Rate of quantum tunnelling measured in a cold ion-molecule reaction

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1 Astrophysical motivation

The hydride anion, H^-, is suspected to exist in the interstellar medium (ISM) and have played an important role in stellar formation. In particular, it likely is the source of molecular hydrogen, through the pathway[1]

$$H + e^- \longrightarrow H^- + \gamma \tag{1a}$$
$$H^- + H \longrightarrow H_2 + e^- \tag{1b}$$

Its presence can also help to explain the observation of the cyanide anion CN^- in the ISM. Rate calculations for radiative electron attachment are too slow to explain the concentration observed in the ISM[2]TODO: Check this is true However, the pathway proposed inTODO: when I have vpn access can help to explain the observation of cyanide:

$$H^- + HCN \longrightarrow H_2 + CN^- \tag{2}$$

since hydrogen cyanide is produced in stellar ejecta[3].

In general, it is very difficult to observe anionic species in the ISM, as UV radiation fields can very easily remove the extra electron. Case in point, the hydride anion has only a single bound state, and thus has no spectral lines which can be used as a convincing marker. Rather, the species ${H_3}^-$ could be used as a tracer[4] due to its IR vibrotational spectrum. While this species has not been observed yet, it is still interesting to ask the question of what is its formation rate?

2 Chemistry

The reaction that allows this is

$$H_2 + H^- \rightleftharpoons {H_3}^- \tag{3}$$

TODO: Figure out why this isn't studied, probably from[5], that the low potential well means that the molecule can easily be broken apart.

While ${H_3}^-$ has a binding energy of 13 meV, which means it can in principle be isolated at $\lesssim 150\,\mathrm{K}$ it is easier instead to consider the analogue

$$H_2 + D^- \longrightarrow \left[H_2D^-\right]^\ddagger \longrightarrow HD + H^- \tag{4}$$

since the heavier mass of deuterium decreases the vibrational zero point energy of the products on the RHS, driving the reaction forward through a release of energy. However, electrically, H^- and D^- are almost identical, and so we expect the attack on the LHS to be very similar to Eq. 3. Furthermore, it is much easier to measure the rate of this reaction, since the end products don't back-react to recreate the starting material, and all anionic species can very easily be separated by their charge-to-mass ratio by either time of flight or cyclotron radius. Combined, these two features make the determination of the rate constant significantly easier.

In particular TODO: something about photo deionization and cold. In particular, the environment of the ISM is very sparsely populated and cold, so TODO: idk lol. In such conditions, given the experimentally determined reaction barrier of about 330 meV[6], the reaction can only proceed incredibly slowly via tunnelling. Estimates for an upper boun on the reaction rate by [7]

References

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