1. Introduction

The study of the process of proton transfer in hydrogenous materials is important for understanding the dynamic behavior of molecules. In this context, the focus is on the proton transfer reaction in water. The reaction is typically described by the following equations:

\[ d + Z^+ \rightarrow Z + d^- \]
\[ d + Z^- \rightarrow Z + d^+ \]

These reactions involve the movement of protons between water molecules. The study of this process can provide insights into the behavior of hydrogen bonds and the dynamics of water in various environments, which is crucial for understanding phenomena in biological systems and materials science.

Abstract

Proton transfer reactions are of fundamental importance in various fields of chemistry, physics, and materials science. In this context, the focus is on the proton transfer processes in hydrogenous materials. The study of these processes can provide insights into the behavior of hydrogen bonds and the dynamics of water in different environments. The reaction is typically described by the following equations:

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These reactions involve the movement of protons between water molecules. The study of this process can provide insights into the behavior of hydrogen bonds and the dynamics of water in various environments, which is crucial for understanding phenomena in biological systems and materials science.
found that during the atomic cascade process, 2% of negative kaons stopped in liquid helium were "trapped" in metastable states with an overall lifetime of about 40 ns [5]. It would be very interesting to verify if a similar effect exists for \( \pi^- \)’s.

The second unique aspect of pionic hydrogen is the nature of its demise. If the \( \pi^- \) is not transferred to another atom, it will eventually be absorbed by the proton. This nuclear capture proceeds through one of two branches [6]:

\[
\begin{align*}
\pi^- + p &\rightarrow \gamma + n \quad (39.3\%) \\
\pi^- + p &\rightarrow \pi^0 + n \quad (60.7\%)
\end{align*}
\]

(3)

The observation of a \( \pi^0 \) from the charge-exchange reaction is a very clean signature of nuclear capture on hydrogen. For other nuclei the production of \( \pi^0 \)'s from \( \pi^- \)'s captured at rest is either kinematically forbidden, or strongly suppressed (\( \leq 10^{-5} \) branching ratio [7]). Pion absorption for these nuclei leads instead to emission of energetic neutrons, charged particles and occasionally high-energy (\( \sim 100 \) MeV) \( \gamma \) rays. The two exceptions to the rule are \(^3\)He and the deuteron, with branching ratios for the charge-exchange reaction at rest of (12.8 \( \pm \) 1.2\%) [9,10] and (1.45 \( \pm \) 0.19) \( \times 10^{-4} \) [8] respectively. The potential experimental problem of background from in-flight (\( \pi^- , \pi^0 \)) reactions can be eliminated by using an incident pion beam of low energy (\(< 25 \) MeV). This experimental advantage of being able to select \( \pi^- \)'s that have been absorbed by hydrogen is very useful tool, and is another reason that pionic hydrogen is an attractive system to study.

Molecular and chemical bond effects in pion capture can be quite large. As an example, the capture probability on hydrogen in hydrazine (\( N_2\text{H}_4 \)) is 30 times less than in a gaseous mixture of \( N_2 + 2H_2 \) [11]. These effects are usually understood in terms of the model of large mesic molecules, introduced by Ponomarev [1]. In this picture, the \( \pi^- \) (or \( \mu^- \)) initially captures into a molecular orbital by ejecting an Auger electron. These molecular orbitals are similar to those of the ejected electron, hence the sensitivity to electronic wavefunctions and chemical bonds. Imanishi et al. [12] have recently extended this model to account for Auger effects in the subsequent de-excitation.

Despite a considerable body of data on pion capture in various hydrogenous materials and mixtures, there are still a considerable number of unanswered questions. In condensed systems, there is even controversy about the basic mechanism of pion transfer. Part of the difficulty lies in the fact that the available models typically have a sufficient number of undetermined parameters to fit a large range of data. Also contributing to the problem is the fact that there are relatively few quantities that are experimentally accessible; typically these are pionic \( \times \)-ray yields and the charge-exchange probability. One is therefore obliged to select carefully systems that can shed light on particular aspects of the problem. The high-quality low-momentum \( \pi^- \) beams available at TRIUMF, along with an excellent detection system for \( \pi^0 \)’s produced at rest, have enabled us to improve on some of the older measurements and to begin to answer some of the outstanding questions in the field.

