

POLYAROMATIC HYDROCARBONS WITH AN IMPERFECT AROMATIC SYSTEM AS CATALYSTS IN INTERSTELLAR HYDROGEN FORMATION

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Introduction

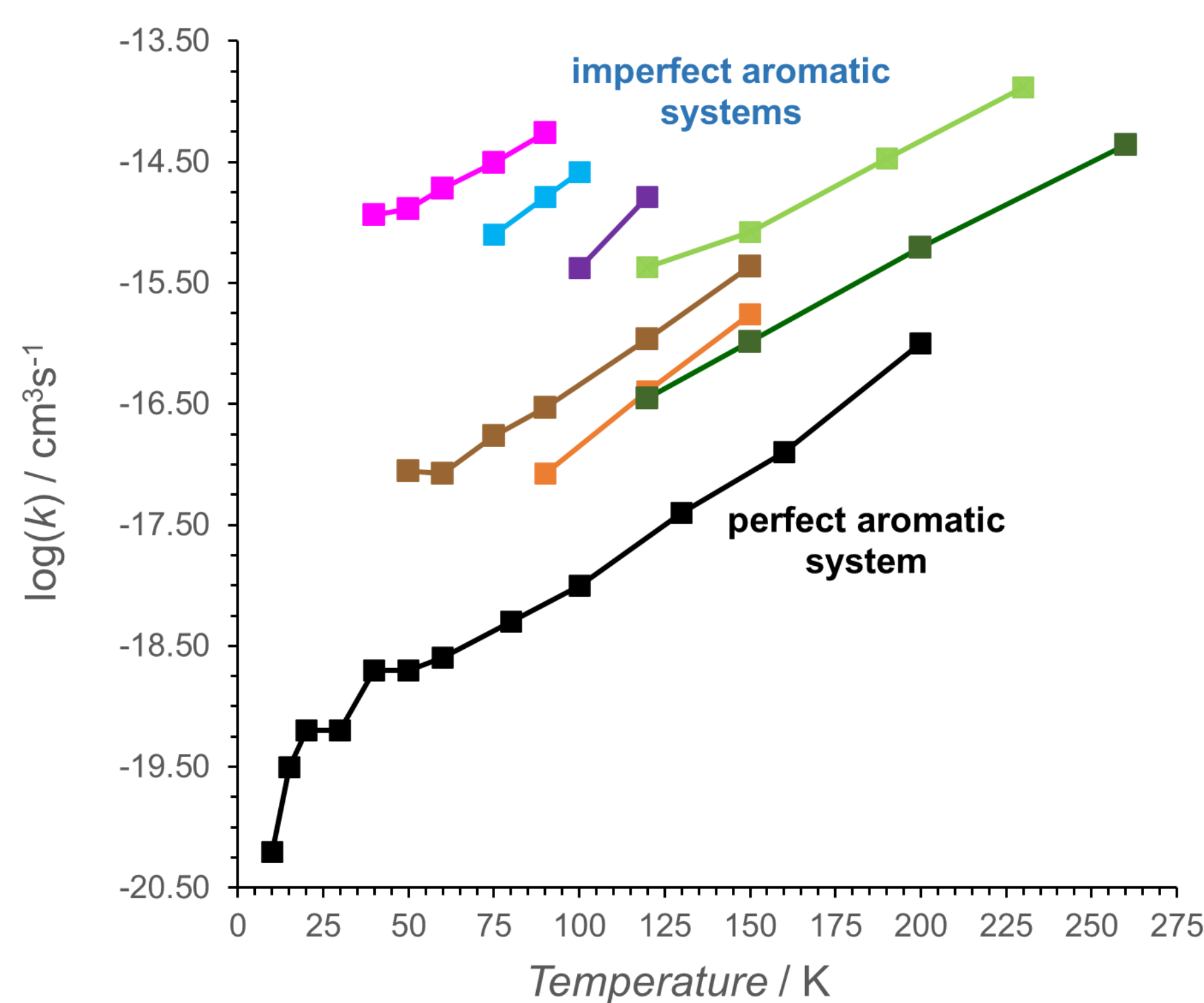
Although H_2 is the smallest and the most abundant molecule of the interstellar medium (ISM), its formation in the present Universe is still not fully understood. A possible solution can be chemisorption on the surface of icy grains. In this case, the hydrogen molecule is formed in subsequent hydrogen-atom-abstraction and addition or subsequent hydrogen-atom-addition and abstraction reactions. Therefore, this process can be considered a catalytic cycle [1]. Usually, one of the reaction steps has a barrier, while the other reaction is barrierless. Polyaromatic hydrocarbons can act as a catalyst [2]. Schneiker et al. [3] have suggested that in the case of PAHs with an imperfect aromatic system, such as phenalene, the barrier of the reaction with an H atom can be smaller and therefore, these can be better catalysts than PAHs with a perfect aromatic system.

