土卫六大气中 H₂ 和 N⁺反应的动力学研究

葛素红 [1,2]　　　董光兴 [1]　　　程新路 [2,*]　　　杨向东 [2]

(¹ 河西学院物理系, 甘肃 张掖　734000;　² 四川大学原子分子物理研究所, 成都　610065)

摘要　依据 Titan 大气的压强和温度条件计算了 N⁺+H₂→NH⁺+H 反应的热化学函数. 结果发现, 该反应是一个吸热反应, 在 Titan 的低温环境中不具有反应自发性. 运用量子化学理论计算研究了反应的动力学性质, 发现该反应在 300 K 温度下的反应速率 k=4.16×10⁻¹⁰ cm³·mol⁻¹·s⁻¹, 在实验室温度下(298.15 K)的反应势垒是 109.847 kJ·mol⁻¹. 依据Titan电离层气压温度条件计算了90 Pa压强条件下1 K到5000 K温度范围内(极低温度和极高温度)的反应活化能和反应速率, 研究发现低温下该反应的反应速率非常低, 而且, 随着温度的降低, 反应速率急剧降低. 理论计算值和文献中的实验值也符合得较好, 理论计算数据可以为星际分子的模拟实验提供一定的参考.

关键词：Titan,　动力学,　活化自由能,　反应速率

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Reaction of H₂ and N⁺ Ion under Titan′s Atmosphere

GE, Su-Hong[1,2]　　　DONG, Guang-Xing[1]　　　CHENG, Xin-Lu[2,*]　　　YANG, Xiang-Dong[2]

(¹*Department of Physics, Hexi University, Zhangye　734000, P. R. China*;

²*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu　610065, P. R. China*)

Abstract　The thermochemical properties of reaction N⁺+H₂→NH⁺+H have been computed under Titan′s atmosphere conditions. It is observed that this reaction is an endothermic reaction and cannot proceed forward spontaneously under low temperature. The rate for this reaction at 300 K has been calculated as k=4.16×10⁻¹⁰ cm³·mol⁻¹·s⁻¹. The reaction barrier is 109.847 kJ·mol⁻¹ at 298.15 K, which is probably too high to allow this reaction to occur in the atmosphere of Titan. The kinetic properties of the reaction are calculated at a pressure of 90 Pa and a temperature ranging from 1 to 5000 K. It is found that this reaction has very low reaction rate under low temperature in Titan′s atmosphere and that the rate decreases drastically with decreasing temperature. This result should be applicable to interstellar place of the low temperature values. The results are compared with those obtained from experiments.

Keywords：Titan,　Thermodynamic,　Activation free energy,　Reaction rate

　　Eight of the nine planets in our solar system have significant atmosphere. Of these, four have been investigated by planetary probes and/or rockets equipped with mass spectrometers. Mass spectrometric analysis has provided details on the atmospheric com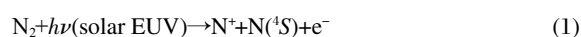position of the outer atmosphere of Venus, Earth, Mars, and Jupiter down to below the one-Pa pressure level. There are more than 40 moons that orbit the planets of the solar system, among these, only three　(Titan, Io, and Triton) were shown to have sufficient atmosphere for mass spectrometric　analysis during a flyby. Titan, orbiting Saturn, has by far the largest at-

mosphere and is a significant focus of the NASA/ESA Cassini-Huygens mission to Saturn[1]. Titan has a well established atmosphere; the composition of this atmosphere near the surface is as follows: more than 97% is molecular nitrogen, the remainder is methane and other minor species[2]. Titan′s upper atmosphere and ionosphere are quite complex chemically[3-6]. Theoretical investigations have been carried out to describe the structure[7-9] and the composition of this atmosphere[10-13]. A large amount of information available from laboratory studies of ion-molecule reactions relevant to Titan′s ionosphere has been collected by Anicich and McEwan[1], a profile of chemical sources of haze formation in Titan′s atmoshpere has been described by Wilson and Atreya[14], and a concise review of the understanding of the ionosphere of Titan, based on observation constraints and theoretical models, has been presented by Nagy and Cravens[15]. The results of plasma discharge in the N_2-CH_4 mixture, with ammonia and oxirane production, have been reported by Bernard et al.[16-17]. Bernard et al. showed that ammonia was the main product in the experiments designed to simulate the upper atmosphere of Titan. They had experimentally studied the reaction chemistry of a Titan-simulated atmosphere in the presence of carbon monoxide (n_{N_2}: n_{CH_4}:n_{CO}=98:2:0.01), and had found that ammonia was clearly identified as one of the major products in the Titan atmosphere simulations. According to the Bernard′s article, no theoretical models have taken the NH_3 photochemical cycle into account in Titan′s atmosphere. Atreya (1986) proposed a mechanism to produce NH_3 (ammonia) in the ionosphere[18]:

$$N_2+h\nu(\text{solar EUV})\rightarrow N^++N(^4S)+e^- \tag{1}$$

$$N^++H_2\rightarrow NH^++H \tag{2}$$

$$NH^++H_2\rightarrow NH_2^++H \tag{3}$$

$$NH_2^++H_2\rightarrow NH_3^++H \tag{4}$$

$$NH_3^++H_2\rightarrow NH_4^++H \tag{5}$$

$$NH_4^++e^-\rightarrow NH_3+H \tag{6}$$

Reaction (2) has once again attracted the attention of researchers for its roles as a possible first step in the synthesis of ammonia in interstellar clouds. This hydrogen atom transfer reaction has served as a model system in the study of the kinetics and dynamics of ion-molecule reactions. Knowledge of the temperature dependence and kinetic energy dependence of the reaction is important for modeling the chemistry of nitrogen-containing species under the conditions of interstellar space. The experimental reaction rates for reaction (2) at 300 K are tabulated in Table 1. The experiments at very low temperatures have estab-

lished that the reaction rate decreases rapidly with decreasing temperature[19]. Reaction (2) has been studied from 8 to 70 K in a supersonic gas jet[20] and from 11 to 20 K in a low temperature ion trap[21]. In the study by Ervin and Armentrout[19], guided ion beam techniques were used to examine the kinetic energy dependence of the integral reaction cross sections.

The thermochemical and kinetic properties of above-mentioned reaction have not been studied, and hence, the calculated results are of utmost interest. To bridge this gap, we have decided to calculate as accurate values as possible, while keeping the computational cost in mind. Since reaction (2) is almost thermoneutral, the expected temperature dependence of the rate depends on the magnitude and the direction of the reaction enthalpy[19]. The thermochemical and kinetic properties of reaction (2) were calculated in accordance with Titan′s condition[22]. Recently, the coupled cluster singles and doubles (CCSD) model has been shown to be highly efficient[23]. Therefore, in this study, the thermochemical properties of reaction (2) were calculated at a pressure of 90 Pa and at different temperatures, respectively, using the CCSD method together with the standard cc-pvdz basis set implemented in the Gaussian 98 program. The kinetic properties of the reactions were calculated at a pressure of 90 Pa and at different temperatures, respectively, using MP2/6-311g(d) method.

1 Computational methods

During the last decade, the coupled cluster method has been recognized as the most efficient means to describe the dynamical correlation effects for systems dominated by a single reference configuration. CCSD includes the effects of all single and double excitations out of the reference configuration, which is usually chosen as the Hartree-Fock self-consistent-field (SCF) wave-function. The calculation on the present work was performed in two steps. First, an optimization of geometry was performed using HF/6-31g*, b3lyp/6-311++g($3df$, $3pd$), and ccsd/cc-pvdz respectively, and the most stationary point was obtained. At the final geometries, the zero-point vibrational effects were obtained by calculating Hessians at the ccsd/cc-pvdz level and

Table1 $N^++H_2\rightarrow NH^++H$ experimental reaction rates (300 K)

Rate coefficient ($cm^3 \cdot s^{-1}$)	Reference	Rate coefficient ($cm^3 \cdot s^{-1}$)	Reference
$(3.9\pm0.8)\times10^{-10}$	[19]	4.7×10^{-10}	[34, 36]
$(5.0\pm0.2)\times10^{-10}$	[1]	4.8×10^{-10}	[35]
6.2×10^{-10}	[32]	6.4×10^{-10}	[33]

vibrational frequencies were computed to verify that each reactant and product was at the minimum of its potential energy surface, no structures having imaginary frequencies were found. In the second step, the E_e, H, G, and S of each reactant and product were computed at the ccsd/cc-pvdz level. In this article, the energies are the ground state energies of each group; especially for N^+, its electronic state is ^3P. The feasibilities of the reactions have also been discussed.

