

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

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 original source of molecular hydrogen, before dust grains allowed surface chemistry, through the pathway[1]



This is because three-body collisions are heavily suppressed by low densities while vibrational/rotational transitions are dipole forbidden due to no transition/permanent dipole moment respectively[2]. 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[3]. However, the pathway studied in [4] can help to explain the observation of cyanide:



since hydrogen cyanide is produced in stellar ejecta[5] and H^- is produced by heterolytic cleavage of H_2 by a cosmic ray[4].

In general, it is very difficult to observe anionic species in the ISM, as UV radiation fields can very easily remove the extra electron. Even more challenging, the hydride anion has only a single bound state at 0.77 eV, and thus has no spectral lines which can be used as a convincing marker. Rather, in cold, dense regions of the ISM with low a low ionization fraction, the species H_3^- could be produced in meaningful quantities and used as a tracer[6] due to its IR vibrotational spectrum. Supposing this species will be eventually observed with high enough sensitivity, its chemistry can be used to probe the amount of H^- in the ISM.

2 Chemistry

The reaction that allows this is the formation of the complex



H_3^- has a binding energy of about 13 meV, which means it can in principle be isolated at $\lesssim 150$ K. However, the strong voltages used to manipulate the ions can very easily rip this complex apart. Rather, it is easier to experimentally benchmark the ab initio calculations using the isotopologue reaction



since the heavier mass of deuterium decreases the vibrational zero point energy of the products on the RHS by about 25 meV, driving the reaction forward through a release of energy.

Electrically, since H^- and D^- are almost identical, quantifying the PES of the isotopologous reaction should inform the validity of the H_3^- calculations. 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 studying the tri-hydrogenic anion's chemical properties much easier.

The reaction is done cryogenically. In such conditions, given the experimentally determined reaction barrier of about 330 meV[7], the reaction can only proceed incredibly slowly via tunnelling. Estimates for an upper bound on the reaction rate by [8] indicated the need for both high concentrations and long reaction times in able to obtain the necessary reaction rates. Further, since the reaction can only proceed through quantum tunnelling, it serves as an experimental test for theoretical cross-sections derived through quantum-mechanical scattering calculations.

3 Experiment

3.1 Manipulating and Measuring Ions

3.1.1 Electrostatics and Wiley-Maclauren spectrometer

Naturally, as charged particles, ions can be manipulated using electric fields produced by applying a voltage to an electrode. As a prototypical example, let us consider the Wiley-Maclauren spectrometer. The negative ions are accelerated by a Wiley-Maclauren spectrometer, and separated by time-of-flight. In essence, the Wiley-Maclauren spectrometer is a parallel plate capacitor that accelerates charged particles proportional to their charge to mass ratio. As they fly, undesirable q/m particles can be deflected electrostatically, e.g., via quadrupole deflector or simple plate deflectors, before they enter the trap. Chromatographically separate by time-of-flight.

3.1.2 MCP

Charged semiconductor with diagonal holes. Charged species crash into hole wall, eject ions, get accelerated, crash into wall again and so forth, multiplying single anions to appreciable currents. Integrate peaks on detector to determine number.

3.2 Multipole Trap and Cooling

D^- is produced in a plasma discharge, and separated chromatographically using the Wiley-Maclauren spectrometer before loading into the MP trap.

Trap is probably loaded axially then static field to trap. Assuming that the apparatus used is an upgraded version of the one used in [9].

Once loaded into the trap, cooling has to be done by thermalization with the container walls via a buffer gas. This is because neither D^- nor H_2 have accessible transitions for optical cooling. The buffer gas cooling is most effective at high multipole order because the RF heating of the ion by the alternating electric field is limited to a narrow, sharp region at the boundary, rather than a broad shallow field over the entire trap. The temperature is not measured directly, but inferred based on a combination of thermalization with the known copper housing.

A buffer gas of H_2 is used. While hot D^- will react with the H_2 buffer gas, enough is cooled down quickly enough where an appreciable amount can build up in the trap. To monitor the trap population, a small voltage is used to kick a small piece of the ion cloud out of the trap.

Of course, at the beginning of cooling, there will be enough thermal energy to overcome the reaction barrier leading to a small initial H^- peak. However, Once cooled though, the amount of buffer gas is quite low so continued reaction rates are negligible. A portion of the cloud can be extracted from the trap and sent into another ToF spectrometer, with a MCP detector. Integrated current gives population.

Calibrated against typical loss rates. MP traps have to satisfy an adiabaticity condition, but collisions with buffer gas and other dynamical properties cause loss of all anionic species. This is measured and calibrated.

