

# Phosphorus monofluoride cation (PF<sup>+</sup>) expected in atmospheres of the gas giant planets Jupiter and Saturn

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**Abstract.** The rate coefficient for the radiative association of phosphorus ion and fluoride atom to form the phosphorus monofluoride cation (PF<sup>+</sup>) is estimated as a function of temperature. The total rate coefficient can be represented by the relation  $k(T) = a_0 + a_1T + a_2T^2 + a_3T^3$ , where  $a_0$ ,  $a_1$ ,  $a_2$ , and  $a_3$  are equal to  $3.25 \times 10^{-18} \text{ cm}^{-3} \text{ s}^{-1}$ ,  $7.55 \times 10^{-22} \text{ cm}^{-3} \text{ s}^{-1} \text{ K}^{-1}$ ,  $-8.23 \times 10^{-27} \text{ cm}^{-3} \text{ s}^{-1} \text{ K}^{-2}$ , and  $2.80 \times 10^{-30} \text{ cm}^{-3} \text{ s}^{-1} \text{ K}^{-3}$ , respectively, over the 300-14000 K range. This rate constant is found to increase monotonically with increase of temperature and is higher than the corresponding radiative association rate coefficient for PF over the entire temperature range.

**Resumo.** Foram estimados os coeficientes de reação para a formação do íon monofluoreto de fósforo (PF<sup>+</sup>) através da associação radiativa do íon de fósforo e o átomo de flúor. Os coeficientes de taxa variam de acordo com a expressão  $k(T) = a_0 + a_1T + a_2T^2 + a_3T^3$ , onde,  $a_0$ ,  $a_1$ ,  $a_2$ , and  $a_3$  são iguais a  $3,25 \times 10^{-18} \text{ cm}^{-3} \text{ s}^{-1}$ ,  $7,55 \times 10^{-22} \text{ cm}^{-3} \text{ s}^{-1} \text{ K}^{-1}$ ,  $-8,23 \times 10^{-27} \text{ cm}^{-3} \text{ s}^{-1} \text{ K}^{-2}$  e  $2,80 \times 10^{-30} \text{ cm}^{-3} \text{ s}^{-1} \text{ K}^{-3}$ , respectivamente, para temperaturas compreendidas no intervalo de 300 a 14000 K. O coeficiente de taxa aumenta monotonicamente com o aumento da temperatura e é maior que o correspondente coeficiente de reação para a formação do PF via associação radiativa.

**Keywords.** Astrochemistry – Molecular processes – Planets and satellites: atmospheres

## 1. Introduction

Elemental phosphorus (P) has been identified towards dwarf and giant stars, diffuse clouds, comets, and young supernova remnant Cas A (Lebouteiller et al. 2005; Koo et al. 2013; Caffau et al. 2016; Maas et al. 2017; Gardner et al. 2020), while P-bearing molecules have been found towards the circumstellar material of the evolved stars, including PO, PN, CP, HCP, CCP, NCCP, SiP, and PH<sub>3</sub> (Guélin et al. 1990; Halfen et al. 2008; Milan et al. 2008; Tenenbaum & Ziurys 2008; Agúndez et al. 2014a,b; Koelemay et al. 2022). In addition, PO, PO<sup>+</sup>, and PN have been observed in molecular clouds (Lefloch et al. 2016; Fontani et al. 2016; Rivilla et al. 2022). PN is also identified in extragalactic sources (Haaslet et al. 2022), PO in comets (Altwegg et al. 2016), and PH<sub>3</sub> in the atmospheres of Jupiter and Saturn (Gillett & Forrest 1974; Ridgway et al. 1976). In the upper atmospheres of these giant planets, the abundance of PH<sub>3</sub> is above than that of the solar composition ( $4.8 \pm 0.3$  on Jupiter and  $15.9 \pm 0.3$  on Saturn) and several order of magnitude higher than those predicted by chemical models (Trujillo et al. 2021).

To investigate the formation mechanisms of P-molecules in the upper atmospheres of the giant planets and other astronomical environments, and help to interpret future observations, the rate constants for the various involved chemical processes should be included. Thus, we have studied the formation of PF<sup>+</sup> by radiative association of P<sup>+</sup>(<sup>3</sup>P) + F(<sup>2</sup>P) atoms to form the phosphorus monofluoride cation (PF<sup>+</sup>).

