Observation of Ortho-Para H_3^+ Selection Rules in Plasma Chemistry

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(Received 25 November 1996)

Intensity ratios of infrared spectral lines of ortho- and para-H_3^+ have been measured in hydrogen plasmas using normal and para-H_2. Large dependences of the intensity ratios on the parent gases have been observed, indicating the spin memory of protons even after chemical reactions. The results clearly demonstrate the existence of selection rules on nuclear spin modifications in chemical reactions theoretically anticipated by M. Quack [Mol. Phys. **34**, 477 (1977)]. [S0031-9007(97)03170-0]

PACS numbers: 33.15.–e, 33.20.Ea, 34.90.+q

Selection rules that relate quantum states before and after various physical and chemical processes are fascinating subjects which reflect both the symmetry and the orders of magnitude of the physicochemical interactions. It is well known that the ordinary radiative processes of atoms and molecules, spectroscopy, obey the most rigorous selection rules [1] while collisional processes obey less rigorous selection rules [2]. This is because (a) molecules retain higher symmetry in a more homogeneous field in the former processes than in the latter, and (b) the magnitude of interaction is much smaller in the former, thus its higher order effect is negligible. In both processes, however, the selection rules related to the nuclear spin quantum numbers, which result from the invariance of both interactions for permutations of identical nuclei, hold most rigorously. In this paper we give experimental evidence that such selection rules hold even for the most violent of molecular processes, that is, chemical reaction in gases. In contrast to radiative and collisional processes where molecules retain their identities, atoms are rearranged in chemical reactions. Most quantum numbers pertinent to reactants have lost their meaning in products. Nuclear spins, however, keep their memory throughout the process because of the weakness of nuclear magnetic interactions, and therefore manifest some selection rules.

The existence of such selection rules has been anticipated in the classic theoretical paper by Quack [3]. However, the photodissociation study of formaldehyde by Schramm, Bamford, and Moore [4], in which they showed that only ortho-H_2 results from ortho-H_2CO, seems to be the only experimental verification of this theme [5]. The para-H_2 induced polarization observed in NMR spectroscopy [6,7] is a manifestation of such an effect in the condensed phase.

In this paper we report our observation of the selection rules related to ortho- and para-H_3^+ in pure hydrogen plasmas. Our work is qualitatively different from the previous work mentioned above and addresses Quack's paper more directly because (a) we study a chain of ion-neutral reactions in the plasmas in which protons are scrambled rather than the single photodissociation step in which H_2 is kept as a unit, and (b) we study nonthermal ratios of spin modifications of a *polyatomic* molecule, H_3^+. In this latter respect our work is related to the extensive experimental studies of Chapovsky and his colleagues [8,9] on CH_3F which, however, do not involve chemical reactions. The problem of the conversion between ortho- and para-H_3^+ is significant [10] in discussing the thermalization of interstellar H_3^+, which has just been discovered [11], and H_3^+ in planetary ionospheres [12].

The gist of our experiment is quite simple. We observe relative intensities of infrared spectral lines of ortho-H_3^+ ($I = \frac{3}{2}$ with spin weight 4) which occupies rovibrational states with A_2 symmetry, and para-H_3^+ ($I = \frac{1}{2}$ with spin weight 2) which occupies states with E symmetry in the ν_2 fundamental band [13] using normal [75% ortho-H_2 ($I = 1$) and 25% para-H_2 ($I = 0$)] and pure para-H_2 as discharge gases. If there exists spin selection rules in chemical reactions such as those discussed by Quack [3], we should observe different relative intensities for the two gases. This experiment was earlier tried using a crude experimental setup without a clear outcome [14]. We have carried out more elaborate experiments using a hollow cathode cell with both continuous ac discharge and pulsed discharge, and a positive column cell with a continuous ac discharge. All experiments showed that the ratio of para-H_3^+ to ortho-H_3^+ was significantly increased when pure para-H_2 was used instead of normal H_2, clearly demonstrating the existence of spin selections rules in ion-neutral reactions.

A result of a hollow cathode pulsed discharge experiment is shown in Fig. 1. The two upper traces show the time variation of the intensity of the $R(1,1)^+$ transition of para-H_3^+ at 2726.219 cm^{-1} when 1.85 Torr of n-H_2 (left) and para-H_2 (right) are used. The two lower traces show the time variation of the $R(1,0)^+$ transition of ortho-H_3^+ at 2725.898 cm^{-1}. In these experiments, the frequencies of tunable infrared radiation from our difference frequency laser system is set at the maximum of the respective H_3^+ absorption, and its power is monitored as the discharge current is pulsed. Figure 2 represents the corresponding hollow cathode discharge current. It

