

## **Influence of exchange symmetry on low temperature ion - molecule reactions**

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### **Symmetry selection rules**

In general, molecular systems change their quantum numbers under the influence of an external interaction. Depending on the symmetry of the Hamiltonian of the unperturbed system and the strength and the properties of the perturbation, there can be correlations between the set of quantum numbers before and after the interaction. Well-known examples include the rather stringent selection rules in a bound-bound transition via emission or absorption of a photon, or the propensity rules governing autoionization. A rather complicated situation is the interaction of two molecules during a collision, especially if they undergo a chemical reaction. If this happens in the gas phase, at least the total energy, the total momentum, the total angular momentum and the parity are good quantum numbers. If one assumes, in addition, that the nuclear spin is separately conserved, more restrictive selection rules are found to occur in systems involving identical nuclei, a consequence of permutation symmetry. Applications to collision systems involving two or three identical atoms are rather trivial while the consequences for reactions of polyatomic systems are more complicated to predict. A rigorous theoretical description how to obtaining selection rules for state specific or state-to-state reactions has been presented by Quack [qua77].

In some collision processes, even more restrictive selection rules can be found if additional dynamical constraints limit the accessible phase space. For example, in a direct inelastic collision the exchange of identical nuclei may be incomplete because of a too short interaction. Another extreme concerns long lived and strongly coupled intermediates, in which all degrees of freedom are completely mixed. In this situation the scattering process can be described by a suitable statistical theory. Such a theory has to account for all conserved quantum numbers, including the symmetry corrections and nuclear spin statistics. So far, only a few reactions have been treated thoroughly in this way, e.g.,  $\text{H}^+ + \text{H}_2$  and isotopic variants (see [ger02b] and references therein).

### **Interstellar chemistry**

A wide field, where symmetry selection rules in reactions play a fundamental role, is the chemistry of the interstellar medium which is quite different from other chemical systems since low densities ( $< 10^7 \text{ cm}^{-3}$ ) and low temperatures (10 K in dense molecular clouds) prevail. There are two major reasons for that. One is the presence of o- $\text{H}_2$  (almost exclusively  $\text{H}_2(j=1)$ ) with a non-thermal probability, affecting not only the overall energy content but carrying also the total nuclear spin  $I = 1$ . The other is the existence of deuterium. Although the typical D / H abundance is only a few  $10^{-5}$ , a wide variety of deuterated molecules has been observed with much higher abundances. For example an  $\text{H}_2\text{D}^+ / \text{H}_3^+$  abundance ratio of 0.2 can be achieved, if one assumes an HD/ $\text{H}_2$  ratio of  $4 \times 10^{-5}$  and utilizes recently published data from low temperature measurements [ger02a]. In the past, the isotope enrichment in a cold environment has been predominantly explained by the differences in zero point energies, but it is now known that also restrictions imposed by the permutation symmetry and which are released when identical atoms are substituted by distinguishable isotopes, determine the outcome of such reactions [ger02b]. In addition, dynamical effects such as the mass dependence of centrifugal barriers restricting the scrambling within the collision complex, can affect the outcome of a chemical reaction.

In this contribution an overview of ion molecule reactions involving identical atoms (mainly H and D) is given. Experimental evidence is presented that, at low temperatures, traces of o-H<sub>2</sub> can lead to significant perturbations in the state population of molecules containing two or more hydrogen atoms. It is also pointed out, that one needs state specific rate coefficients not only for the formation and destruction of the molecules of interest but also for inelastic collisions, especially with H<sub>2</sub>(j=1), in order to predict quantitatively the intensities observed, e.g., by radio astronomers.

### Experimental approaches

So far only a few experimental studies could actually proof the influence of selection rules in chemical reactions. In principle, highly sophisticated crossed beam experiments or laser based studies are able to provide results on a state to state level required usually for observing such effects. One simple but convincing experimental proof of nuclear spin conservation is the exothermic but slow ortho-para conversion reaction  $H^+ + H_2(j=1) \rightarrow H^+ + H_2(j=0)$  observed in a differential scattering experiment using translational spectroscopy [ger90]. Observing the relative intensities of o-H<sub>3</sub><sup>+</sup> and p-H<sub>3</sub><sup>+</sup> absorption lines, ortho-para conversion via H<sub>3</sub><sup>+</sup> + H<sub>2</sub> collisions has been observed experimentally in a hydrogen plasma [cor00]. Using pure p-H<sub>2</sub> and n-H<sub>2</sub> as discharge gases some evidence for the influence of nuclear spin selection rules has been obtained.