3.3 Reaction, Detection and Measurement

Then pump with H_2 to reaction concentration and allow to react at constant pressure for pseudo-first-order reaction. Fixed time, pressure, then pump down to not overwhelm MCP.

The detector is an MCP, a type of secondary emission multiplier, where a charged particle collides with a substrate, ejects more charged particles, and those charged particles are accelerated into another substrate, leading to a cascade of charged particles that can be detected as a current.

Naturally, such a detection is highly sensitive to the number of gas molecules, as the high voltages used to accelerate ions in the MCP can easily ionize the molecular hydrogen and overwhelm the detector. Thus, before measurements, the chambre is pumped down to a low H_2 pressure. Then, a small amount of the trapped ions is “kicked” from the multipole trap with a deflector electrode, accelerated by another WM spectrometer, and separated by ToF before measurement by the MCP. The current can be integrated to compare the fraction of ions that are hydrogen to deuterium.

Then, from this fraction, loss rates can be determined. Assuming particles have a fixed probability of leaving the trap, the rate of change in particle number of each species can be written

$$\frac{dH}{dt} = kD - x_H H \tag{5a}$$

$$\frac{dH}{dt} = -(k + x_D)D \tag{5b}$$

or

$$\frac{d}{dt} \begin{pmatrix} H \\ D \end{pmatrix} = \begin{pmatrix} -x_H & k \\ 0 & -(k+x_D) \end{pmatrix} \begin{pmatrix} H \\ D \end{pmatrix} \quad (6)$$

which has two eigenvectors,

$$\begin{pmatrix} H \\ D \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} -\frac{k}{k+x_D-x_H} \\ 1 \end{pmatrix} = V, U$$

with time evolutions

$$V = V_0 e^{-k_H t} \\ U = U_0 e^{-(k+x_D)t}$$

Therefore, the initial condition of (H_0, D_0) gives $U_0 = D_0$, $V_0 = \frac{k}{k+x_D-x_H} D_0 + H_0$, which evolves as

$$\frac{H}{D_0} = -\frac{k}{k+x_D-x_H} (e^{-(k+x_D)t} - e^{-x_H t}) + \frac{H_0}{D_0} e^{-x_H t} \quad (7a)$$

$$\frac{D}{D_0} = e^{-(k+x_D)t} \quad (7b)$$

These of course can be combined as

$$\frac{H}{D} = \frac{k}{x_H - k - x_D} (1 - e^{-(x_H - k - x_D)t}) + \frac{H_0}{D_0} e^{-(x_H - k - x_D)t} \quad (8)$$

however, the authors did not do this analysis. Rather, they expanded out the growth and decay of each of the H^- and D^- peaks to second order in Taylor series, since each of these rates are $\ll 1/t$, and fit the two peaks. This gives the pseudo-first-order reaction constant k , which can be used to determine the reaction constant $k_r = k/n_H$ by dividing out the roughly fixed hydrogen density.

4 Results and analysis

Due to radio-frequency heating, the distribution of reactants is not a Boltzmann distribution and thus has a different rate behaviour than reactants in thermal equilibrium. To model the non-equilibrium distribution of the ions, a Tsallis distribution is used

$$f(v_i) \sim \left(1 + (q-1) \frac{\frac{1}{2} m v_i^2}{k_B T} \right)^{\frac{1}{1-q}} \quad (9)$$

In the limit of $q \rightarrow 1$ this recovers the Boltzmann distribution, and at $q > 1$ a power-law tail is developed at the high end of the velocity distribution. The trajectories are numerically integrated with random collisions with a thermal buffer gas. These simulations show a nonlinear dependence in the $[H_2]$ concentration, which were in fair agreement with experimental measurements, showing the impact of the RF heating at very high densities. Indeed, the effects of the RF heating are observed as a faster-than-linear growth of the rate with respect to density, as RF heating leads to a lower effective barrier height. Thus, to mitigate this non-thermal effect, a linear fit was done for the lowest reactant densities. The rate they determined was $5.2(16) \times 10^{-20} \text{ cm}^3 \cdot \text{s}^{-1}$, which is the slowest reaction rate ever measured.

