

Phosphorus monofluoride (PF) expected on gas giants Jupiter and Saturn by radiative association

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Abstract. The thermal rate constants for formation of the phosphorus monofluoride (PF) by radiative association of P(⁴S) and F(²P) atoms are estimated for temperatures ranging for 300 to 14,000 K. The coupling of the phosphorus and fluoride atoms mainly occurs through the A³Π state, which can decay to the ground X³Σ⁻ state of PF. The rate coefficients were found to vary according to the expression $k(T)=2.101\times 10^{-18}(T/300)^{0.268}\exp(-3990/T)\text{ cm}^3\text{ s}^{-1}$. These results indicate that only a small amount of PF-molecule can be formed by radiative association in the upper atmospheres of the giant planets.

Resumo. As constantes de reação para a formação do monofluoreto de fósforo (PF), via associação radiativa dos átomos de P(⁴S) e F(²P), foram estimadas para temperaturas variando de 300 a 14.000 K. O acoplamento dos átomos de fluor e fósforo pode ocorrer principalmente através do estado A³Π, o qual pode decair para o estado fundamental X³Σ⁻ do PF. Os coeficientes de taxa obtidos variam de acordo com a expressão $k(T)=2.101\times 10^{-18}(T/300)^{0.268}\exp(-3990/T)\text{ cm}^3\text{ s}^{-1}$. Os resultados indicam que apenas uma pequena quantidade de moléculas de PF pode ser formada nas camadas mais altas das atmosferas dos planetas gigantes.

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

1. Introduction

Phosphine (PH₃) is the only phosphorus compound to have been detected in the upper atmospheres of Jupiter and Saturn (Larson et al. 1977; Kaye & Strobel 1984; Fletcher et al. 2009) at abundances (4.8 ± 0.3 on Jupiter and 15.9 ± 0.3 on Saturn above solar composition) several orders of magnitudes higher than those predicted by thermodynamic equilibrium (Fletcher et al. 2009). PH₃ is thought to form in the hotter deep layers of the atmosphere and is brought to the top of the atmosphere through convective transport (Trujillo et al. 2021). The overabundance of PH₃ in the high observable layers occurs because chemical equilibrium timescales are long when compared to convective timescales. The chemical models considered abundances of the atmospheric P-molecules that could be spectroscopically observed, PH₃, PH₂, PH, P₄O₆, P₄O₇, P₄O₈, P₄O₉, P₄O₁₀, PS, P₂, P, PO, PO₂, PF, PC, PCl, PN, P₄, and P₃ (Barshay & Lewis 1978; Borunov et al. 1995; Fletcher et al. 2009).

In order to model these phenomena, one needs to know the rate coefficients for the various involved processes. Three-body association reactions strongly depend on the density, while the radiative association does not. As a consequence, the former reactions are only efficient in the lower atmosphere and the latter can therefore still be important in the upper atmosphere of planets (Dalgarno, Babb & Sun 1992; Sun & Dalgarno 1992; Vuitton et al. 2012). Hence, to investigate the presence and formation mechanisms of PF on Jupiter and Saturn, and help to interpret future observations of planetary atmospheres, we study the process of radiative association in the collision of P + F to form the PF-molecule in gas giants atmospheres by radiative association of P(⁴S) and F(²P) atoms.

2. Radiative association

The radiative association rate coefficient, k , is defined as the formation rate of phosphorus monofluoride, PF, in the reaction P +

F → PF + $h\nu$, by the expression $dn(\text{PF})/dt = k n(\text{P})n(\text{F})$, where n is the number density of P, F and PF, respectively.

A semiclassical treatment of the nuclear motion may be adequate for collisions of massive reactants (Dalgarno et al. 1990). A convenient method for estimating the rate coefficient has been proposed by Bates (1951). In this approximation, the cross section for the radiative association of two species at a relative motion of energy E , $\sigma(E)$, is given by

$$\sigma(E) = 4\pi \left(\frac{\mu}{2E} \right)^{1/2} P \int_0^\infty b \int_{r_c}^\infty \frac{A(r)}{\sqrt{1 - \frac{V_i(r)}{E} - \frac{b^2}{R^2}}} db dr, \quad (1)$$

where, μ is the reduced mass of the colliding atoms, r_c is the classical distance of the closest approach, r is the internuclear separation, b is the impact parameter, $V_i(r)$ is the potential energy curve through which the colliding particles unite, $A(r)$ is the Einstein coefficient for spontaneous emission and P is the probability of approach along the $V_i(r)$ state.