Low temperature ion trapping techniques are not only well-suited for studying collision processes of astrochemical relevance but also can give information on the influence of selection rules in reactions. For example, association rate coefficients measured for CH<sub>3</sub><sup>+</sup> + H<sub>2</sub> collisions in different ion traps, have been under debate for some time. Meanwhile, reliable results for CH<sub>5</sub><sup>+</sup> formation are available for both p-H<sub>2</sub> and o-H<sub>2</sub> [ger95], although it is interesting to read the semi-quantitative discussion of heating via ortho-hydrogen by Bates [bat91]. Several new results for H<sup>+</sup>, H<sub>3</sub><sup>+</sup>, C<sub>2</sub>H<sub>2</sub><sup>+</sup> and CH<sub>3</sub><sup>+</sup> ions colliding with well-defined mixtures of p-H<sub>2</sub>, o-H<sub>2</sub> and HD or D<sub>2</sub> have been discussed recently [ger02b].

The four-atomic system  $H_2^+ + H_2 \rightarrow H_3^+ + H$  has been treated theoretically in [qua77]. It has been shown that p-H<sub>3</sub><sup>+</sup> can be formed exclusively if both reactants are in the para-form. If, however, one or both molecules are in an odd rotational state, the situation is less obvious. A simple reaction model has been discussed in [cor00], based on the questionable assumption that one can distinguish between proton hopping and atom exchange and that these simple reactions mechanisms are connected with additional nuclear spin selection rules. A correct statistical consideration must start with formation of complexes having total nuclear spins I = 0, 1, or 2 with weights 2I + 1. Those with I = 0 can only decay to p-H<sub>3</sub><sup>+</sup>, and those with I = 2 only to o-H<sub>3</sub><sup>+</sup>. The decay of I = 1 complexes can contribute to both channels, at high temperatures with equal weight. Another problem, also discussed in [cor00], is the inelastic scattering and scrambling reaction in H<sub>3</sub><sup>+</sup> + H<sub>2</sub> → H<sub>3</sub><sup>+</sup> + H<sub>2</sub> collisions. For example, the equilibrium o-H<sub>3</sub><sup>+</sup> / p-H<sub>3</sub><sup>+</sup> at a fixed o-H<sub>2</sub> / p-H<sub>2</sub> ratio and a given translational temperature is still an open question.

Such information can be obtained by combining low temperature trapping methods with suitable lasers. The population of specific states can be obtained via laser-induced reactions, e.g., infrared laser induced reconversion of H<sub>2</sub>D<sup>+</sup>. Another approach is the time dependent modification of the stored ion ensemble by optical pumping providing state-to-state rate coefficients.

### H<sub>3</sub><sup>+</sup> + H<sub>2</sub> and deuterated analogues

The singly deuterated H<sub>2</sub>D<sup>+</sup> ion which is of special importance in interstellar chemistry for deuterating other molecules, was detected recently in emission via the 1<sub>10</sub>-1<sub>11</sub> ortho-transition at 372 GHz [sta99]. It is formed via the proton - deuteron exchange reaction



which is exothermic by 232 K in the left-to-right direction. The exothermicity is sufficient to produce  $\text{H}_2(j=1)$  or to form  $\text{H}_2\text{D}^+$  in its excited  $1_{01}$ ,  $1_{11}$ ,  $1_{10}$ ,  $2_{02}$ , and  $2_{12}$  states, of which  $1_{11}$  is the lowest state of ortho symmetry. Reaction (1) has been studied in a low temperature multipole ion trap at 10 K [ger02a]. The rate coefficient for the forward reaction has been found to be significantly smaller than previously accepted. The rate coefficient for the backward reaction has been determined for n- $\text{H}_2$  and p- $\text{H}_2$  (purity 99%±1%) and found to be much higher than the values derived from the equilibrium constant. Although all energy levels of the involved molecules and the potential energy surface of the collision complex are well known, there exist no detailed calculation of the reaction dynamics describing the formation and destruction of  $\text{H}_2\text{D}^+$ . In addition, as discussed in [pag92] and emphasized in [ger02a], also the inelastic collisions of  $\text{H}_2\text{D}^+$  are not yet well-enough understood, especially the pumping o- $\text{H}_2\text{D}^+$  via collisions with traces of o- $\text{H}_2$ . It is a consequence of nuclear spin restrictions that relaxation of o- $\text{H}_2\text{D}^+(1_{11})$  in collisions with p- $\text{H}_2(j=0)$  is not efficient since the exothermic product channels p- $\text{H}_2\text{D}^+(0_{00})$ +p- $\text{H}_2(j=0)$  and p- $\text{H}_2\text{D}^+(1_{01})$ +p- $\text{H}_2(j=0)$  are forbidden and formation of p- $\text{H}_2\text{D}^+(0_{00})$ +o- $\text{H}_2(j=1)$  is endothermic. Collisions of o- $\text{H}_2\text{D}^+(1_{11})$  with o- $\text{H}_2(j=1)$  can lead to even higher energies in the ion and, finally, to an efficient destruction of  $\text{H}_2\text{D}^+$  via the endothermic reverse reaction (1).