In the present study we investigated polyaromatic hydrocarbons with different aromatic characters: benzene [4], cyclopentadiene, cycloheptatriene, indene and phenalene. Among these, benzene was identified in the ISM in 2001 [5], while cyclopentadiene and indene in 2021 [6].

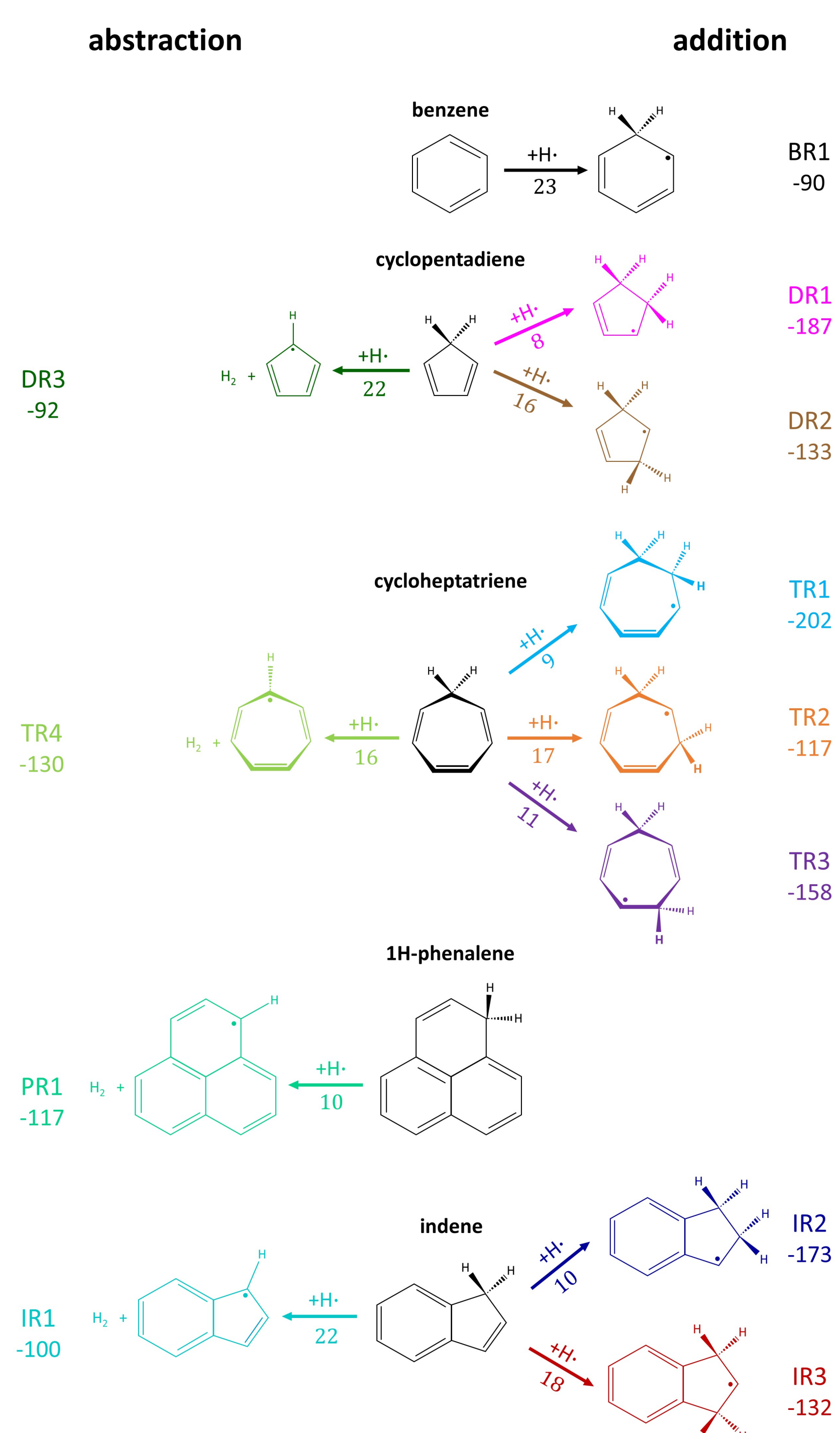
Computational methods

In the present study computations were performed for the H-atom-abstraction and H-atom-addition reactions using Gaussian [7], i-PI [8] and FHI-aims [9] program systems. Heights of reaction barriers and reaction rates were determined for the investigated molecules with density functional theory (MPWB1K/cc-pVTZ). Furthermore, the reaction path and the tunneling reaction rates were determined at different temperatures using ring-polymer instanton theory for cyclopentadiene and cycloheptatriene.

