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Capture and transfer of stopped pions in alcohols

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The pion charge-exchange probability in hydrogen for stopped π^- has been measured for a series of alcohols. The relative atomic capture probabilities for hydrogen in different chemical environments as well as for the other molecular constituents were extracted from the data using a phenomenological approach. The results allow the prediction of the charge-exchange probability in other molecules of similar chemical structure. The charge-exchange probability in deuterated methanols was measured and compared to the prediction of our model. A comprehensive picture is obtained if pion transfer from hydrogen to deuterium is included.

I. INTRODUCTION

In recent years much work has been devoted to the study of the capture of stopped negative pions in complex molecules. It is now well established that pion nuclear capture ratios depend not only on the nuclear charge of the atoms concerned but also depend strongly on the electronic environment in the molecule in which they are embedded [1–3]. This is understandable since the incident pion must pass through, and therefore interact with, the molecular electron cloud before passing into atomic orbitals near the nucleus from which nuclear capture predominantly occurs. However, the understanding of the precise way in which the molecular electrons affect the pion capture process is far from complete. Attempts to incorporate molecular effects into calculations of capture ratios in various kinds of molecule have met with partial success but fail to reproduce the experimental data satisfactorily in a number of cases [4]. Furthermore, there is continuing disagreement about the role of pion transfer from hydrogen onto heavier atoms. The generally accepted model favors collisional (external) π^- transfer by diffusion of a breakaway neutral $\pi^- p$ system through the material followed by the transfer of the π^- in a collision with a higher-Z atom [1], whereas the model proposed by Jackson and co-workers [5,6] assumes π^- transfer by tunneling of the π^- along a bond between hydrogen and a neighboring heavier atom (internal transfer). In general molecular systems containing hydrogen atoms bonded to higher-Z atoms, these two modes of pion transfer are difficult to distinguish experimentally and the relative importance of the two modes is therefore still unclear. However, external transfer has been observed in mixtures of both H_2 and noble gases [7], and CH_4 and noble gases [3]. Furthermore, a recent experiment [8] has found evidence for external transfer in mixtures of hydrogenous and nonhydrogenous liquids.

The experimental data in this field generally fall into one of two categories: either capture ratios on atoms of different nuclear charge (usually obtained from pionic x-ray measurements) or charge-exchange probabilities (π^-, π^0) (obtained from the $\pi^0 \rightarrow 2\gamma$ signal following pion capture on hydrogen). In either case, the main problem in interpreting the data is that the capture ratio or charge-exchange probability is an average over the chemically different atoms of the same nuclear charge within the molecule. Isolating the changes in pion capture on atoms of a particular Z that may be due to molecular effects is thus a rather difficult task. The results of analyzing the data on charge-exchange probabilities, for instance, to extract transfer parameters, often depend upon the particular model adopted to describe the initial pion capture on the different atoms within the molecule. Since this process itself is rather poorly understood, it would be useful in future work on pion chemistry if it were possible to establish an empirical scale of pion capture ratios on atoms in specific electronic environments. Such a scale would be analogous to the scale of chemical shifts which is derived from measurements of proton and ^{13}C NMR spectra. As in the case of the chemical shift scale, the position on the pion capture scale would be a function of the electron density around the capturing atom, especially the valence density to which the capture process appears to be particularly sensitive. Furthermore, since the nuclear capture rates are the net result of atomic capture followed by any transfer processes (if they occur), knowledge of the position of hydrogen atoms in different environments on the pion capture scale would be useful in extracting information on the pion transfer process.

In this paper we describe one approach to setting up such a pion capture scale and report the results of a recent experiment at TRIUMF in which the charge-exchange probability was measured for a series of alcohols. The results from the study are analyzed to yield relative capture rates on atoms in different chemical environments which are then interpreted in terms of simple ideas about the electronic environment in different regions of the molecule. We also report measurements of the pion charge-exchange probability in the deuterated methanols CD_3OH and CH_3OD and compare these with the value for the nondeuterated isomer CH_3OH. An investigation of the effect of deuteration on the charge-exchange probability in this system allows further examination of the model.