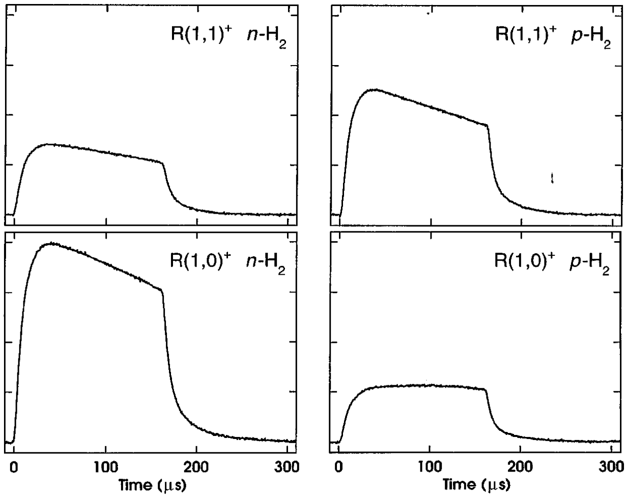

FIG. 1. Observed time variation of the peak intensities of the $R(1,1)^+$ para-H_3^+ infrared absorption (upper traces) and the $R(1,0)^+$ ortho-H_3^+ absorption (lower traces) when normal H_2 (left traces) and para-H_2 (right traces) were used as discharge gases. The copper hollow cathode cell [12] with a 3.8 m length and 3.5 cm inner diameter was used with a 16-pass optical arrangement. The difference frequency laser system was used as the tunable radiation source with power of ~200 μW. Each trace is the average of ten scans. The absorption intensities are in an arbitrary scale which is common to all four traces.

is noted in Fig. 1 that the para-H_3^+ to ortho-H_3^+ intensity ratio increases drastically from ~0.35 for the n-H_2 discharge to ~2.3 (30 μs after the beginning of the pulse) for the para-H_2 discharge, clearly demonstrating the existing selection rules. The signals reach maximum at about 40 μs after the onset of the discharge current and decrease after that because of the heating of the plasma and the resulting reduction of the H_3^+ population in the $J = 1$ rotational levels. For the para-H_3^+ signal generated in para-H_2 (upper right of Fig. 1), the decrease is enhanced by the conversion of para- to ortho-H_3^+, while for the ortho-H_3^+ signal (lower right of Fig. 1), the decrease is approximately compensated by the conversion, resulting in an approximately constant signal. Similar results were obtained for the ortho-para pair $R(4,3)^-$-$R(4,4)^-$ of H_3^+ transitions. In this case, the heating tends to increase the signal because of the high energy of the $J = 4$ levels $[E(J = 4,\ K = 3) - E(J = 1,\ K = 1) = 823\ \mathrm{K}]$. A more detailed analysis of the results and the experimental procedure will be published in a separate paper. For continuous ac discharges, the increase is not as drastic as for pulsed discharges because the longer duration of these discharges thermalizes more ortho- and para-H_3^+, but the effect is still clearly discernible.

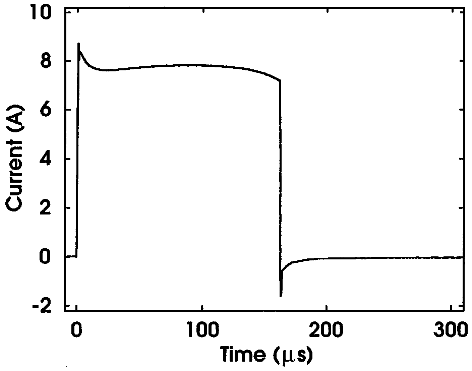

FIG. 2. The current pulse of the hollow cathode discharge. The pulse was generated by using a high voltage dc power supply and a high current transistor switch circuit. The pulse width was adjustable from 5 μs to 2 ms, and the pulse interval (1 s) was sufficiently long that the discharge gas products from the last pulse had been completely pumped off when a new discharge started. Observed time dependence of the signals for all pulse widths were reproduced by the rates and rate constants given in the text.

The observed variations of the para- to ortho-H_3^+ ratio for both pulsed and continuous ac discharges are explained by studying each step of the chain of plasma chemical reactions, paying special attention to spin modifications. Here we discuss the clear-cut case of plasmas in pure para-H_2, assuming Quack's prediction. The resultant approximate agreement between the calculated and observed values demonstrates that the prediction is indeed valid.

First, the ionization reaction by electron bombardment,

$$H_2 + e \longrightarrow H_2^+ + 2e\,, \tag{1}$$

initiates the plasma chemistry by producing pure para-H_2^+. The ionization process is so fast and the nuclear spin reorientation due to the electron-nuclear spin interaction is so slow that no appreciable ortho-H_2^+ is produced. This is followed by the well-known [12], efficient ion-neutral reaction,

$$H_2^+ + H_2 \longrightarrow H_3^+ + H\,, \tag{2}$$

which produces H_3^+. Quack showed [3] that only para-H_3^+ is produced from para-H_2^+ and para-H_2. The para-H_3^+ thus produced go through a series of proton hop reactions,