Closer inspection of the PES reveals that, for  $\text{H}_5^+$ , the five H atoms are not equivalent in the collision complex. The "structure" may be better described as an  $\text{H}_3^+-\text{H}_2$  cluster ion or as an agglomerate where one proton can jump back and forth between two hydrogen molecules. As can be seen from the calculations, each jump requires a readjustment of the two H-H distances between the two values which are close to those of the free  $\text{H}_2$  and  $\text{H}_3^+$  molecule, 0.075 nm and 0.083 nm, respectively. The approximate picture that only the positive nucleus is transferred and that two electrons remain predominantly on "each side" is in accordance with the *ab initio* calculations.

### **$\text{CH}_3^+ + \text{H}_2$ and deuterated analogues**

Protonated methane,  $\text{CH}_5^+$ , is a so-called hypercoordinated carbocation, i.e. the proton is bound to the methane via a three-center-two-electron (3c-2e) bonding. It is the prototype of a strongly bound but very floppy molecule. Despite many spectroscopic efforts culminating in high-resolution infrared spectra [whi99], the structure of this fluxional molecular ion is an object of an ongoing debate [kra99] since the spectra are still awaiting an assignment. One of the basic questions is, whether all five hydrogen atoms are chemically equivalent or whether the 3c-2e bond favors a specific structure, e.g., a separate  $\text{H}_2$  sub-unit bound to a  $\text{CH}_3^+$  ion [mar99]. In order to correctly interpret the outcome of scrambling collisions, the symmetry selection rules must be known.

There are various reactions proceeding via, leading to, or starting with  $\text{CH}_5^+$ . The exothermic reaction  $\text{H}^+ + \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{H}_2$  has been discussed in [qua77]. Probably it is a direct reaction but, even with complete scrambling of the protons, selection rules restrict the outcome. For example there will be no creation of p- $\text{H}_2$  with  $\text{CH}_3^+$  in a degenerate state if  $\text{CH}_4$  were initially in a totally symmetric state. Formation of  $\text{CH}_5^+$  via radiative association has been mentioned above [ger95] while the reaction  $\text{CH}_4^+ + \text{n-H}_2 \rightarrow \text{CH}_5^+ + \text{H}$  has been studied only recently in a variable temperature 22-pole ion trap from room temperature down to 15 K [asv03a]. The reaction is rather slow at 300 K but significantly faster at 15 K. This behavior is tentatively explained with dynamical restrictions but also may be caused by statistical factors.

An interesting result, probing directly the  $\text{CH}_5^+$  ion, has been obtained by storing this ion in pure HD at low temperatures. No H-D scrambling could be observed at all (rate coefficient

smaller than  $5 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ ) indicating the closed shell structure of this floppy molecular ion [asv03b]. In contrast efficient deuteration has been measured in the collision



In this 370 K exothermic reaction, the detailed structure of the  $\text{CH}_5^+$  ion is probably less important because the total energy of the collision complex is above the dissociation limit. Nonetheless there are strong indications that symmetry selection rules play an important role as indicated by a comparison of the following three different experimental results:

**Table 1.** Rate coefficients for deuteration of  $\text{CH}_3^+$  at 15 K using different relaxation conditions.

Reaction	$k / \text{cm}^3 \text{s}^{-1}$	Remarks
a) $(\text{CH}_3^+)_a + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2$	$(1.65 \pm 0.1) \times 10^{-9}$	pure HD
b) $(\text{CH}_3^+)_b + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2$	$(0.4 \pm 0.2) \times 10^{-9}$	relaxation in p- $\text{H}_2$
c) $(\text{CH}_3^+)_c + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2$	$(1.5 \pm 0.8) \times 10^{-9}$	relaxation in n- $\text{H}_2$

In case a) pure HD has been used [asv03] while in the other two cases,  $\text{CH}_3^+$  was stored in hydrogen containing HD just in the global terrestrial abundance of  $[\text{HD}] / [\text{H}_2] = 3 \times 10^{-4}$ . In case b) the hydrogen was converted into p- $\text{H}_2$  while in case c) n- $\text{H}_2$  was used [ger02b]. Comparison of the rate coefficient determined in case a) with the collisional rate reveals that all primary ions are immediately deuterated, i.e., the reaction is so fast, that there is no relaxation or ortho-para conversion. It is important to note that the number of primary ions undergo a mono-exponential decay over three orders of magnitude and that collisional cooling with He does not change significantly the results. Storing  $\text{CH}_3^+$  ions in n- $\text{H}_2$  does not change the rate coefficient. Of course, the errors are rather large since only a small fraction of the collisions are with HD and since the data evaluation has to account for backward reactions. Despite the resulting large errors it is clear that relaxation of  $\text{CH}_3^+$  in p- $\text{H}_2$  reduces the reactivity by a significant factor.

It is not yet understood why p- $\text{CH}_3^+$  does not so easily undergo an exchange reaction with HD. As discussed above for reaction (1) the rate coefficient is determined by the mobility of H, D or also HD in the collision complex. Theoretical calculations of the potential energy surface indicate [mar99] that binding to the central C-atom seems to make all five hydrogen atoms rather equivalent and that there are no barriers hindering an efficient exchange. Is result b) a hint to a nuclear-spin protected structure in the p- $\text{CH}_3^+$ -HD collision complex?

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