II. THEORY

We shall now outline the simple model first proposed by Smith and co-workers [9,10]. One starts from the assumption that atoms of a given nuclear charge, which occur in similar chemical environments in the molecule but in different physical regions, have similar pion capture rates. The nuclear capture rate (including all transfers) on an atom of nuclear charge Z_i in an environment labeled α will be denoted $R^{\alpha}_{Z_i}$. If there are $n^{\alpha}_{Z_i}$ such atoms in the molecule, the nuclear capture ratio $R(Z_i, Z_j)$ for the two atoms whose nuclear charges are Z_i and Z_j can be written

$$R(Z_i, Z_j) = \frac{\sum_{\alpha} n_i^{\alpha} R_{Z_i}}{\sum_{\beta} n_j^{\beta} R_{Z_j}} . \tag{1}$$

The summations are over all chemically different environments, α and β, in which the Z_i and Z_j nuclei are found within the molecule. In general, the choice of classifying atoms into chemically different groups will depend to some extent on the nature of the particular functional groups present within the molecule. Specific examples are given below.

Using this approach, the total nuclear capture probability, P_{Z_i}, for the nucleus Z_i becomes

$$P_{Z_i} = \frac{\sum_{\alpha} n_i^{\alpha} R^{\alpha}_{Z_i}}{\sum_{\alpha} n_i^{\alpha} R^{\alpha}_{Z_i} + \sum_{j\,(\neq i)} \sum_{\beta} n_j^{\beta} R^{\beta}_{Z_j}} . \tag{2}$$

In this work, the observable of particular interest is the charge-exchange reaction

$$p + \pi^- \rightarrow n + \pi^0 \tag{3}$$

which occurs with a probability of $\sim 60\%$ for π^- capture on hydrogen nuclei [11]. The observation of a π^0 is an unambiguous signal for pions stopping in hydrogen, since—apart from $\pi^{-3}He$ with $\sim 15\%$ [12,13]—the charge exchange (π^-, π^0) is suppressed $(< 10^{-4})$ in any other $\pi^- Z$ [14,15]. From Eq. (2) the total nuclear capture probability in hydrogen can be written as

$$W_H = \frac{\sum_{\alpha} n_H^{\alpha} R_H^{\alpha}}{\sum_{\alpha} n_H^{\alpha} R_H^{\alpha} + \sum_{Z\,(\neq 1)} \sum_{\beta} n_Z^{\beta} R_Z^{\beta}} , \tag{4}$$

where the measured charge-exchange probability $P_{\rm cex}$ and W_H are related by $P_{\rm cex} = 0.6 W_H$. Suppose we consider a generalized molecule of the form

$$CH_3(CH_2)_m CH_2 CH_2 X , \tag{5}$$

where X is some (polarizing) functional group such as —C=O, —C=O$_2$H, —OH, —NH$_2$, or —CH =CH$(CH_2)_n CH_3$. We expect that the carbon and hydrogen atoms that are located closest to the functional group X (environment α) and possibly in the next position along the carbon chain (environment β) may have electron densities which are somewhat different from those around the corresponding atoms in the nonpolar side chain $CH_3(CH_2)_m$. The pion capture rates on these α (and β) carbons and hydrogens may therefore differ significantly from those in the nonpolar side chain. However, because of the nonpolar nature of the side chain $CH_3(CH_2)_m$, the pion capture rates on all carbon atoms (or hydrogen atoms) within this group should be similar. On this basis, it should be possible to express the nuclear capture probability for a series of molecules of the same kind (that is with the same X group but different lengths of the side chain) in terms of a relatively small number [$\sim$ 6 for molecules of form (5)] of nuclear capture rates R.

Since it is the relative rather than absolute capture rates that are of primary interest, it would be convenient to define a standard capture rate on a particular reference nucleus in a specific electronic environment in terms of which all other capture rates could be expressed. In this respect, the capture rate on a carbon atom in a methylene or methyl group in a nonpolar side chain appears to represent a convenient choice for such an internal reference rate. These carbon-containing groups are commonly encountered in organic molecules and often occur in a side chain which is isolated from the electron-distorting effects of other functional groups by several intervening carbon atoms. The electronic environment around such carbon atoms should not therefore differ significantly from one kind of molecule to another. The capture rate on one of these standard carbon atoms will be denoted R^S_C. If the charge-exchange probabilities are known for a set of molecules with a common X but varying length side chain, these can be fitted to give estimates of the nuclear capture ratios R^{α}_H / R^S_C, R^{β}_H / R^S_C, and R_X / R^S_C.

A particular simple (and rather special) example of the above procedure will now be considered. When the functional group X corresponds to the hydrogen atom the molecular series is just the series of alkanes. The charge-exchange probabilities for a number of different chain lengths have been measured previously by Petrukhin *et al.* [16] and Krumshtein *et al.* [17] and the results are summarized in Table I. (It should be noted that the values given in this table were normalized to a W_H value for

TABLE I. Pion capture probabilities in hydrogen for alkanes. The data are taken from Petrukhin *et al.* (Ref. [16]) and Krumshtein *et al.* (Ref. [17]) renormalized to $W_H(CH_2) = 12.9 \times 10^{-3}$. In the last column the calculated values are presented using Eq.(6) with the parameter given in the text.