According to the thermochemical theories, at room temperature and $1.01×10^5$ Pa pressure, the enthalpy of an ideal gas can be noted as[24]

$$H=E_e+E_n+pV=E_e+E_n+RT \quad (E1)$$

where E_e is the electronic structure energy and E_n is the molecular thermal energy. By assuming that any molecule is an ideal gas, the values of H, E_e, and E_n can be computed at any temperature. The Gibbs free energy G is defined as follows:

$$G=H-TS \quad (E2)$$

or
$$\Delta G=\Delta H-T\Delta S \quad (E3)$$

where S is the entropy , and ΔG is the free energy of the reaction. The partition function from any component can be used to determine the entropy contribution from that component using the following relation:

$$S=Nk_B+Nk_B\ln(\frac{q(V,T)}{N})+Nk_BT(\frac{\partial \ln q(V,T)}{\partial T})_V \quad (E4)$$

The partition function $q(V, T)$ for the corresponding component of the partition function includes the translational, rotational, vibrational, and electronic motions. Because entropy and enthalpy are both status functions, their calculated values vary with temperatures. In this article, the enthalpy, Gibbs free energy, the entropy for each reaction, as well as the equilibrium constant $K(T)$ were computed using the formula (E5)[25-26]:

$$K(T)=e^{\frac{-\Delta G}{RT}} \quad (E5)$$

The converted temperature of the reaction was also calculated using the formula (E3). The key equation for calculating the reaction rates is[26]

$$k(T)=\frac{k_BT}{hc^0}e^{\frac{-\Delta^{\ddagger}G^0}{RT}} \quad (E6)$$

where $c^0=1$ mol·L^{-1} is used for the concentration, $\Delta^{\ddagger}G^0$ is the activation free energy of the reaction.

In this article, the energies that were computed are the ground state energies of each group, for N^+, its ground state is ^3P, and for H_2, its ground state is $X^1\Sigma_g^+$ The deviation of computational thermochemistry and kinetics is mainly attributed to the zero-point vibrational energies. The scale factor of frequencies was determined to be appropriate for reproducing fundamental frequencies. The minimum factor was equal to 0.893. Thus, the error bars for activation barriers of reactions are expected to be considerably better than 11%.

However, in this study, the calculations have been carried out using the theory of quantum simulation of molecules. This theory is based on the hypothesis of the Born-Oppenhimer approximation, and this reaction has been dealt with as an adiabatic process. Electronically, nonadiabatic processes and their dynamical effects on chemical reactions have recently become very interesting issues and considerable efforts have been made toward the development of experimental techniques and theoretical fields[27-29]. The endothermic proton transfer reaction has been investigated over a broad rage of reactant vibrational levels by Tang *et al.*[30]. The accurate *ab initio* potential-energy surface has been investigated by Palmieri *et al.*[31]. These theoriesare of considerable interest, and efforts are been made to study the reaction by considering it as a nonadiabatic process in our subsequent researches.

2　Results and discussion

2.1　The thermochemical properties of reaction (2) at 90 Pa and at different temperatures

Because the pressure of 90 Pa corresponds to the conditions in Titan′s middle stratosphere and the temperature at this pressure level is about 170 K. So, in this article, the thermochemical

Table 2　Thermochemical properties of reaction (2) at various temperatures (ccsd/cc-pvdz)

T/K	ΔH/(kJ·mol^{-1})	ΔG/(kJ·mol^{-1})	ΔS/(J·mol^{-1}·K^{-1})	$K(T)$
5	20.217	20.159	11.242	$1.58×10^{-211}$
8	20.213	20.125	11.242	$2.93×10^{-132}$
15	20.217	20.050	11.247	$1.29×10^{-70}$
20	20.217	19.991	8.983	$5.45×10^{-53}$
40	20.217	19.765	11.247	$1.46×10^{-26}$
50	20.213	19.652	11.242	$2.89×10^{-21}$
70	20.213	19.426	11.251	$3.09×10^{-15}$
100	20.213	19.092	11.247	$1.04×10^{-10}$
150	20.213	18.527	11.242	$3.48×10^{-7}$
170	20.213	18.305	11.242	$2.34×10^{-6}$
200	20.213	17.966	11.242	$2.01×10^{-5}$
273	20.217	17.142	11.242	$5.23×10^{-4}$
283	20.217	17.033	11.242	$7.16×10^{-4}$
293	20.217	16.916	11.242	$9.63×10^{-4}$
303	20.213	16.807	11.247	$1.26×10^{-3}$
353	20.217	16.426	11.242	$3.70×10^{-3}$
453	20.217	15.117	11.251	$1.79×10^{-2}$
1000	20.439	8.924	11.510	0.343
1500	21.133	3.029	12.062	0.784
1800	21.627	−0.636	12.368	1.043
2000	21.953	−3.134	12.544	1.208
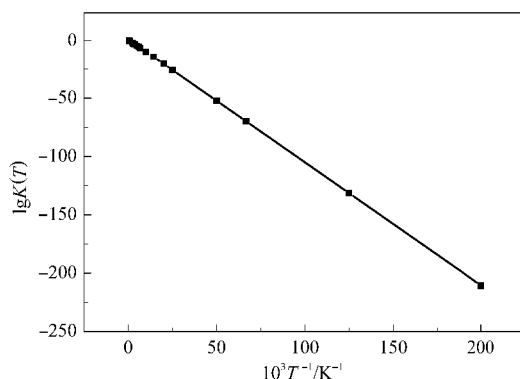
Fig.1 van′t Hoff plots of the equilibrium $K(T)$ for reaction $N^{+}+H_2 \rightarrow NH^{+}+H$

