, in a case (a) limit, whenever either a Born[12] or infinite-order-sudden[13] description of the dynamics is valid. This more restrictive propensity rule will also apply here, to transitions within the $\Omega = 1$ and $\Omega = 2$ manifolds.

With increasing J, the orbit-rotation terms in the molecular Hamiltonian will mix together more strongly the three spin-orbit manifolds, so that a pure case (a) description is no longer appropriate.[6,9] The two propensity rules derived here will then no longer apply. Recently, Alexander and Dagdigian[4] have investigated symmetry selection rules for collisions of molecules in $^3\Sigma$ electronic states, in the general case of intermediate coupling. A similar approach could be applied to collisions of $^3\Pi$ molecules.

Obviously, it would be desirable to have experimental verification of the selection rules derived here. In recent studies of the reaction of Mg atoms with N_2O, Field and co-workers[14] have observed differences in the e/f level populations in MgO($a\,^3\Pi$) molecules formed in a flame. It is intriguing to speculate whether the underlying kinetics reflect, to some extent, the propensity for e/f conservation discussed in the present article.

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Laboratory measurements in the energy range 0.02–1 eV of the rate constants of ion–molecule reactions involving CS+

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The kinetics of ion–neutral reactions involving sulfur-bearing ions is of interest for the interpretation of molecules synthesized in the interstellar medium. To the present date ten molecules containing sulfur have been detected within dense clouds in the interstellar medium. Oppenheimer and Dalgarno[1] have proposed a chemical scheme for the creation and destruction of interstellar molecules that contain sulfur. In a recent paper Duley *et al.*[2] pointed out the difficulties encountered in using gas phase chemistry to explain the formation of several molecules. Moreover, they have recalculated the abundances of sulfur-bearing molecules using the reaction