Molecule	Formula	W_H (units of 10^{-3})	Calculated W_H (units of 10^{-3})
Methane	CH_4	24.73 ± 0.53	24.42 ± 0.30
Ethane	CH_3CH_3	18.77 ± 0.53	18.42 ± 0.23
Propane	$CH_3CH_2CH_3$		16.41 ± 0.21
Pentane	$CH_3(CH_2)_3CH_3$	14.15 ± 0.49	14.79 ± 0.19
Hexane	$CH_3(CH_2)_4CH_3$	14.77 ± 0.48	14.39 ± 0.18
Dodecane	$CH_3(CH_2)_{10}CH_3$	13.52 ± 0.62	13.37 ± 0.17
Heptadecane	$CH_3(CH_2)_{15}CH_3$	12.46 ± 0.46	13.08 ± 0.16
Cyclohexane	C_6H_{12}	12.72 ± 0.49	12.36 ± 0.16
Polythene	$(CH_2)_n$	12.90 ± 0.36	12.36 ± 0.16

polythene equal to $(12.9\pm1.8)\times10^{-3}$ which is the mean of three independent absolute measurements [18–20] and is slightly lower than the value quoted in Ref. [16]. The preferred value of 12.9×10^{-3} is used for consistency throughout this article in order to facilitate comparison of capture rates in different molecules.) Since there is no polarizing group in the molecule one expects that all carbon atoms are essentially equivalent as far as pion capture is concerned (ignoring the slight difference between methyl and methylene groups). Similarly all hydrogens may be expected to be equivalent with respect to pion capture. The six values of W_H for molecules with formula $C_{n_C}H_{n_H}$ can then be fitted with one hydrogen capture rate and one carbon capture rate using an expression of the form

$$W_H = \frac{n_H R_H}{n_H R_H + n_C R_C^S}. \qquad (6)$$

The data give a least-squares fit with a χ^2 per point of 1.0 for a ratio of R_H/R_C^S equal to $(6.26 \pm 0.08) \times 10^{-3}$. The reasonable fit for these data with just one adjustable parameter confirms the assumption of the equivalence of the different carbon (and hydrogen) atoms in the molecular series with respect to pion capture. The capture ratio R_H/R_C^S obtained from the alkane series agrees with the pion capture probability in hydrogen for polythene, i.e., $W_H(CH_2) \approx 2R_H/R_C^S$ (see Table I). The calculated values for the alkanes are listed in the last column of Table I using Eq. (6). The agreement with the measured values is good. It is interesting to note that the apparent constancy of the ratio R_H/R_C^S for the molecular series in Table I and for polythene shows that the capture ratio is phase independent since this group of molecules contains gases, liquids, and solids. Since the capture rate on hydrogen is the net result of atomic capture followed by transfer we are led to the conclusion that if transfer is significant then the transfer rate is independent of the phase in which the molecule is present.

In Table I the pion capture probability for propane is calculated in the absence of an experimental value. This is very useful information because it can be compared with the capture probability by hydrogen in propane for kaons and antiprotons available from bubble-chamber studies. For kaons we have the results of Van der Velde-Wilquet *et al.* of 4.0±0.4% [21] and of Murphy *et al.* of 3.2±0.4% [22], which have to be compared with 1.6% for pions. The results are close yet the values for kaons are significantly higher than for pions indicating that kaons do not exhibit such a strong suppression of absorption by the hydrogen. For antiprotons the value of 11 ± 3% was found by Pawlewicz *et al.* [23] again higher than for kaons. The trend is quite clear and speaks for itself, although further confirmation of these data would be important.

For a more general molecular series of the kind $CH_3(CH_2)_mCH_2CH_2X$, it may be necessary to use two or three unknown hydrogen ratios R_H/R_C^S, one or two carbon ratios R_C/R_C^S, and one or more additional ratios to describe capture in the X group. In this case one requires values for W_H in five or more different members of a homologous series in order to extract useful estimates of the capture ratios. This has provided the motivation for the present experimental study of charge-exchange probabilities in a series of alcohols as well as for an earlier study on acid anhydrides [9].

