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STUDY OF THE $P^+ + H_2 \rightarrow PH_2^+ + h\nu$ AND $PH_2^+ + H_2 \rightarrow PH_4^+ + h\nu$ REACTIONS IN THE INTERSTELLAR MEDIUM

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Abstract. Phosphorus plays a crucial role in biochemistry but its interstellar chemistry remains poorly understood, with only PN, PO and PO^+ detected in the interstellar medium so far, leaving open the question of its main reservoir(s). In this work, we investigate two new reactions pathways that can occur in translucent clouds: $P^+ + H_2 \rightarrow PH_2^+ + h\nu$ and $PH_2^+ + H_2 \rightarrow PH_4^+ + h\nu$. Our quantum chemical calculations reveal that both reactions are exothermic and barrierless, which would make them efficient in the ISM, but in practice they are dominated by back dissociation according to reaction rate estimates. Using the `Nautilus` gas-grain chemistry code, we show that these two reactions have no long-term impact on phosphorus chemistry and that PH_3 on/in ices remains the most abundant P-bearing species in dense environments.

Keywords: Astrochemistry, Phosphorus, Molecules, Radiative association, Modeling, ISM: clouds

1 Introduction

Phosphorus is a key element for life, e.g., through P-O bonds in DNA, yet its interstellar journey remains poorly constrained. Only PN, PO and PO^+ have been detected in star-forming regions so far, raising questions about its reservoir(s). Indeed, those molecules do not recover the expected abundance of phosphorus in such regions. In translucent clouds, phosphorus is expected to be in the form of P^+ and could react with H_2. We then consider two new reactions pathways: $P^+ + H_2 \rightarrow PH_2^+ + h\nu$ and $PH_2^+ + H_2 \rightarrow PH_4^+ + h\nu$, that could occur in the translucent cloud stage. Our purpose is to complete the current chemical network regarding phosphorus chemistry, and to assess the influence of these new reactions on phosphorus chemistry using a chemical model, `Nautilus` (Ruaud et al. 2016).

2 Quantum chemical calculations

We characterized both reactions using ab initio calculations to map their potential energy surfaces (PES). For $P^+ + H_2 \rightarrow PH_2^+ + h\nu$, the four triplet states of the C_{2v} symmetry point group (SPG) were scanned, while for $PH_2^+ + H_2 \rightarrow PH_4^+ + h\nu$ the PES were explored on the singlet surface in C_s SPG. The calculations were performed with the aug-cc-pVTZ basis set with Complete Active Space and Multi-Configurational Self-Consistent Field (CASSCF and MCSCF) methods on `Molpro` (Werner et al. 2020), considering active spaces of 6 electrons/6OM for PH_2^+ and 8 electrons/8OM for PH_4^+.

The results show the formation of weakly bound intermediates in both reactions, as shown in the reaction diagrams in Figure 1. In both cases, the reaction is exothermic and the transition state (TS) is submerged, which makes the pathways barrierless, which is necessary for a gas phase reaction to occur under ISM conditions (Fontani 2024). Once this geometry is reached, three scenarios are possible: (1) stabilization by photon emission, (2) back dissociation, or (3) conversion toward a more stable geometry. However, both reactions should be dominated by back dissociation. The low gas densities in translucent clouds avoid system relaxation through collisions, and photon emission is too slow compared to the lifetime of such intermediates. This interpretation is consistent with the low reaction rates estimates we have: $k = 6.2 \times 10^{-16}$ cm^3 s^{-1} from the KIDA database for the first reaction (Wakelam et al. 2012), and $k = 1.2 \times 10^{-14}$ cm^3 s^{-1} for the second reaction, that we estimated based on Hébrard et al. (2013). In both cases, the efficiency of radiative association is expected to be low compared to back dissociation.

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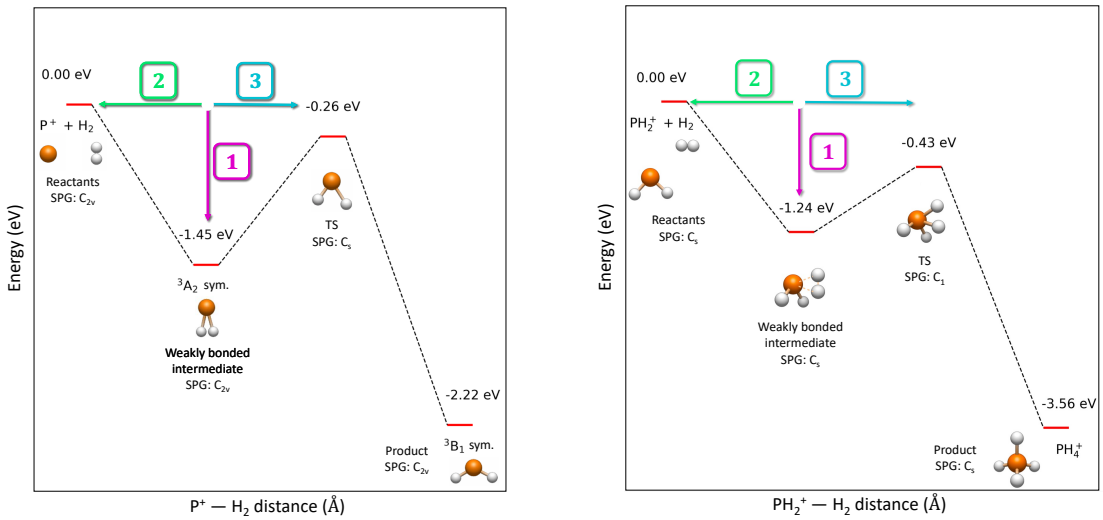

Fig. 1. Left: Reaction diagram of $P^+ + H_2 \rightarrow PH_2^+ + h\nu$. **Right:** Reaction diagram of $PH_2^+ + H_2 \rightarrow PH_4^+ + h\nu$. The (1), (2) and (3) processes are mentioned in the text.

3 Astrochemical modeling

We used `Nautilus`, a three-phase gas-grain code that models the evolution of chemical abundances in a given environment to assess the impact of both reactions in our current chemical network. This code considers the evolution of the chemistry in the gas phase, on the surface of the grain and in the icy mantle of the grain, as well as the exchanges between these three phases. We included both reactions using the reaction rates mentioned before. We assumed the physical conditions of a dense environment with a density of 5×10^4 cm^{-3}, a temperature of 10 K and a cosmic-ray ionization rate of 1.3×10^{-17} s^{-1}. We simulate the evolution of chemistry in a dense molecular cloud during 10^7 years.

At 10^5 yrs, the typical age of a dense molecular cloud, the PH_2^+ abundance is $\sim$ 100 times higher with the updated chemical network than the initial one. The abundance of PH_4^+ shows less than a factor 3 difference between the two models. We also focused on PH_3, phosphine, as it was the most abundant P-bearing species before the addition of both reactions. For phosphine, we can clearly see that the abundances are only impacted at the early times ($<10^3$ yrs) in the gas phase. Based on the other P-bearing species in the network, we can conclude that there is no significant impact from the updated chemical network on the phosphorus chemistry in dense molecular clouds.

4 Conclusions

We have shown that the two reactions studied here could occur under ISM conditions, as they are barrierless and exothermic, but back dissociation should dominate. The addition of both reactions does not influence much the phosphorus chemistry of a dense cloud according to our model. PH_3 in/on ices remains the most abundant P-bearing species in dense environments according to our study.

References

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