2. Gaseous Mixtures

Perhaps the simplest possible system to consider is a gaseous mixture of hydrogen with other elements. The pion transfer reaction has been extensively studied, largely by the Dubna group, for mixtures of hydrogen with noble gases (He, Ne, Ar, Kr, Xe) [13,14], and simple molecules such as \( D_2, CO, N_2, \) and \( CO_2 \) [14,15,16]. We have chosen to study the \( H_2 + D_2 \) system [17], which is particularly interesting because of the relation to similar processes in muon-catalyzed fusion.

The pion transfer is studied by measuring the variation of the \( \pi^0 \) yield as the relative concentration of \( H_2 \) and \( D_2 \) is varied. Figure 1 shows the experimental setup, which is essentially the same for all our measurements. The production of \( \pi^0 \)'s is signalled by the decay \( \pi^0 \rightarrow \gamma \gamma \) (98.8% branching ratio). The two \( \gamma \)'s are produced back-to-back and with equal energies in the rest frame of the \( \pi^0 \); however the \( \pi^0 \) has a small kinetic energy of 2.9 MeV. Therefore the photons are Doppler-shifted in the lab frame and so have a small distribution about 180° and energies of between 55 MeV and 83 MeV. The \( \gamma \)'s are detected by two large NaI(Tl) scintillators (TINA \( \phi \) 46 cm x 51 cm; MINA \( \phi \) 36 cm x 36 cm) at 180° to each other. Plastic scintillators (S1, S6) in front of TINA and MINA enable us to reject signals due to charged particles.

The incident \( \pi^- \) beam was at a momentum of 78 MeV/c (kinetic energy of 20 MeV) with
\[ \frac{(z/A)_{\text{corr}}\text{m}}{M} = n \times \frac{E_{\text{kin}}}{E_{\text{kin}}^*} \]

Figure 3 shows the relative production of the concentration of deuterium (C) is in...

![Diagram of data sets and no transfer process](image)

**Figure 2:** Spectrum of the product of the F+H reaction from a hydrogen target. The diagram illustrates the data sets and the no transfer process.
Figure 4: Transfer probability $Q$ versus relative concentration for $\text{H}_2 + \text{D}_2$ mixtures. The dashed curves are the fits to Eq. (7) for the two data sets, and the solid curve is the common fit, which yielded the parameters listed in Table 1.

relative concentrations of hydrogen and deuterium respectively. The model can be expressed in terms of only two parameters $\kappa = \beta_{pd}/\beta_{pp}$ and $\Lambda = \lambda_{pd}/\beta_{pp}$. Defining the concentration ratio $C = C_d/C_p$, one has

$$W_H = \frac{1 + \kappa C}{(1 + C)(1 + \kappa C + \Lambda C)}.$$  

(6)

Similarly, the net transfer probability $Q$ can be written

$$Q = \frac{\beta_{pd}C_d}{\beta_{pp}C_p + \beta_{pd}C_d + \lambda_{pd}C_p} = \frac{\Lambda C}{1 + \kappa C + \Lambda C},$$

(7)

from which it is easy to see that the transfer probability is simply related to $W_H$:

$$W_H = \frac{1 - Q}{1 + C}.$$  

(8)

This transfer probability is plotted as a function of $C$ in Fig. 4. The data were obtained during two separate running periods which were analyzed independently to determine our systematic errors. The results of the two fits are shown, as well as a common fit to all our data. Table 1 displays the parameters extracted from the latter fit, and compares them to those obtained by Petrokhin and Prokoshkin [15]. The agreement is reasonable, although our data point to a somewhat larger asymptotic value for the transfer. Two other measurements for $W_H$ are available [18,19]; both are more precise than our data, but both were only taken at one value of the concentration. Inclusion of these two datum ("World fit" in Table 1) changes the extracted values for $\Lambda$ and $\kappa$ somewhat. This reflects the fact that these two parameters are fairly highly correlated in the fit. The values for $\kappa/\Lambda$ and $Q(C \to \infty)$ are essentially unchanged however. The result $\kappa/\Lambda > 1$ indicates that in $\pi^- p + d$ collisions, the probability for capture is higher than that for collisions since $\kappa/\Lambda > 1$, the probability of pion capture in hydrogen is similar for $\pi^- p + d$ collisions.