III. EXPERIMENTAL TECHNIQUE AND DATA ANALYSIS

The experiment was performed in the M13 low-energy pion channel at TRIUMF. The setup used in this experiment is very similar to that described in detail elsewhere [24]. A beam of 78 MeV/c pions was stopped in a target holder containing the liquids. A coincidence of signals from three plastic scintillation counters S1, S2, and S3 defined a beam particle and an anticoincidence with a scintillation counter S4 (i.e., $123\bar{4}$) behind the target signaled the stopping of the particle in the target. In order to eliminate the π^0 background from π^- stopping in S3, this counter was made of deuterated scintillator. If a stopped π^- is captured by a proton in hydrogen, then a π^0 is produced 60% of the time. The decay γ rays from the π^0 were detected using a π^0 spectrometer consisting of two large NaI crystals TINA (TRIUMF iodide of natrium, 46 cm in diameter, 51 cm long) and MINA (Montreal iodide of natrium, 36 cm in diameter, 36 cm long). Each NaI was kept at a distance of ~ 80 cm from the target in order to be able to distinguish between neutrons and γ rays using the time-of-flight technique. Charged particles entering TINA and MINA were rejected by plastic scintillation counters in front of the two NaI detectors.

The purity of the chemicals used for the present experiment exceeded 99%. All targets used in this experiment were contained in cylindrical target holders, 133 mm in diameter, 15.5 mm long, with 25-μm-thick stainless-steel windows. The fraction of incident pions stopping in the target windows was determined by measuring the pion stops as a function of target thickness. For this purpose various thicknesses of CH_2 were used as target material. The fraction of pions stopping in the windows turned out to be less than 3%. The beam momentum was selected to optimize stopping in the liquid target.

A histogram of $E_T E_M$, where E_T is the energy deposited in TINA and E_M is the energy deposited in MINA, was generated to determine the π^0 yield, N_{π^0}. Since

$$E_T E_M = \frac{M_{\pi^0}^2}{4\sin^2\frac{\psi}{2}}, \tag{7}$$

where M_{π^0} is the mass of the π^0 and ψ is the angle between the two γ rays, the π^0 events show up as a peak in this histogram (see Ref. [24] for a figure). The number of π^0's produced in each target was determined by fitting a function

$$f(E) = A\exp\frac{(E-B)}{D}\left(1-\operatorname{erf}\frac{E-B}{C}\right)+\mathcal{B}, \tag{8}$$

where $E = E_T E_M$ and $\mathcal{B}$ is a background term. A, B, C, and D are amplitude, energy and width related parameters [24]. Integration of the π^0 peak above the background gave N_{π^0}.

The number of π^-'s stopping in the target, N_{π^-}, was obtained using the technique described in Ref. [24]. The relative charge-exchange probability for each concentration was obtained as N_{π^0}/N_{π^-} and was then normalized to that measured in CH_2. The stability of the data was checked by repeating the measurements with CH_2 at regular intervals.

The pion capture probability in hydrogen, W_H, for each target was calculated from

$$W_H(\mathcal{T}) = W_H(CH_2)\frac{T(\mathcal{T})}{T(CH_2)}, \tag{9}$$

where $W_H(CH_2)$ is the pion capture probability for polythene and $T(\mathcal{T})$ is the ratio of N_{π^0}/N_{π^-} for a particular target. $T(CH_2)$ was calculated from the mean of 17 measurements made at regular intervals during the course of the present experiment. The value for $W_H(CH_2)$ was taken to be $(12.9 \pm 1.8) \times 10^{-3}$. In calculating the errors of the W_H values, only the errors in $T(\mathcal{T})$ and $T(CH_2)$ were taken into account. The error in $W_H(CH_2)$ was not included since it is the relative W_H values which are of primary interest.

IV. RESULTS

The values of N_{π^0} and W_H calculated by means of Eq. (9) for the different targets are listed in Table II. The W_H values for the primary alcohols and water are plotted against the number of carbon atoms in the molecule, n_C, in Fig. 1 and show a monotonic rise with n_C. The W_H values for this alcohol series asymptotically approach the value $W_H(CH_2)$ which is indicated as a straight line. The capture probabilities for all the primary alcohols (excluding the deuterated methanols) and water were fitted with an expression of the form

$$W_H = \frac{n_H^\alpha R_H^\alpha + R_H^O + n_H^\beta R_H^\beta}{n_H^\alpha R_H^\alpha + R_H^O + n_H^\beta R_H^\beta + n_C R_C + R_O}. \tag{10}$$

Here R_H^α is the rate for pion capture on a hydrogen atom bound to a carbon atom which is in the α position with respect to the OH group. R_H^O is the rate for pion capture on a hydrogen atom of the OH group. R_H^β is the rate for pion capture from all other hydrogen atoms. R_C is the rate for pion capture on a carbon atom and R_O is the rate for pion capture on an oxygen atom. The n_H and n_C factors are the relative numbers of the respective atoms in the given molecule.