A Dipole Approximation

Recall that a charged particle in an electromagnetic field has the hamiltonian

$$H = \frac{(\mathbf{p} - \frac{q}{c}\mathbf{A})^2}{2m} + qV \quad (10)$$

Fixing Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$, we can expand about a small perturbing vector potential,

$$H = -\frac{\hbar^2 \nabla^2}{2m} + qV + \frac{i\hbar q}{mc} \mathbf{A} \cdot \nabla \quad (11)$$

with $\nabla^2 V(\mathbf{r}) = -4\pi\rho(\mathbf{r})$. Under the Coulomb gauge, solutions are given

$$\mathbf{A} = A\hat{\mathbf{e}}e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \quad (12)$$

which are exactly planewave, or polarized beams of light. In particular, in terms of the spectral intensity

$$I(\omega) = \frac{\omega^2}{2\pi c} |A|^2 \quad (13)$$

we can simplify the expansion of Fermi's Golden Rule

$$R = \frac{2\pi}{\hbar} \rho_f(E_f) |\langle f|V_1|i\rangle|^2 \quad (14)$$

as

$$R = \frac{4\pi^2 e^2}{m^2 c \omega^2} I(\omega) \begin{cases} \left| \int d^3r \psi_f^* e^{i\mathbf{k}\cdot\mathbf{r}} \hat{\mathbf{e}} \cdot \nabla \psi_i \right|^2 & \omega = +\omega_{fi} & \text{absorption} \\ \left| \int d^3r \psi_f^* e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{\mathbf{e}} \cdot \nabla \psi_i \right|^2 & \omega = -\omega_{fi} & \text{emission} \end{cases} \quad (15)$$

Typically, we will have $\lambda \sim \text{nm} \gg R_{\text{atom}} \sim \text{\AA}$, and so we can approximate $\mathbf{k} \cdot \mathbf{r} \sim R_{\text{atom}}/\lambda \ll 1$. The leading orders are the *dipole* and *quadrupole* operators

$$e^{\pm i\mathbf{k}\cdot\mathbf{r}} \approx 1 + i\mathbf{k} \cdot \mathbf{r} + \mathcal{O}[(\mathbf{k} \cdot \mathbf{r})^2]$$

Using

$$[\mathbf{r}, H_0] = \frac{i\hbar}{m} \mathbf{p}$$

we can write

$$\langle f|\hat{\mathbf{e}} \cdot \nabla|i\rangle = -\frac{m\omega_{fi}}{\hbar} \langle f|\hat{\mathbf{e}} \cdot \mathbf{r}|i\rangle \quad (16)$$

to obtain selection rules.

A.1 Vibrotational

To second order in the quantum numbers ν, ℓ , the harmonic oscillator gains an anharmonic correction

$$H_{AHO} = \hbar\omega_e \left(\nu + \frac{1}{2} \right) - \omega_e \chi_e \left(\nu + \frac{1}{2} \right)^2$$

the rigid rotor gains centrifugal distortion term

$$H_{NRR} = B_e \ell(\ell + 1) + D_v [\ell(\ell + 1)]^2$$

and a vibrotational coupling is added

$$H_{RV} = -hc\alpha_e \left(\nu + \frac{1}{2} \right) [\ell(\ell + 1)]$$

This is of course much more difficult to treat analytically, but if we treat these as perturbations about H_{SHO} and H_{RR} , we can inherit those selection rules.

B Hydrogen Chemistry and Spectroscopy

Ab initio calculations determine that H_3^- has nine bound states, five in the A'_2 irrep and four in the A'_1 irrep. These should have transitions ranging from 1–10 meV, 0.1–1 mm, or 0.3–3 THz. The ground state is bound by about 13 meV.

Redshift of ~ 1000 for dark ages, density of $\text{H}\cdot$ is $\sim 0.1\text{--}10^2 \text{ cm}^{-3}$ and of H_2 is $10^2\text{--}10^6 \text{ cm}^{-3}$ depending on region. Ionization rate constant $\zeta \approx 3 \times 10^{-17} \text{ s}^{-1}$ is the rate at which cosmic rays ionize diffuse molecular clouds 10^2 cm^{-3} . H_2^+ is rapidly stabilized into H_3^+ with rate constant $2 \times 10^{-9} \text{ cm}^3 \cdot \text{s}^{-1}$. Each collision causes a fractional loss of $\sim \frac{m_e}{m_{\text{H}_2}}$ before the electron thermalizes to $\sim 100 \text{ K}$ after ~ 6200 collisions. However, above 3.7 eV, the electron has a chance to disassociatively attach via $\text{e}^- + \text{H}_2 \longrightarrow \text{H}\cdot + \text{H}^-$. This occurs with a cross-section of about $\sigma_{DA} \sim 3 \times 10^{-21} \text{ cm}^2$ at 4 eV, while elastic collision occurs with a cross-section of about $\sigma_{\text{el}} \sim 1.7 \times 10^{-15} \text{ cm}^2$. Assuming $\mathcal{O}(1000)$ collisions occur before DA, the fraction of electrons that form H^- is $f_{\text{DA}} = \sigma_{\text{DA}}/(\sigma_{\text{el}}/1000) \sim 1.8 \times 10^{-3}$. Modelling loss by neutralization $\sim k_0 n_+ n[\text{H}^-]$ we arrive at a steady state, etc. From [6], an approximate formula can be written **TODO: learn this**