In an ancillary experiment, we have searched for a pressure dependence of the transfer, and found none, in agreement with previous observations [18]. In fact, the asymptotic transfer is in good agreement with the value $Q = (28 \pm 13)\%$ at $C = 0.84$ measured at liquid hydrogen densities [20]. As emphasized by Horváth [21], this is important because any non-collisional processes would induce a virtual density (pressure) dependence for $W_H$. The absence of such a dependence is strong evidence that collisional processes dominate the capture and transfer as assumed in our analysis.

### Table 1: The parameters of Eq. (7), extracted from the present data, compared to those obtained by Petrokhin and Prokoshkin [15], and those obtained by a fit to our data as well as the data from Aniol et al. [18] and Kravtsov et al. [19] ("World fit").

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>$\Lambda$</td>
<td>0.65 ± 0.07</td>
<td>0.4 ± 0.1</td>
<td>0.45 ± 0.04</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>1.40 ± 0.22</td>
<td>1.3 ± 0.4</td>
<td>0.93 ± 0.14</td>
</tr>
<tr>
<td>$\kappa/\Lambda$</td>
<td>2.2 ± 0.4</td>
<td>3.3 ± 1.3</td>
<td>2.1 ± 0.4</td>
</tr>
<tr>
<td>$Q(C \to \infty)$</td>
<td>(32 ± 3)%</td>
<td>(23 ± 4)%</td>
<td>(33 ± 3)%</td>
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</tbody>
</table>

3. Alcohols

Since the nuclear capture rate of a $\pi^-$ on a hydrogen atom is the net result of atomic capture followed by any transfer processes (if they occur), it is often difficult to disentangle the two effects. The analysis of data on pion charge-exchange probabilities to extract transfer rates, often depends on assumptions about the initial pion capture on the different atoms within the molecule. In a complex molecule, the pion charge-exchange probability is an average over the
The calculation of the degree of protonation and reaction quotient involves understanding the equilibrium of the system. The protonation constant, $K_a$, can be used to calculate the degree of protonation, $\alpha$, as follows:

$$\alpha = \frac{[H^+][OH^-]}{[H_2O]}$$

where $[H^+]$ and $[OH^-]$ are the concentrations of hydrogen ions and hydroxide ions, respectively, and $[H_2O]$ is the concentration of water.

The reaction quotient, $Q_r$, is a measure of the ratio of the concentrations of the products to the concentrations of the reactants in a reaction at a given time.

$$Q_r = \frac{[H^+][OH^-]}{[H_2O]}$$

The equilibrium constant, $K_e$, can then be determined from the reaction quotient at equilibrium, where $Q_r = K_e$.

$$K_e = \frac{[H^+][OH^-]}{[H_2O]}$$

The degree of reaction, $\eta$, can be calculated using the relationship:

$$\eta = \frac{[H_2O]}{[H_2O]_0}$$

where $[H_2O]_0$ is the initial concentration of water.

Table 2 provides examples of the degree of protonation and reaction quotient for several common acids and bases.

<table>
<thead>
<tr>
<th>Acid/Base</th>
<th>Degree of Protonation, $\alpha$</th>
<th>Reaction Quotient, $Q_r$</th>
<th>Equilibrium Constant, $K_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>$\alpha = 0.1$</td>
<td>$Q_r = 10^{-5}$</td>
<td>$K_e = 10^{-5}$</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>$\alpha = 1$</td>
<td>$Q_r = 1$</td>
<td>$K_e = 1$</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>$\alpha = 0$</td>
<td>$Q_r = 10^{-14}$</td>
<td>$K_e = 10^{-14}$</td>
</tr>
</tbody>
</table>

The figure shows the relationship between the number of carbon atoms and the molar weight of the compound. The solid curve represents the trend observed in the data, indicating the increase in molar weight with the number of carbon atoms.

By plotting the data, it can be observed that there is a direct proportionality between the molar weight and the number of carbon atoms. This trend is evident in the figure, where the molar weight increases linearly with the number of carbon atoms.
Table 3: Best fit capture ratios determined from the primary alcohols.

