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 the origin of life as we know it. Indeed, this element plays an important role in biochemistry (e.g., through P-O bonds in DNA and ATP molecules) and is part of the well-known CHNOPS, the key elements for life on Earth. Thus, understanding its interstellar journey from its initial carriers in the diffuse interstellar medium (ISM), through its depletion onto the dust grains in dense cores, until its delivery to planet forming systems is important. However, phosphorus bearing molecules are poorly detected in star-forming regions, with only three different molecules detected: PN, PO and PO^+. In this work, we investigate phosphorus reservoirs by completing the chemical network of phosphorus in the ISM. We consider new reactions pathways that can occur in translucent clouds: $P^+ + H_2 \rightarrow PH_2^+ + h\nu$ and $PH_2^+ + H_2 \rightarrow PH_4^+ + h\nu$. These reactions could be precursor of phosphorus chemistry in the ISM. We used *Complete Active Space Self-Consistent Field* (CASSCF) and *Density Functional Theory* (DFT) computational methods. We used the Nautilus (Ruaud et al., 2016) gas-grain chemistry code with an updated chemical network considering both reactions studied to assess their influence on phosphorus chemistry. These results give new insights on the possible phosphorus reservoir in the ISM.

I. Calculations

Goal: to study 2 reactions pathways and to include them to current chemical network