Two fits of the data were performed, each with slightly different data samples. In both cases the deuterated methanols were excluded from the fits as pion transfer from hydrogen to deuterium complicates the situation there. We shall address this problem later. In fit I only the primary alcohols plus water were included, whereas in fit II all the alcohols from Table II plus water were employed. The values of the best-fit capture ratios (relative to R_C) are given in Table III. The result of fit I gives a χ^2 per point of 0.77 and will be discussed first. The result for R_H^β/R_C, the capture ratio for hydrogen atoms far from the polarizing OH group, is $(6.72 \pm 0.05) \times 10^{-3}$ which is a little higher than the value for the alkanes of $R_H/R_C^S = (6.26 \pm 0.08) \times 10^{-3}$. The alcohol result gives $(13.44 \pm 0.10) \times 10^{-3}$ for polythene, which is satisfactory though not perfect. The value for R_H^α/R_C, the capture ratio for hydrogen atoms bound to carbon which is in the α position to the OH group is $(6.28 \pm 0.08) \times 10^{-3}$, slightly lower than the value of R_H^β/R_C. This is con-

TABLE II. Pion capture probabilities in hydrogen for alcohols (present data). In the last column the calculated values are presented using Eq.(10) and the parameters of fit I given in Table III.

Molecule	Formula	N_{π^0}	W_H (units of 10^{-3})	Calculated W_H (units of 10^{-3})
Water	H_2O	3802	3.52 ± 0.07	3.52 ± 0.05
Methanol	CH_3OH	10438	7.47 ± 0.09	7.47 ± 0.10
Ethanol	CH_3CH_2OH	4305	8.88 ± 0.16	9.04 ± 0.08
Propan-1-ol	$CH_3(CH_2)_2OH$	5975	9.98 ± 0.17	9.90 ± 0.07
Butan-1-ol	$CH_3(CH_2)_3OH$	6838	10.70 ± 0.17	10.47 ± 0.08
Pentan-1-ol	$CH_3(CH_2)_4OH$	6569	10.95 ± 0.18	10.87 ± 0.08
Hexan-1-ol	$CH_3(CH_2)_5OH$	6565	11.03 ± 0.18	11.17 ± 0.08
Heptan-1-ol	$CH_3(CH_2)_6OH$	5796	11.29 ± 0.19	11.41 ± 0.08
Octan-1-ol	$CH_3(CH_2)_7OH$	7211	11.54 ± 0.17	11.59 ± 0.08
Decan-1-ol	$CH_3(CH_2)_9OH$	5160	11.96 ± 0.22	11.87 ± 0.08
Deuterated Methanol	CD_3OH	807	0.845 ± 0.031	1.17 ± 0.02
Deuterated Methanol	CH_3OD	3884	5.55 ± 0.11	6.31 ± 0.10
Butan-2-ol	$CH_3CH_2CH(OH)CH_3$	7471	10.85 ± 0.17	10.54 ± 0.08
2-Methyl-propan-2-ol	$(CH_3)_3COH$	6256	10.66 ± 0.18	10.61 ± 0.09
Cyclohexanol	$(CH_2)_5CHOH$	3143	8.23 ± 0.18	9.57 ± 0.07

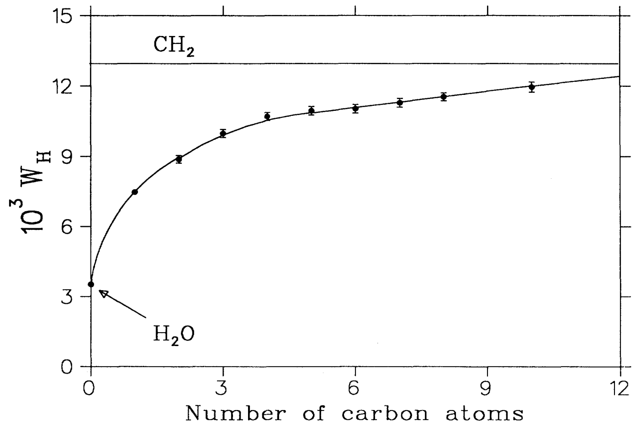

FIG. 1. Pion capture probabilities in hydrogen, W_H, of alcohols and water. W_H for CH_2 is indicated with a straight line. The solid curve is a spline fit through the fitted values.

sistent with the lower electron density expected around hydrogen atoms of a methylene group adjacent to a hydroxyl group due to the strongly electronegative character of the oxygen atom. Since the atomic capture process is thought to be dominated by Auger transitions, the capture rate on an atom is expected to be a function of the electron density around that atom. The value

TABLE III. Best-fit capture ratios for alcohols. Fits I and II are described in the text.