<table>
<thead>
<tr>
<th>Capture Ratio</th>
<th>Fitted value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{H}^{d}/R_{C}$</td>
<td>$(6.72 \pm 0.05) \times 10^{-3}$</td>
</tr>
<tr>
<td>$R_{H}^{p}/R_{C}$</td>
<td>$(6.28 \pm 0.08) \times 10^{-3}$</td>
</tr>
<tr>
<td>$R_{H}^{d}/R_{C}$</td>
<td>$(3.48 \pm 0.07) \times 10^{-3}$</td>
</tr>
<tr>
<td>$R_{O}/R_{C}$</td>
<td>$1.97 \pm 0.02$</td>
</tr>
</tbody>
</table>

ol, which has a very different structure than the primary alcohols, also reproduces the data well. However, the calculation does rather poorly for cyclohexanol. Whether this is related to its ring structure or is a problem with the measurement is not yet clear. We have applied a similar model to the existing data on alkanes [22,23] and found no effects due to ring structures [24].

The results for the deuterated methanols CD$_3$OH and CH$_3$OD are particularly interesting. The sum of the capture probabilities in CD$_3$OH and CH$_3$OD is considerably less than the probability for CH$_3$OH. This is also seen by comparing the individual $W_H$ values of the deuterated methanols with the predictions of our model (c.f. Table 2). This is clearly evidence of transfer. However, we can correct for the effect of transfer using the $\pi^-p + d \rightarrow \pi^-d + p$ transfer parameters determined from our H$_2$/D$_2$ measurements, or perhaps more applicably, the H$_2$O/D$_2$O data discussed below. After this correction the $W_H$ values are $1.33 \times 10^{-3}$ and $6.24 \times 10^{-3}$ for CD$_3$OH and CH$_3$OD respectively, in quite reasonable agreement with the predictions of our model.

Finally, we have attempted to apply the model parameters deduced from the alcohols to existing data on a very different system, a series of sugar isomers. Earlier work at TRIUMF measured charge-exchange probabilities $W_H$ for several hexose and pentose isomers of sugars, and found evidence of an inverse correlation between $W_H$ and the melting point [25,26]. It was suggested that this correlation was indicative of hydrogen bonding causing a higher melting point and reducing the electron density around the hydrogen atoms and hence reducing the pion capture probability. The present model applied to the sugar data overestimates the $W_H$ values by about a factor of two. This could be considered as additional evidence of the effect of hydrogen bonding on pion capture.

4. Dibromoalkanes

Charge-exchange probabilities were also measured for the first five primary dibromoalkanes (chemicals of the form Br(CH$_2$)$_n$Br). The results are shown in Fig. 6; the curve is simply a

Figure 6: Capture probability in hydrogen for dibromoalkanes. The line is a guide to the only.

guide to the eye. The $W_H$ values increase dramatically as the chain length increases. This again shows the important effect of a very electronegative group (the Br atoms in this case) on the probability of the $\pi^-$ capturing on a hydrogen atom. As the chain lengthens, less of the molecule is affected by the distortions in the electron density due to the Br atoms on the ends. Unlike the alcohols series, the curve shows no signs of flattening out, probably indicating that the Br atoms have considerable influence throughout the molecule, even in the case of dibromopentane (Br(CH$_2$)$_3$Br). Notice that the $W_H$ value for dibromopentane is still far below the value for (CH$_3$)$_n$ (12.9 $\times$ 10$^{-3}$). Unfortunately, it appears that there is not sufficient data with only 5 species investigated to apply a model similar to the one used for the alcohols (Eq. (9)) and get meaningful results.

5. Transfer in H$_2$O/D$_2$O Mixtures

The results on pion charge-exchange probabilities in mixtures of gases, for example the H$_2$/D$_2$ mixtures discussed above, clearly indicate that the $\pi^-$ is transferred from one molecule to another. This can be labelled an “external” transfer process. The data are quite consistent with the collisional picture described above, in which the small, neutral $\pi^-p$ atom breaks away from the molecule and is transferred in a subsequent collision, i.e. $\pi^-p + Z \rightarrow \pi^-Z + p$. In more complicated molecules than H$_2$, the collisional transfer could conceivably also proceed
If the mucosal supporting structures are independent of inflammation, then the tissue-dependent process isn't required.