$$n(\text{H}_3^-) = \frac{k_{\text{RA}} \zeta f_{\text{DA}}}{(k_{\pm})^2} \left(\frac{n(\text{H}_2)}{n_+} \right)^2 \quad (17)$$

C Star formation

Star formation requires gravitational and external pressures to overcome internal energies and pressures. This can be stated[2]¹ as the *virial equation*

$$\begin{aligned} \ddot{I} = & \int_V dV \left(\frac{1}{2} \rho v^2 + \frac{3}{2} P \right) + \int_{\partial V} r^i \Pi_{ij} dS^j + \frac{1}{8\pi} \int_V B^2 dV \\ & + \int_{\partial V} r^i T_{ij} dS^j - \int_V dV \rho \mathbf{r} \cdot \nabla \phi - \frac{1}{2} \int_{\partial V} \rho r^2 \mathbf{v} \cdot d\mathbf{S} \end{aligned} \quad (18)$$

¹derived from MHD

where the first line \mathcal{T} are the kinetic and thermal energy, the second line \mathcal{T}_S is the confining pressure $\Pi_{ij} = \rho v_i v_j + P \delta_{ij}$ from ram and thermal pressure respectively, the third line \mathcal{B} is the difference between the internal magnetic pressure and the external magnetic pressure/tension from the Maxwell stress tensor T_{ij} , the fourth line \mathcal{W} is the energy due to the gravitational potential ϕ , and the final term is the rate of change of the momentum flux. If magnetic and surface effects are negligible and the system is in hydrostatic equilibrium, we obtain a virial ratio

$$\alpha_{\text{virial}} = \frac{2T}{|W|} \quad (19)$$

where for $\alpha_{\text{virial}} > 1$ implies $\ddot{I} > 0$ and vice-versa. If there is only thermal pressure, this leads to the *Jeans criterion*

$$\mathcal{T} \approx \frac{3}{2} M c_s^2 \quad \mathcal{W} \approx -a \frac{GM^2}{R} \quad \Rightarrow \quad R \gtrsim \frac{c_s}{\sqrt{G\rho}}$$

for a stable gas cloud. If this is violated, the cloud begins to collapse. More rigorous linearized perturbation of the hydrodynamics and self gravity determine a dispersion relationship

$$\omega^2 = c_s^2 k^2 - 4\pi G \rho_0 \quad (20)$$

which at $\omega = 0$ yields a critical point

$$\lambda_J = \frac{2\pi}{k} = \sqrt{\frac{\pi c_s^2}{G\rho_0}} \quad (21)$$

above which perturbations grow exponentially, and below which perturbations are stabilized. In particular, the dispersion relation gives a timescale of freefall, $\tau \sim 1/|i\omega|$.

C.1 Early Stars

In order to reduce \mathcal{T} to allow star formation, the early gas clouds had to cool. However, these clouds were comprised mostly of ^1_1H and ^4_2He , whose atomic transitions occurred at roughly $10\text{ eV} \sim 10^5\text{ K}$; below this temperature, atomic lines are inefficient at cooling. The $J = 2$ transition of molecular H_2 has a characteristic temperature of about 500 K , and can cool to about 200 K . This phase is the *loitering phase*, but as the region at 200 K grows larger, the rate of three body recombination increases, allowing for the density to increase until an equilibrium between the heating from binding energy release competes with cooling from quadrupole line emission. Eventually, the density increases to the point where they are thick to the H_2 lines, so heating dominates, and the star can begin collapsing/fusing.

D RF Traps

This section primarily follows [10]. Recall the Lorentz force,

$$m\ddot{\mathbf{r}} = q\mathbf{E} + q\dot{\mathbf{r}} \times \mathbf{B} \quad (22)$$

For cryogenic temperatures, i.e. slow atoms, the effect due to the magnetic field is going to be heavily suppressed by the magnitude of $\dot{\mathbf{r}}$, so it is neglected. The electric field can be engineered such that it can be separated into an RF and a DC component.