## 2. Cross section and rate constants

The radiative association process, P<sup>+</sup> + F → PF<sup>+</sup> + hν, involves the formation of an unstable complex stabilized against redissoc-

iation by emission of a photon. The thermal rate coefficient at a given temperature  $T$  to form PF<sup>+</sup> by such a process is given by

$$k(T) = \left(\frac{8}{\mu\pi}\right)^{1/2} \left(\frac{1}{K_B T}\right)^{3/2} \int_0^\infty E \sigma(E) e^{-E/K_B T} dE \quad (1)$$

where  $K_B$  is the Boltzmann constant,  $\mu$  is the reduced mass of the P<sup>+</sup> + F system,  $E$  is the collision energy, and  $\sigma(E)$  is the cross section.

In a semi-classical scheme (Bates 1951; Dalgarno et al. 1990), the cross section is given by

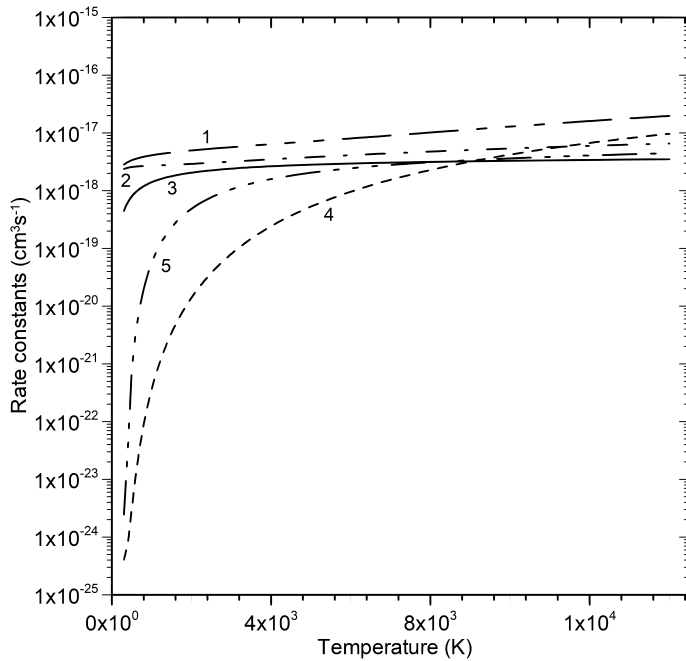
$$\sigma(E) = 2\pi g \left(\frac{2\mu}{E}\right)^{1/2} \int_0^\infty b \int_{r_c}^\infty \frac{A(r)}{\left(1 - b^2/r^2 - U_i(r)/E\right)^{1/2}} dr db \quad (2)$$

where,  $g$  is the statistical weight factor,  $r$  is the internuclear distance,  $r_c$  is the classical turning points for the impact parameter  $b$ ,  $U_i(r)$  is the potential energy curve in the entrance channel, and  $A(r)$  is the radiative transition probability (in s<sup>-1</sup>).

## 3. Radiative association and results

The PF<sup>+</sup> cation has been observed in laboratory for the first time by Douglas & Frackowiak (1962). It consist of the rotational resolved spectrum of the A<sup>2</sup>Σ<sup>+</sup>-X<sup>2</sup>Π transition of PF<sup>+</sup>. Later, Berkowitz et al. (1984) determined the ground-state dissociation energy  $D_0$  to be larger than  $5.24 \pm 0.02$  eV. There are also some theoretical studies on the structure of PF<sup>+</sup> (Nguyen 1986; Kim & Hirst 1995; Li et al. 2015; Liu et al. 2017), including potential energy curves, spectroscopic parameters, transition dipole moments, and vibrational properties of PF<sup>+</sup>.