![Diagram](image-url)
Figure 8: The ratio of the number of pionic x-rays from Cl and Br divided by the relative concentration C, vs. C, for mixtures of bromodecane and carbon tetrachloride. The line is a guide to the eye.

as an explanation for effects seen in the charge-exchange yield. It also allows us to correct the charge-exchange data for the relative stopping probabilities in the two types of molecules in the mixture, without having to make any assumptions. With Eq. (3), the number of $\pi^+$ events detected is given simply by

$$ N_{\pi^+} = 0.607 \epsilon_{\pi^+} P_{\alpha} P_{\gamma}(1 - T_T) , $$

where $\epsilon_{\pi^+}$ is the $\pi^+$ detection efficiency, $P_{\alpha}$ is the probability of a $\pi^-$ stopping on the hydrocarbon molecule (bromodecane), $P_{\gamma}$ is the probability that a $\pi^-$ stopping on the bromodecane will go to a hydrogen atomic orbital and $T_T$ is the total transfer probability to other (higher-Z) atoms. Similarly, the number of bromine $4f \to 3d$ x-ray transitions observed is given by

$$ N_{Br}^{4f \to 3d} = \epsilon_{Br} P_{\alpha} P_{Br} P_{4f \to 3d} , $$

where $\epsilon_{Br}$ is the detection efficiency for the Br x-ray, $P_{Br}$ is the probability, given a $\pi^-$ stopping on the bromodecane molecule, of the $\pi^-$ going to a bromine atomic orbital and $P_{4f \to 3d}$ is the probability of the $4f \to 3d$ transition in the cascade in Br. By considering the ratio of $N_{\pi^+}/N_{Br}^{4f \to 3d}$, the dependence on the molecular stopping probability $P_{\alpha}$ cancels out.

The transfer probability $T_T$ can be decomposed into three terms:

$$ T_T = T_1 + T_2 + T_3 . $$

Figure 9: a) The pion capture probability in hydrogen $W_H$ vs. the relative concentration C, and b) the ratio of the number of $\pi^+$s to the number of Br x-rays, for mixtures of bromodecane and carbon tetrachloride. The lines are to guide the eye.

Here $T_1$, the "internal" transfer term, is the probability for the $\pi^-$ to transfer to different atoms in the same molecule (i.e. the bromodecane). Note that this could represent the barrier penetration mechanism of Jackson et al., the collisional process, a combination of the two, or possibly other unspecified mechanisms. The terms $T_2$ and $T_3$ represent "external" transfer, to atoms in different bromodecane molecules ($T_2$) or to atoms in a CCl$_4$ molecule ($T_3$). The internal transfer probability $T_1$ should be independent of the molecular ratio $C = n_{Br}/n_{H}$, whereas $T_2$ and $T_3$ are expected to depend (in different ways) on the molecular ratio. In the simplest approximation, the external transfer probability to a molecule of a particular kind is proportional to the mole fraction for that molecule in the mixture. Therefore we have $T_2 = \frac{A_{Br} n_{Br}}{n_1 + n_{Br}}$ and $T_3 = \frac{A_{CCl_4} n_{CCl_4}}{n_1 + n_{CCl_4}}$, where $A_{Br}$ and $A_{CCl_4}$ are transfer constants for $\alpha$ (bromodecane) and $\beta$ (carbon tetrachloride) molecules respectively. We make no assumption here as to the mechanism for external transfer. Together with (10)-(12) this gives

$$ \frac{N_{\pi^+}}{N_{Br}^{4f \to 3d}} = \epsilon \left[ 1 - T_1 - \frac{A_{Br}}{1 + C} \frac{A_{CCl_4}}{1 + (1/C)} \right] , $$

where the factor $\epsilon$ is defined by

$$ \epsilon = 0.607 \frac{\epsilon_{\pi^+} P_{\gamma}}{\epsilon_{Br} P_{\alpha} P_{4f \to 3d}} , $$

$$ \epsilon = 0.607 \frac{\epsilon_{\pi^+} P_{\gamma}}{\epsilon_{Br} P_{\alpha} P_{4f \to 3d}} . $$