Capture ratio	Fit I	Fit II
R_H^{β}/R_C	$(6.72 \pm 0.05) \times 10^{-3}$	$(6.53 \pm 0.12) \times 10^{-3}$
R_H^{α}/R_C	$(6.28 \pm 0.08) \times 10^{-3}$	$(5.90 \pm 0.34) \times 10^{-3}$
R_H^{O}/R_C	$(3.48 \pm 0.07) \times 10^{-3}$	$(3.11 \pm 0.31) \times 10^{-3}$
R_O/R_C	1.97 ± 0.02	1.76 ± 0.17

for R_H^O/R_C, the capture ratio for a hydrogen atom in an OH group, is significantly less than both R_H^β/R_C and R_H^α/R_C. This is consistent with the significant reduction in electron density around a hydrogen atom attached directly to an electronegative oxygen atom. Inclusion of W_H for H_2O is crucial for the fit because it largely determines R_H^O/R_C. If $W_H(H_2O)$ is discarded then R_H^O/R_C is compatible with 0 and the overall errors for the fit are much worse. Finally, the ratio R_O/R_C is in agreement with other values reported for O:C capture ratios in hydroxyl-containing molecules such as saccharides [9]. The quality of the fit becomes evident if W_H is calculated using Eq.(10) with the parameters given in Table III. The calculated values are listed in the last column of Table II and agree with the measurement very well except for the deuterated methanols, which will be discussed below in more detail, and cyclohexanol where the calculation is $\sim$ 15% higher than the measurement. The ring structure of this molecule might change the electron distribution in a manner such that the applicability of our model is limited. However, no effect of the ring structure was found for the alkanes hexane and cyclohexane as can be seen from Table I and the only difference is that cyclohexanol contains a polarizing functional group. Hence we are left with a slight puzzle whether the observed suppression of W_H is real and due to the ring structure or whether the effect may be due to misbehavior of the apparatus or some contaminant of the cyclohexanol. A future measurement W_H in cyclopentanol might help clarify the situation. The location of the hydroxyl group (Butan-1-ol and Butan-2-ol) seems not to influence the W_H values very much which is confirmed by the calculation. Also the calculation for 2-methyl-propan-2-ol, which has a fairly different structure than the primary alcohols, is very close to the measured value.

The result of fit II gives a χ^2 per point of 6.7. The quality of this fit is worse as manifested by the χ^2 and the error bars of the capture ratios. However, the general trend of the fit II is the same as for fit I and the results agree within the error bars. The difference is caused by the inclusion of W_H for cyclohexanol in fit II, where fit I fails to predict the capture probability on hydrogen atoms satisfactorily as mentioned above. We recommend fit I for use in predicting W_H values for alcohols of similar chemical structure as the primary alcohols. The error bars, however, given for fit I in Table III are strictly valid only for primary alcohols. The error bars of fit II give an idea of what the error bars for alcohols of similar structure are.

It is interesting to compare the present results to the results of a recent study of pion capture in acid anhydrides and saccharides [10]. For the anhydrides, it was found that the relative probability of pion capture in hydrogen attached to a carbon atom in the α position with respect to the C_2O_3 group was approximately half the relative probability for capture on hydrogen attached to carbons further from the C_2O_3 group. The large effect of the C_2O_3 group on the capture rates contrasts with the relatively small difference observed in the present experiment between the values of R_H^β and R_H^α for alcohols. This difference between the anhydrides and alcohols is a reflection of the stronger charge distortion of nearby atoms by the C_2O_3 group than by the OH group.

The saccharides whose pion capture probabilities were reported in Ref. [10] contain just CH, CH_2, O, and OH groupings. The close relationship between the structures of the saccharides and alcohols suggests that it might be feasible to use the pion capture parameters extracted in the present work to predict W_H values for the saccharide isomers measured in Ref. [10], by means of Eq. (4). However, if this simple approach is adopted, one finds that the predicted W_H values for the saccharides are approximately twice the experimental values. In Ref. [10], a dependence of W_H on the melting point was suggested, which was interpreted as an indication that the pion capture rate in hydrogen is reduced due to the effects of hydrogen bonding between molecules. If this is indeed the case, then the atomic capture ratios derived from studies on alcohols may not be directly applicable to systems, such as the saccharides, in which hydrogen bonding plays a somewhat different role. Hence the fact that the parameters derived from the alcohols overestimate the W_H values for the saccharides is not unexpected.