The coupling of P<sup>+</sup>(<sup>3</sup>P) ion and F(<sup>2</sup>P) atom can occurs mainly through the A<sup>2</sup>Σ<sup>+</sup>, B<sup>3</sup>Π, and C<sup>2</sup>Σ<sup>-</sup> states of the phosphorus monofluoride cation (PF<sup>+</sup>) and then radiate via a strong



**FIGURE 1.** Radiative association rate constants. 1-PF<sup>+</sup>(Total), 2-PF<sup>+</sup>(B-X), 3-PF<sup>+</sup>(A-X), 4-PF<sup>+</sup>(C-X), and 5-PF<sup>+</sup>(A-X)

dipole transition to the X<sup>2</sup>Π ground state of PF<sup>+</sup>. For these transitions, the statistical weight factors are  $g = 4/54$  for B<sup>2</sup>Π-X<sup>2</sup>Π, and  $g = 2/54$  for A<sup>2</sup>Σ<sup>+</sup>-X<sup>2</sup>Π and C<sup>2</sup>Σ<sup>-</sup>-X<sup>2</sup>Π. The potential energy curves of these states and transition moments needed for the thermal rate constants calculations are taken from Li et al. (2015) and Liu et al. (2017). Their calculations are well consisted with the experimental data (Douglas & Frackowiak 1962; Berkowitz et al. 1984; Butcher et al. 1988).

The thermal rate coefficients for the formation of the PF<sup>+</sup> cation through the A<sup>2</sup>Σ<sup>+</sup>-X<sup>2</sup>Π, B<sup>2</sup>Π-X<sup>2</sup>Π, and C<sup>2</sup>Σ<sup>-</sup>-X<sup>2</sup>Π systems are presented in Figure 1. For the temperature range of 300 to 14000 K, the rate constants are found to increase with increase of temperature. The total rate constant can be fitted to the relation  $k(T) = a_0 + a_1T + a_2T^2 + a_3T^3$ , where  $a_0$ ,  $a_1$ ,  $a_2$ , and  $a_3$  are equal to  $3.25 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ ,  $7.55 \times 10^{-22} \text{ cm}^3 \text{ s}^{-1} \text{ K}^{-1}$ ,  $-8.23 \times 10^{-27} \text{ cm}^3 \text{ s}^{-1} \text{ K}^{-2}$ , and  $2.80 \times 10^{-30} \text{ cm}^3 \text{ s}^{-1} \text{ K}^{-3}$ , respectively, within 25 per cent over the 300-500 K range and within 5% applicable up to 500 K. The total rate coefficient can be compared to the one estimated for P(<sup>4</sup>S) + F(<sup>2</sup>P) reaction through the A<sup>3</sup>Π-X<sup>3</sup>Σ<sup>-</sup> system (Andreazza & de Almeida 2022), which is higher than the corresponding radiative association rate coefficient for PF<sup>+</sup> over the entire temperature range (Fig. 1). The A<sup>3</sup>Π state of PF has a hump. Because of the barrier, the rate constant diminishes rapidly at low temperatures. Also, the C<sup>2</sup>Σ<sup>-</sup> state of PF<sup>+</sup> is very weakly bound and is repulsive at nuclear separation inside  $5 a_0$  (Liu et al. 2017), the reaction rate constant is also very small at low temperatures.

In these studies, the fine structure of the fluoride atom was not considered. The maximum splitting in the asymptotic energy curves is  $404.061 \text{ cm}^{-1}$  (578 K). Thus, the predicted rate constants are unreliable at low temperatures. Moreover, semiclassical approximation ignores the quantum effects. These effects may be important at low temperatures (Bain & Bardsley 1972; Smith 1989). It is difficult to estimate the error in our calculations because the rate coefficients are small for the radiative association reaction to be observable in laboratory. In general, the computed rate constants have uncertainties that decrease with the increasing temperature.

## 4. Conclusions

The thermal rate constant for formation of PF<sup>+</sup> cation through the radiative association of P(<sup>3</sup>P) and F(<sup>2</sup>P) is estimated over the 300-14000 K range. The PF<sup>+</sup> cation can be formed through the A<sup>2</sup>Σ<sup>+</sup>-X<sup>2</sup>Π, B<sup>2</sup>Π-X<sup>2</sup>Π, and C<sup>2</sup>Σ<sup>-</sup>-X<sup>2</sup>Π systems. The total rate coefficients are found to increase monotonically with increase of temperature. These values are low as expected for the formation of PF<sup>+</sup> in upper atmospheres of giant planets and other astronomical environments, however, higher than the corresponding radiative association rate coefficient for PF over the entire temperature range.

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