$$H_3^+ + \tilde{H}_2 \longrightarrow H_2 + \tilde{H}_2H^+\,, \tag{3}$$

and hydrogen exchange reactions,

$$H_3^+ + \tilde{H}_2 \longrightarrow \tilde{H}H_2^+ + H\tilde{H}\,, \tag{4}$$

where tildes over the H discriminate hydrogen atoms originally in H_2. Quack's theory shows that only para-H_3^+ results from the proton hop reaction (3) if para-H_3^+ and para-H_2 react. The hydrogen exchange reaction (4), however, introduces ortho-H_3^+ even when para-H_3^+ and para-H_2 react. For such a case, the branching ratio of the para-H_3^+ and ortho-H_3^+ production is calculated to be 2 : 1. To find this ratio, we first calculate the overall branching ratios of spin modification based on a statistical counting of nuclear spin states using permutation groups, without taking into account the complexity of chemistry, by a procedure similar to that given by Quack in section 6 of his paper. We obtain values summarized in Table I. We

TABLE I. Branching ratios of spin modifications based on statistical treatment.

$H_2 + H_2^+ \longrightarrow H_3^+ + H$

Spin[a] species	Weight	*o*	*p*
oo	9	6	3
op	3	1	2
po	3	1	2
pp	1	0	1

[a] *oo*, etc., denotes reactions of ortho-H_2 and ortho-H_2^+, etc.

$H_3^+ + H_2 \longrightarrow H_3^+ + H_2$

Spin[b] species	Weight	*oo*	*op*	*po*	*pp*
oo	12	37/5	1	14/5	4/5
op	4	1	1	2	0
po	12	14/5	2	28/5	8/5
pp	4	4/5	0	8/5	8/5

[b] *oo*, etc., denotes reactions of ortho-H_3^+ and ortho-H_2, etc. in that order.

then split the reaction into identity (with weight 1), proton hop (weight 3), and proton exchange (weight 6). After going through many reactions of (3) and (4), H_3^+ are destroyed by dissociative recombination

$$H_3^+ + e \longrightarrow H + H + H \quad \text{or} \quad H_2 + H \qquad (5)$$

or ambipolar diffusion to the wall. The decay of the signal at the end of the pulse in Fig. 1 is due to these processes.

The magnitude and the time dependence of the observed signals shown in Fig. 1 can be explained from time-dependent simultaneous rate equations by using the following standard values of rate, rate constants, and number densities: the rate of ionization [15] 3.0 s^{-1}, rate constants of reactions (2) [16] $k_2 = 2.0 \times 10^{-9}$ $cm^3\,s^{-1}$, reactions (3) and (4) together [18] $k_3 = 1.3 \times 10^{-9}$ $cm^3\,s^{-1}$, reaction (5) [17] $k_r = 1.8 \times 10^{-7}$ $cm^3\,s^{-1}$, and number densities of charges $[e] = [H_3^+] = 1.0 \times 10^{12}$ cm^{-3}. The calculated ratio of para-H_3^+ to ortho-H_3^+ depends most critically on the branching ratio of the proton hop reaction (3) to the hydrogen exchange reaction (4) since the latter is the only reaction in the chain which introduces ortho-H_3^+. We have found that a branching ratio of (3) to (4) of 2.4 : 1 fits our results best. Gerlich [18] has studied this ratio mass spectroscopically using the $D_3^+ + H_2$ reactions and reported that the ratio depended critically on the collision energy of the reactants. Using Fig. 10 of Ref. [18], we note that our branching ratio of 2.4 : 1 corresponds to the collision energy of 58 meV ~ 670 K, which is higher than the estimated temperature of ~300–400 K in hollow cathode plasmas. In view of the fact, however, that in Gerlich's $D_3^+ + H_2$ reactions the deuteron hop reaction is more endothermic than the H-D exchange reaction by ~100 K, while in our $H_3^+ + H_2$ reactions both are thermoneutral, we may regard this as good agreement. In addition to the main channel of reactions (1)–(5), the spin conversions in plasmas are caused by the slow conversion of para-H_2 to ortho-H_2. This proceeds partly because the H_2 produced in reactions (3)–(5) are no longer completely para-H_2 and partly because of the recombination on the copper wall of H atoms produced in (2) and (5) and dissociation due to electron bombardment. Since the analysis of this effect is not as clear cut as that in the gas, we treated this by introducing an overall lifetime of the para-H_2 to ortho-H_2 conversion in the plasma. We find that the lifetime of 1.0 ms fits the experimental results shown in Fig. 1. This is a small effect as far as the para-H_3^+–ortho-H_3^+ ratios are concerned for the pulsed experiment since our pulse duration is much shorter.

In conclusion, the observed strong dependence of the ortho-H_3 and para-H_3 abundance ratio clearly demonstrates the existence of spin selection rules in plasma chemistry. The analysis based on the assumption of the theoretical prediction given by Quack explains the observed results quantitatively.

We would like to acknowledge the help of K. E. Kerr, R. M. Dickson, and Y. Zhang for the para-H_2 preparation.

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