Fig.2 van′t Hoff plots of the rates of reaction $N^{+}+H_2 \rightarrow NH^{+}+H$

properties of reactions are calculated at a pressure of 90 Pa and a temperature ranging from 5 to 2000 K at the CCSD/cc-pvdz level. The data are listed in Table 2.

Reaction (2) is an endothermic reaction with $\Delta H > 0$ and $\Delta G > 0$, which indicates that it cannot occur forward spontaneously. The values of ΔH and ΔS are positive, and the converted temperature is 1797.6 K. It implies that reaction (2) cannot carry on forward spontaneously at $T < 1797.6$ K. The equilibrium constants $K(T)$ are quite small, especially at lower temperature. Fig.1 shows the van′t Hoff plots for reaction (2). The equilibrium constant of the reaction increases rapidly with the increasing temperature, but the free energies of the reaction decreases with the increasing temperature, and the free energies of the reaction are negative when $T > 1797.6$ K. Thus, when $T < 1797.6$ K, reaction (2) cannot proceed forward spontaneously, whereas at $T > 1797.6$ K, reaction (2) could proceed forward spontaneously. The barrier of this reaction is also calculated at the ccsd/cc-pvdz level. Such a barrier of 109.847 kJ·mol^{-1} is probably too high to allow reaction (2) to occur in the atmosphere of Titan. The rate of this reaction at 300 K has been calculated as: $k=4.16\times10^{-10}$ cm^3·mol^{-1}·s^{-1}. It suggests that the spontaneity has no influence on reaction (2) under this condition. The results are compatible with the results obtained by Ervin et al.[19], and the value of $k= 4.16\times10^{-10}$ cm^3·mol^{-1}·s^{-1} is also in agreement with the results ob-

tained by Tichy[32], Adams[33], Kim[34], Smith[35], and Fehsenfeld[36] et al., respectively (Table 1).

2.2 The kinetic properties of reaction (2) at 90 Pa and at different temperatures

In this study, the kinetic properties of reactions are calculated at a pressure of 90 Pa and a temperature ranging from 1 to 5000 K at the MP2/6-311g(d) level. The activation free energies of reaction (2) at a pressure of 90 Pa and different temperatures are shown in Table 3. It is clear that the activation energies of reaction (2) increase with the increasing temperature. The Arrhenius analysis of these data combined with the different temperatures (Fig.2) indicate that reaction (2) has very low reaction rates under low temperature, and the rates of reaction (2) decrease drastically with the decreasing temperature. This result is in good agreement with the other conclution in literatures.

3 Conclusions

After computing the thermochemical properties of reaction $N^{+}+H_2 \rightarrow NH^{+}+H$, it is found that this reaction is an endothermic reaction and that it cannot proceed forward spontaneously. The rate of this reaction at 300 K is $k=4.16\times10^{-10}$ cm^3·mol^{-1}·s^{-1}, and the reaction barrier is 109.847 kJ·mol^{-1}, which is probably too high to allow reaction (2) to occur in the atmosphere of Titan. In addition, the kinetic properties of reactions are calculated at a pressure of 90 Pa and a temperature ranging from 1 to 5000 K. It is seen that reaction (2) has very low reaction rates under low temperature, and the rates decrease drastically with the decreasing temperature. It is in good agreement with the results obtained in the experiments carried out by Ervin and Armentrout. However, the agreement of the present data with the predictions makes the experiments useful to provide upper bounds to the rate of this reaction at very low temperatures.

Table 3 The activation free energies of reaction (2) at various temperatures (MP2/6-311g(d))

T/K	$\Delta^{\ddagger}G^{0}$/(kJ·mol^{-1})	T/K	$\Delta^{\ddagger}G^{0}$/(kJ·mol^{-1})	T/K	$\Delta^{\ddagger}G^{0}$/(kJ·mol^{-1})
1	101.713	20	104.370	300	156.268
2	101.826	70	112.683	500	196.895
3	101.939	80	114.441	1000	302.679
4	102.064	100	118.018	2000	520.862
5	102.198	150	127.219	3000	742.982
8	102.600	170	130.993	4000	967.663
11	103.027	200	136.708	5000	1194.310

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