Reaction rates



Reactions with hydrogen atom

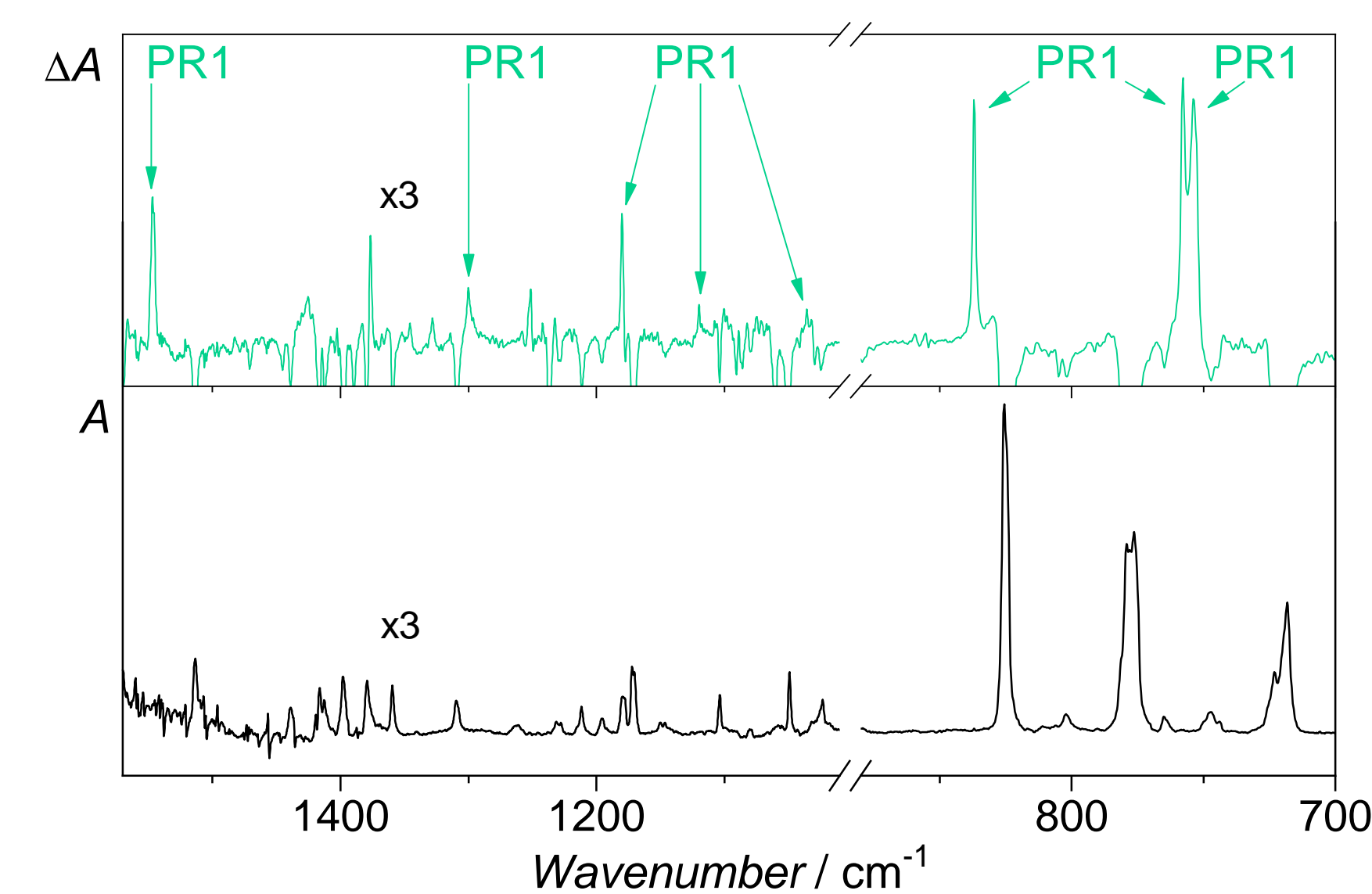


The zero-point-vibrational energy corrected barrier heights are given