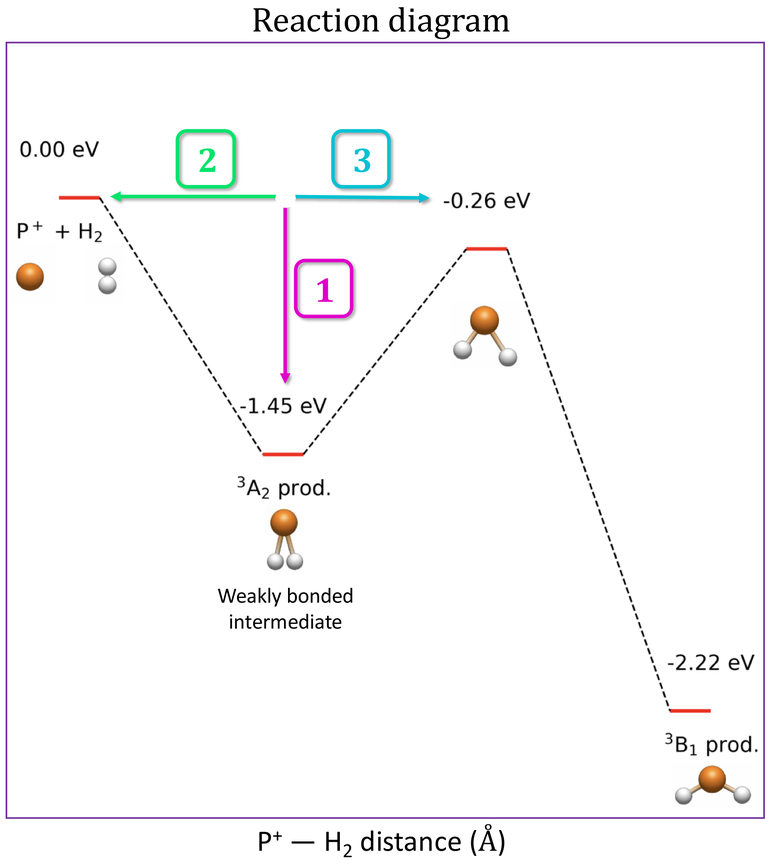
Methodology

- Method: CASSCF ($6e^-$/6OM)
- Basis set: aug-cc-pVTZ
- State: Triplet

- Method: DFT / M06-2X
- Basis set: aug-cc-pVTZ
- State: Singlet

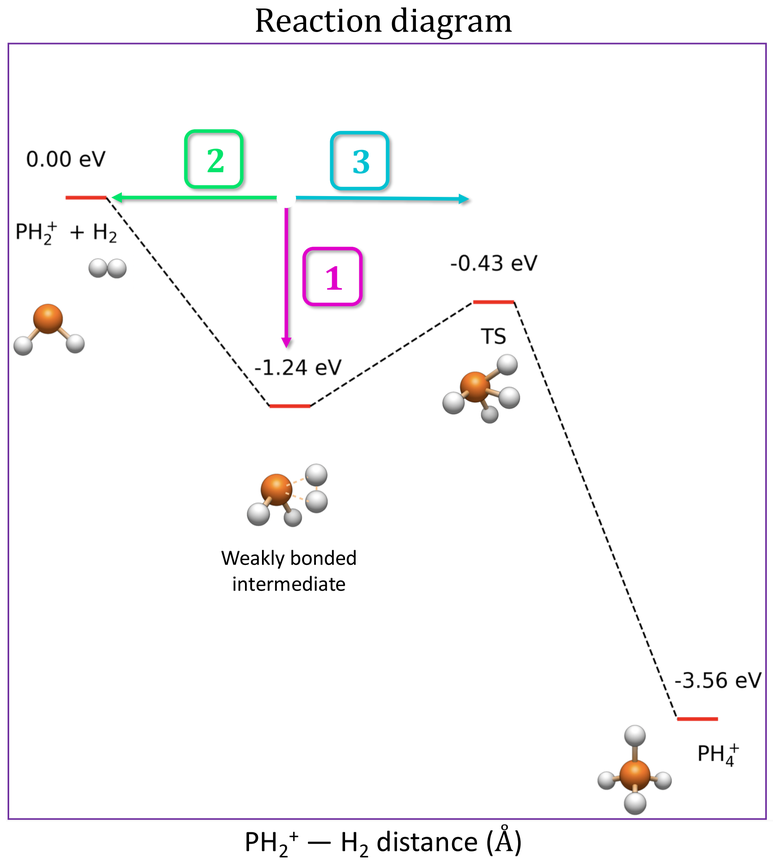
$P^+ + H_2 \rightarrow PH_2^+ + h\nu$

Reaction diagram



$PH_2^+ + H_2 \rightarrow PH_4^+ + h\nu$

Reaction diagram



Results

Once the intermediate geometry is reached, we have **3 possible processes**:

- Photon emission — 1 — Slowest process
- Back dissociation — 2
- Spatial rearrangement — 3

2 and 3: Competitive processes

Reaction rates at 10 K:

- $P^+ + H_2 \rightarrow PH_2^+ + h\nu$

$k = 6.2 \times 10^{-16}$ cm^{-3}.s^{-1}

From KIDA (Wakelam et al., 2012)

- $PH_2^+ + H_2 \rightarrow PH_4^+ + h\nu$

$k = 1.2 \times 10^{-14}$ cm^{-3}.s^{-1}

Estimate based on a model from Hébrard et al., 2013

II. Modeling

Goal: to assess the impact of the two reactions on phosphorus chemistry through chemical modeling

Chemical model

Nautilus (Ruaud et al., 2016)

- 3 phase gas-grain model
- Time evolution of the abundances of species

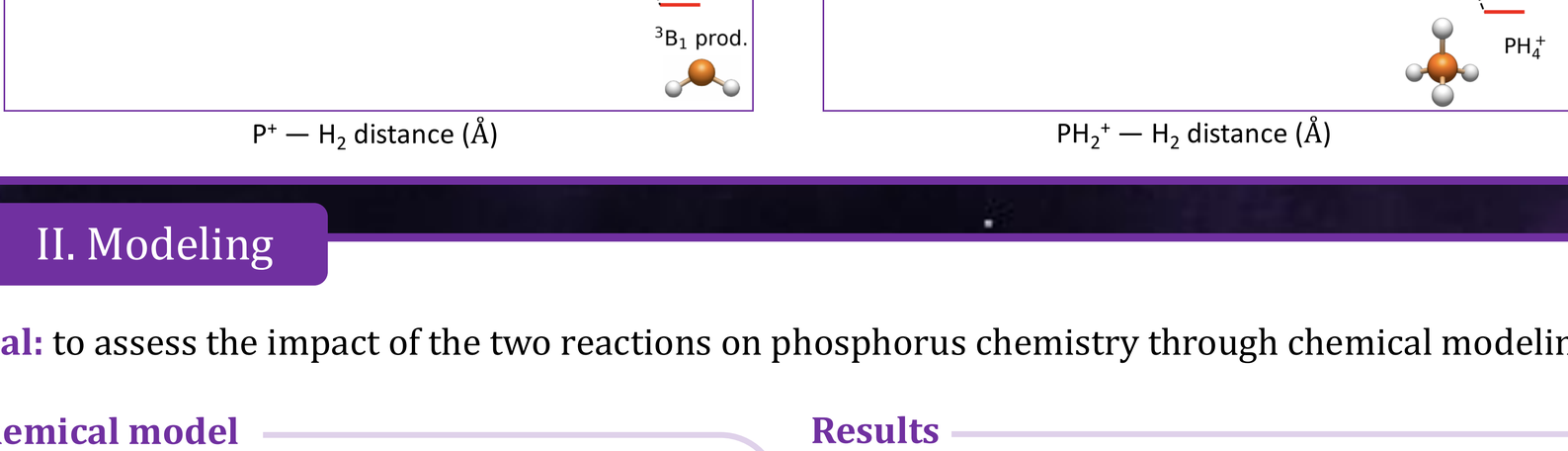
Input: Molecular cloud physical conditions

- $n = 5 \times 10^4$ cm^{-3}
- $T = 10$ K
- $\zeta = 1.3 \times 10^{-17}$ s^{-1}

Results

- Updated chemical network
- Initial chemical network

- Increase of the abundances of PH_2^+, PH_4^+ and PH_3 in the gas phase at early times ($\lesssim 10^5$ yrs)
- No impact on PH_3 in the gas phase after 10^3 yrs
- No impact on solid PH_3



Conclusions

→ Both reactions could occur under ISM conditions, but **back dissociation should dominate** according to the reaction rates

→ **PH_3** in/on ices is the **most abundant** P-bearing species in dense environments according to the model

→ **PH_3 reservoir** of phosphorus?

Perspectives

→ **Update the chemical network** with new phosphorus related reactions

→ **Investigate other molecules** as candidate for the phosphorus reservoir