The thermal rate coefficient, $k(T)$, is obtained at temperature T by calculating an integral over Maxwell-Boltzmann velocity distribution. It is convenient to substitute the mean relative velocity by the collision energy $E = \mu v^2/2$ and so:

$$k(T) = \left(\frac{8k_B T}{\mu\pi} \right)^{1/2} \int_0^\infty x \sigma(xk_B T) \exp(-x) dx, \quad (2)$$

where k_B is the Boltzmann constant and $x = E/Tk_B$.

3. Rate constants

The coupling of the P(⁴S) and F(²P) atoms, both in their ground states, give rise to triplet and quintet molecular states of symmetries Π and Σ^- . The two triplet states (A³Π and X³Σ⁻) have been identified spectroscopically and they are bound, but the two quintet state (1⁵Π and 1⁵Σ⁻) are repulsive (Li et al. 2015) and make little contribution to the rate constants.

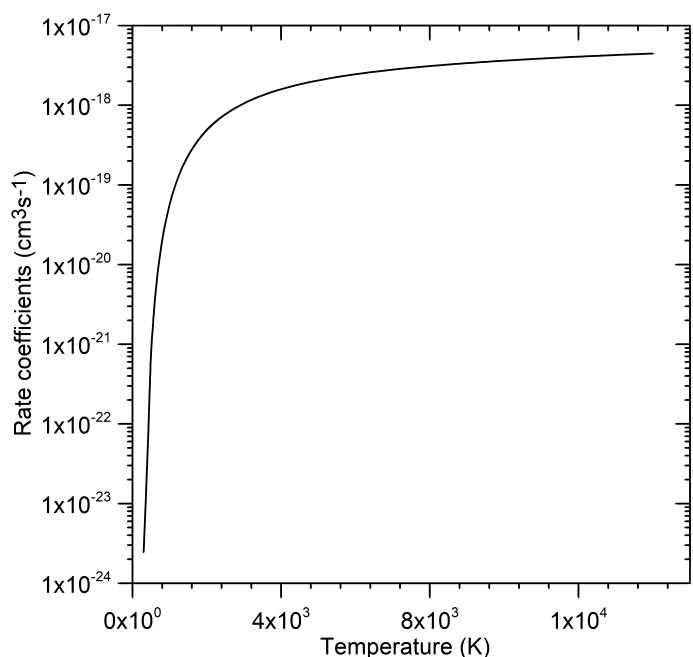


FIGURE 1. Radiative association rate constants

For PF, radiative association of $P(^4S)$ and $F(^2P)$ atoms mainly occurs through the $A^3\Pi$ molecular electronic state, which can decay to the ground $X^3\Sigma^-$ molecular electronic state. The probability of approach along the $A^3\Pi$ state is $6/24$.

The potential energy curves and transition dipole moments adopted in the radiative association calculation for radiative recombination of $P(^4S)$ and $F(^2P)$ atoms were theoretically found by Li et al. (2015) with the high-level configuration interaction method. Their calculations are well consisted with the experimental data (Yamada et al. 1987; Nizamov & Setzer 2002).

The rate coefficients for radiative association of phosphorus and fluorine atoms through the $A^3\Pi-X^3\Sigma^-$ transition system are estimated for temperatures in the range 300-14,000 K. The resulting rate constants increase with the increase in temperature and are shown in Figure 1, which are fitted to the parametric form

$$k(T) = 2.101 \times 10^{-18} \left(\frac{T}{300}\right)^{0.268} \exp\left(\frac{-3990}{T}\right) \text{ cm}^3 \text{ s}^{-1} \quad (3)$$

within 5 per cent over the 300-14,000 K range.

We do not take into account the fine structure of the fluoride atoms. The maximum splitting in the asymptotic potential energy curves is 404.061 cm^{-1} or 578 K. Thus, uncertainties are expected at low temperatures. Moreover, semiclassical calculations ignores the quantum effects (shape resonances and tunneling). Such effects may be important at low temperatures (Bain & Bardsley 1972; Smith 1989). Since radiative association rate coefficients are too small for the reaction to be observable in laboratory, it is difficult to estimate the uncertainties in our calculations. However, the computed rate constants have uncertainties that decrease with the increasing temperature.

4. Conclusions

The rate coefficients for radiative association of $P(^4S)$ and $F(^2P)$ atoms for the formation of PF radical are estimated. The PF-forming transition can occur via the $A^3\Pi$ molecular state, which undergoes radiative transition to the $X^3\Sigma^-$ ground state of PF.

The rate constant values for radiative association in the elastic collision between atoms of phosphorus and fluorine reveal that the reaction $P(^4S) + F(^2P) \rightarrow PF + h\nu$ is inefficient because the estimated rate constants are small. These results indicate that only a modest amount of PF-molecule can be synthesized by radiative association in the upper atmospheres of gas giant planets in the temperature range of 1000-2000 K.

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