The present model was further investigated with the aid of an alternative technique using deuterated methanols. We measured the hydrogen capture probability for CD_3OH, CH_3OD, and CH_3OH. The results for W_H are given in Table IV. The interesting observation is that the sum of capture probabilities in CD_3OH and CH_3OD falls short of the probability for CH_3OH. The same conclusion can be drawn if the individual values W_H for CD_3OH and CH_3OD are compared with the calculated results obtained from the alcohol series which are presented in the last column of Table IV. These calculated values include transfer effects from hydrogen to carbon and oxygen, but do not include transfer effects from hydrogen to deuterium ($\pi^- p + d \rightarrow \pi^- d + p$). However, we can correct for pion transfer from hydrogen to

TABLE IV. Pion capture probabilities in hydrogen for deuterated methanols (all in units of 10^{-3}). The calculated values in the last column are obtained by using Eq.(10) and the parameters of fit I given in Table III.

Molecule	W_H (expt.)	Corrected (H_2-D_2)	Corrected (H_2O-D_2O)	Calculated (Alcohol series)
CD_3OH	0.845 ± 0.031	1.15	1.33	1.17 ± 0.02
CH_3OD	5.55 ± 0.11	6.27	6.24	6.31 ± 0.10
CH_3OH	7.47 ± 0.09	7.42	7.57	7.47 ± 0.10

deuterium which we investigated recently in H_2-D_2 gas mixtures [24] (where the transfer is purely external) and in H_2O-D_2O liquid mixtures [25] as a function of the deuterium concentration. The hydrogen to deuterium transfer contribution can be removed from the experimental pion capture probability by dividing W_{H} by 1-Q, where Q is a factor which is related to the probability for pion transfer from hydrogen to deuterium. For the H_2-D_2 system Q is equal to the H to D transfer probability while for the H_2O-D_2O system it is approximately equal to the H to D transfer probability divided by the probability that the pion is not transferred to an oxygen atom in pure H_2O.

The relative deuterium concentrations for CD_3OH and CH_3OD are 3 and $\frac{1}{3}$, respectively. The corresponding figures for pion transfer at these concentrations were obtained from Ref. [25] and amount to $Q \sim 36\%$ transfer for $C_d/C_p=3$ and $Q \sim 11\%$ transfer for $C_d/C_p = \frac{1}{3}$. These give the corrected values of W_{H} shown in column 4 of Table IV. The corresponding values based on the corrections using the H_2-D_2 [24] data are shown in column 3 of Table IV. The corrected values agree very well with the prediction from the alcohol series as well as with the measurement of $W_{\mathrm{H}}(CH_3OH)$. This supports the whole approach.

V. CONCLUSIONS

The pion capture probabilities for the series of alcohols reported here were analyzed in terms of a simple model of pion capture on atoms in different chemical environments. The model yields values for the relative capture ratios of hydrogen and carbon and oxygen and carbon which are consistent with the known electron distribution in the molecule and with other data on atomic capture ratios. This method of analysis can be applied to systems where charge-exchange probabilities are known for a homologous series of molecules. The (empirical) capture ratios obtained by this method could be used to predict the charge-exchange probabilities in other molecules containing similar functional groups.

The result of the alcohol series was applied to investigate deuterated methanols. It is found that the pion capture probability for CD_3OH and CH_3OD is smaller than the prediction of the model and the W_{H} values for CD_3OH and CH_3OD also do not add up to $W_{\mathrm{H}}(CH_3OH)$. However, if the measured W_{H} values are corrected for pion transfer from hydrogen to deuterium in collisions $\pi^- p + d$ as obtained from our previous studies [24,25] then overall agreement is achieved. This is a verification of the usefulness of the model.