above the arrows, while heats of reactions at 0 K are below the notations. Values are in kJ mol^{-1} .

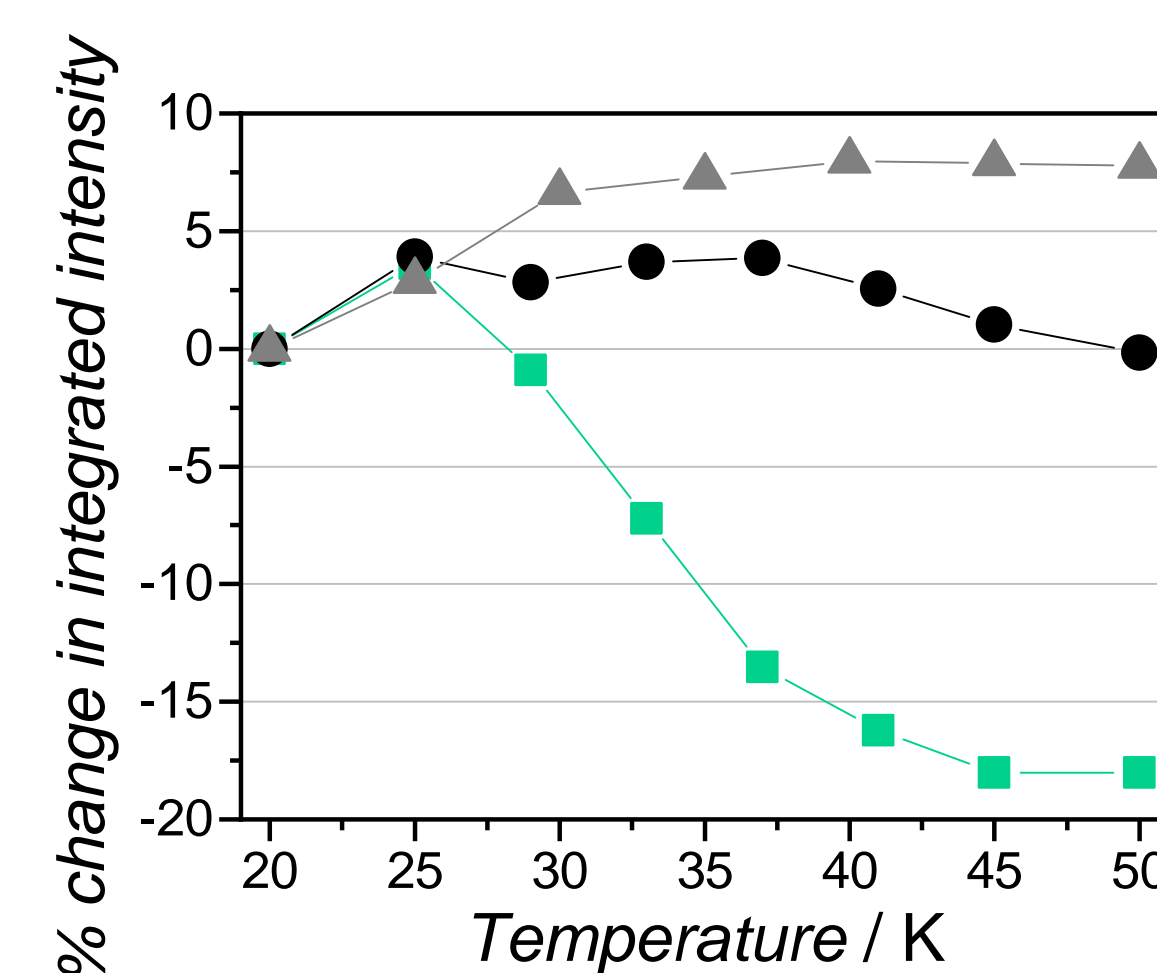
Experimental 1:

1H-Phenalene in Xe matrix

- Deposition** in amorphous Xe matrix at 20 K.
- Irradiations** at 335, 322, 250 and 220 nm.
 - $P \rightarrow PR1 + H$
- Annealing** after photolysis.
 - $PR1 + H \rightarrow P$



black: IR spectrum of 1H-phenalene in a 20 K Xe matrix.
green: Difference spectrum obtained by subtracting the spectrum recorded after deposition from the spectrum recorded after 90 min 220 nm irradiation.

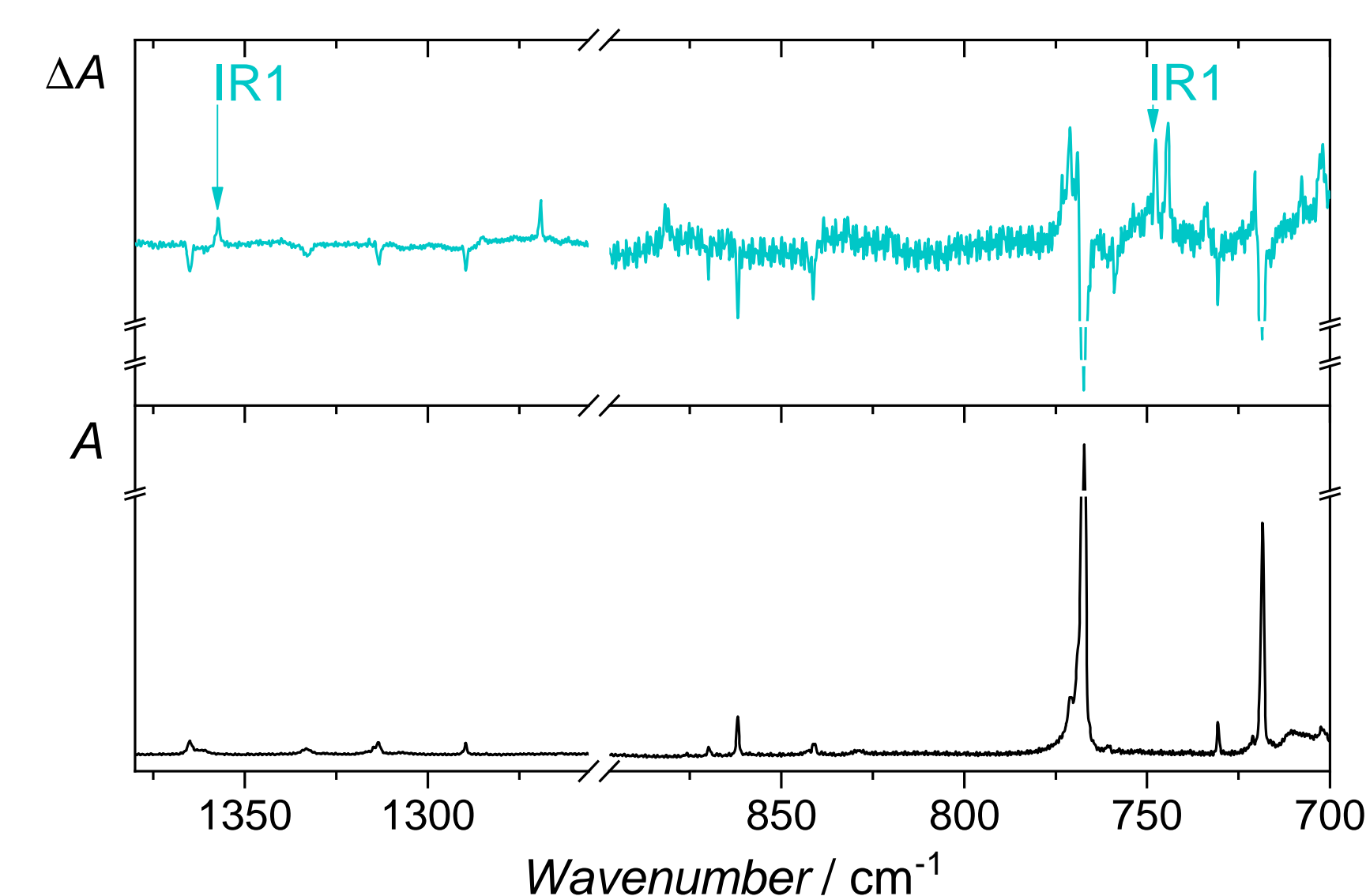


■ Band of phenalenyl radical observed after 250 nm photolysis.
● Band of 1H-phenalene observed after 250 nm photolysis.
▲ Band of 1H-phenalene observed without photolysis.

Experimental 2:

Indene in *para*-H₂ matrix

- Co-deposition** of indene (I) with Cl_2 and *para*- H_2 (for blank experiments without Cl_2) at 3.1 K.
- Exposition to 365 nm light to produce Cl atoms.
 - $Cl_2 \rightarrow 2Cl$
- Irradiation with 2217 nm to **generate H atoms**.
 - $Cl + H_2^* \rightarrow HCl + H$
 - $I + H \rightarrow IR1 + H_2$
- Dark process** (H atom diffusion).
 - $I + H \rightarrow IR1 + H_2$



black: IR spectrum of indene in *para*- H_2 matrix at 3.1 K.
blue: Difference spectrum obtained by subtracting the spectrum recorded after deposition from the spectrum recorded after H atom generation and waiting 11 hours in the dark.

Astrochemical relevance

According to our computations the barriers of the H-atom-addition reactions of the investigated imperfect aromatic systems are smaller than that of benzene. The barriers of the H-atom-abstraction reactions of the investigated systems also have smaller or similar barriers than of the H-atom-addition reaction of benzene. In addition, the tunnelling reaction rates at different temperatures of reactions are larger by 2-4 orders of magnitude for cyclopentadiene and cycloheptatriene than for benzene. Hence, our work suggests that polyaromatic hydrocarbons with an imperfect aromatic system can be better interstellar catalysts than those with a perfect aromatic system.

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Acknowledgement

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