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_{RF}(\mathbf{r}) \cos \Omega t + q\mathbf{E}_{DC}(\mathbf{r}) \quad (23)$$

For convenience, we fix $\mathbf{E}_{DC} = 0$, although it will be used later to create an axial confinement. Additionally we treat inhomogeneities in the RF fields as perturbations to a homogeneous field,

$$\mathbf{E}_{RF}(\mathbf{r}) = \mathbf{E}_0 + \mathbf{E}_I(\mathbf{r}) \quad \mathbf{E}_I(0) = 0 \quad (24)$$

In particular, a solution to the homogeneous field can be trivially found by integration

$$\mathbf{R}_{RF}(t) = -\frac{q\mathbf{E}_0}{m\Omega^2} \cos \Omega t \equiv -\mathbf{a} \cos \Omega t \quad (25)$$

Note that the amplitude of oscillations is suppressed by the frequency of the RF trap. By choosing a relatively high frequency, we can treat the oscillations due to the homogeneous field as a small perturbation superposed on top of the drift due to a weak or slowly varying inhomogeneous field,

$$\mathbf{r}(t) = \mathbf{R}_d(t) + \mathbf{R}_{RF}(t) \quad (26)$$

thus, we can expand the electric field the particle feels as a function of time

$$\mathbf{E}_{RF}(\mathbf{r}(t)) \approx \mathbf{E}_{RF}(0) - (\mathbf{a} \cdot \nabla) \mathbf{E}_{RF}(0) \cos \Omega t + \mathcal{O}(E_I^2)$$

Since the drift velocity is small and the field inhomogeneities are small, we additionally have $\dot{\mathbf{a}} \ll \Omega \mathbf{a}$, $\dot{\mathbf{R}}_d \ll \Omega \mathbf{R}_d$. After substituting, neglecting small terms, and applying the identity

$$(\mathbf{v} \cdot \nabla) \mathbf{v} = \frac{1}{2} \nabla v^2 - \mathbf{v} \times (\nabla \times \mathbf{v})$$

the drift EoM becomes

$$m\ddot{\mathbf{R}}_d = -\frac{q^2}{4m\Omega} \nabla E_{RF}^2 \quad (27)$$

Naturally, as $\mathbf{F} = -\nabla U$, we can write an effective potential

$$U_{\text{eff}} = \frac{q^2}{4m\Omega} E_{RF}^2 + q\Phi$$

We obtain an interpretation that particles tend to drift towards regions with lower field amplitudes. A natural implementation of such a field configuration is the multipole trap

D.1 Multipole Configuration

Solving Laplace's equation, an ideal multipole configuration located at radius r_0 and having a profile $\Phi_n(r_0, \varphi) = \cos n\varphi$, $\Phi_n(0) = 0$, will have a potential

$$\Phi_n(r, \varphi) = \Phi_0 \left(\frac{r}{r_0} \right)^n \cos n\varphi$$

yielding an effective potential

References

- [1] P. J. E. Peebles and R. H. Dicke, The Astrophysical Journal **154**, 891 (1968), Publisher: IOP ADS Bibcode: 1968ApJ...154..891P.
- [2] M. R. Krumholz, Notes on Star Formation, 2016, arXiv:1511.03457 [astro-ph].
- [3] N. Douguet *et al.*, Physical Review A **88**, 052710 (2013), Publisher: American Physical Society.
- [4] M. Satta, F. A. Gianturco, F. Carelli, and R. Wester, The Astrophysical Journal **799**, 228 (2015), Publisher: IOP ADS Bibcode: 2015ApJ...799..228S.
- [5] A. G. G. M. Tielens, Reviews of Modern Physics **85**, 1021 (2013), Publisher: American Physical Society.
- [6] M. Ayouz, R. Lopes, M. Raoult, O. Dulieu, and V. Kokoouline, Physical Review A **83**, 052712 (2011), Publisher: American Physical Society.
- [7] M. Zimmer and F. Linder, Journal of Physics B: Atomic, Molecular and Optical Physics **28**, 2671 (1995).
- [8] E. S. Endres, O. Lakhmanskaya, M. Simpson, S. Spieler, and R. Wester, Physical Review A **95**, 022706 (2017), Publisher: American Physical Society.
- [9] J. Mikosch *et al.*, Physical Review A **78**, 023402 (2008), Publisher: American Physical Society.
- [10] D. Gerlich, Inhomogeneous RF Fields: A Versatile Tool for the Study of Processes with Slow Ions, in *Advances in Chemical Physics*, pp. 1–176, John Wiley & Sons, Ltd, 1992, _eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/9780470141397.ch1>.