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[1] L. I. Ponomarev, Annu. Rev. Nucl. Sci. **23**, 395 (1973).
[2] H. Schneuwly, V. I. Pokrovsky, and L. I. Ponomarev, Nucl. Phys. **A312**, 419 (1978).
[3] D. Horváth, Radiochim. Acta **28**, 241 (1981); Hyperfine Interactions **17-19**, 679 (1984).
[4] D. Horváth and F. Entezami, Nucl. Phys. **A407**, 297 (1983).
[5] D. F. Jackson, C. A. Lewis, and K. O'Leary, Phys. Rev. A **25**, 3262 (1982).
[6] C. Tranquille and D. F. Jackson, Phys. Rev. A **34**, 742 (1986).
[7] V. I. Petrukhin and V. M. Suvorov, Zh. Eksp. Teor. Fiz. **70**, 1145 (1976) [Sov. Phys.—JETP **43**, 595 (1976)].
[8] M. R. Harston, D. S. Armstrong, D. F. Measday, S. Stanislaus, and P. Weber, Phys. Rev. Lett. **64**, 1887 (1990).
[9] J. R. H. Smith, A. S. Clough, D. F. Jackson, K. R. Smith, D. F. Measday, F. Entezami, A. Noble, S. Stanislaus, C. Virtue, M. Salomon, and K. A. Aniol, Nucl. Instrum. Methods **A242**, 465 (1986).
[10] D. Horváth, K. A. Aniol, F. Entezami, D. F. Measday, A. J. Noble, S. Stanislaus, C. J. Virtue, A. S. Clough, D. F. Jackson, J. R. H. Smith, and M. Salomon, Phys. Rev. A **41**, 5834 (1990).
[11] J. Spuller, D. Berghofer, M. D. Hasinoff, R. MacDonald, D. F. Measday, M. Salomon, T. Suzuki, J-M. Poutissou, R. Poutissou, and J. K. P. Lee, Phys. Lett. **67B**, 479 (1977).
[12] A. V. Bannikov, B. Lévay, V. I. Petrukhin, V. A. Vasilyev, L. M. Kochenda, A. A. Markov, V. I. Medvedev, G. L. Sokolov, I. I. Strakovsky, and D. Horváth, Nucl. Phys. **A403**, 515 (1983).
[13] G. Backenstoss, M. Izycki, W. Kowald, P. Weber, H. J. Weyer, S. Ljungfelt, U. Mankin, G. Schmidt, and H. Ullrich, Nucl. Phys. **A448**, 567 (1986).
[14] R. MacDonald, D. S. Beder, D. Berghofer, M. D. Hasinoff, D. F. Measday, M. Salomon, J. Spuller, T. Suzuki, R. Poutissou, J.-M. Poutissou, P. Depommier, and J. K. P. Lee, Phys. Rev. Lett. **38**, 746 (1977).
[15] B. Bassalleck, F. Corriveau, M. D. Hasinoff, T. Marks, D. F. Measday, J.-M. Poutissou, and M. Salomon, Nucl. Phys. **A362**, 445 (1981).
[16] V. I. Petrukhin, V. E. Risin, I. F. Samenkova, and V. M. Suvorov, Zh. Eksp. Teor. Fiz. **69**, 1883 (1975) [Sov. Phys.—JETP **42**, 955 (1976)].
[17] Z. V. Krumshtein, V. I. Petrukhin, V. E. Risin, L. M.

Smirnova, V. M. Suvorov, and I. A. Yutlandov, Zh. Eksp. Teor. Fiz. **65**, 455 (1973) [Sov. Phys.—JETP **38**, 222 (1974)].

[18] M. Chabre, P. Depommier, J. Heintze, and V. Soergel, Phys. Lett. **5**, 67 (1963).

[19] D. Bartlett, S. Devons, S. L. Meyer, and J. L. Rosen, Phys. Rev. B **136**, 1452 (1964).

[20] A. F. Dunaitsev, V. I. Petrukhin, and Yu. D. Prokoshkin, Nuovo Cimento **34**, 521 (1964).

[21] C. Van der Velde-Wilquet, G. S. Keyes, J. Sacton, J. H. Wickens, D. H. Davis, and D. N. Tovee, Nuovo Cimento Lett. **5**, 1099 (1972).

[22] C. T. Murphy, G. Keyes, M. Saha, and M. Tanaka, Phys. Rev. D **9**, 1248 (1974).

[23] W. T. Pawlewicz, C. T. Murphy, J. G. Fetkovich, T. Dombeck, M. Derrick, and T. Wangler, Phys. Rev. D **2**, 2538 (1970).

[24] P. Weber, D. S. Armstrong, D. F. Measday, A. J. Noble, S. Stanislaus, M. R. Harston, K. A. Aniol, and D. Horváth, Phys. Rev. A **41**, 1 (1990).

[25] S. Stanislaus, D. F. Measday, D. Vetterli, P. Weber, K. A. Aniol, M. R. Harston, and D. S. Armstrong, Phys. Lett. A **143**, 239 (1990).