

500/2-80



сообщения  
объединенного  
института  
ядерных  
исследований  
дубна

4/2-80

E14 - 12824

D.Horváth

ON THE CHEMISTRY  
OF THE LIGHTEST EXOTIC ATOMS

1979

**E14 - 12824**

**D.Horváth\***

**ON THE CHEMISTRY  
OF THE LIGHTEST EXOTIC ATOMS**

---

\* Present address: Central Research Institute  
of Physics, Budapest, Hungary.

Хорват Д.

E14 - 12824

О химии легких экзотических атомов

В работе обсуждаются химические аспекты образования трех водородоподобных экзотических атомов: позитрония, мюония и  $p\pi^-$  мезоатома. Для позитрония предсказания по двум механизмам образования, Оре-модель с реакциями "горячего" позитрония и трековая модель сравниваются с экспериментальными наблюдениями в растворах. Примером использования  $p\pi^-$  мезоатома для получения сведений о свойствах химической связи водорода могут служить последние эксперименты, выполненные в ЛЯП ОИЯИ.

Работа выполнена в Лаборатории ядерных проблем ОИЯИ.

Сообщение Объединенного института ядерных исследований, Дубна 1979

Horváth D.

E14 - 12824

On the Chemistry of the Lightest Exotic Atoms

The chemical aspects of formation of three hydrogen-like exotic atoms, positronium, muonium, and pionic hydrogen are discussed. For positronium two formation mechanisms, the Ore model with hot-atom reactions, and the spur reaction model are set against experimental observations in solutions. The use of pionic hydrogen atoms in obtaining information on the bond properties of hydrogen is illustrated by recent experiments performed in JINR.

The investigation has been performed at the Laboratory of Nuclear Problems, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1979

INTRODUCTION

This paper briefly examines the chemical aspects of formation of three hydrogen-like exotic atoms having remarkable chemical applications, positronium ( $Ps = e^+e^-$ ), muonium ( $Mu = \mu^+e^-$ ), and pionic hydrogen ( $p\pi^-$ ). The use of positrons and muons in solid state research will not be treated here, it has been described in recent review articles<sup>1,2/</sup>. On positron annihilation a complete bibliography is available<sup>3/</sup> and an extensive review has been published on positronic and mesonic chemistry quite recently<sup>4/</sup>.

The exotic particles in question, pion, muon, and positron are linked together in a decay chain (Table 1). Pions are obtained in proton accelerators at a few hundred MeV and muons are formed as a result of pion decay in flight

Table 1

Data on the particles discussed in this paper

Particle	Lifetime	mass		decay mode
		$m/m_e$	$m, \text{MeV}$	
$\pi^+$	26 ns	273	139	$\pi^+$
$\mu^+$	2.2 $\mu$ s	207	106	$\mu^+ + \nu_\mu$
$e^+$	stable	1	0.511	$e^+ + \nu_e + \bar{\nu}_\mu$

while for positron sources mainly the  $^{22}\text{Na}$  isotope is used. Among them positron is the least expensive and most popular particle. The use of positronium, muonium, and pionic hydrogen in chemistry is based mainly on the fact that essentially they are unstable hydrogen isotopes (Table 2). In

Table 2

Some properties of hydrogen-like atoms

System	binding energy	reduced mass	free decay mode	lifetime
Ps = e <sup>+</sup> e <sup>-</sup>	6.8 eV	0.5	para-Ps (↑↓) - 2γ ortho-Ps (↑↑) - 3γ	0.125 ns 140 ns
Mu = μ <sup>+</sup> e <sup>-</sup>	13.5 eV	0.995	μ <sup>+</sup> → e <sup>+</sup> + ν <sub>e</sub> + ν̄ <sub>μ</sub>	2.2 μs
H = p e <sup>-</sup>	13.6 eV	1	stable	
pπ <sup>-</sup>	-	238	p + π <sup>-</sup> → { n + γ / 40% / n + π <sup>0</sup> / 60% /	< 1 ps

vacuum Ps decays via self-annihilation; Mu, by muon decay:

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu; \quad (1)$$

and pπ<sup>-</sup>, by pion capture in proton,

$$p + \pi^- \rightarrow \begin{cases} n + \gamma & (40\%) \end{cases} \quad (2)$$

$$\begin{cases} n + \pi^0 \\ \hookrightarrow 2\gamma & (60\%). \end{cases} \quad (3)$$

The investigator registers characteristic 0.511 MeV photons from positron annihilation, energetic (~30 MeV) positrons emitted in muon decay (1), and, usually, pairs of ~70 MeV photons from charge-exchange reaction (3). The experimental data obtained in such a way, the formation and disappearance rates of Ps, Mu, or pπ<sup>-</sup> atoms are believed to give us information on the chemical environment in condensed media.

#### POSITRONIUM

Positron lifetime and γ-γ angular correlation measurements are the common experimental techniques

for monitoring the formation and interactions of Ps atoms in matter. Positron lifetime is measured by the fast-slow coincidence method<sup>1/</sup>, time resolution about 400 ps (full width at half maximum) is considered to be good enough for positronium research. When Ps is formed the positron-annihilation decay curve consists of at least three exponential components. The singlet (para) Ps decays with a mean life

of  $\tau_0 = 0.125$  ns. For the triplet(ortho) Ps the  $2\gamma$  decay is forbidden by the conservation laws, its interactions, however, with the electrons of the medium result in  $2\gamma$  decays with a long lifetime  $\tau_2 = 1-5$  ns (pick-off annihilation). In addition, we always have a component due to the annihilation of free positrons on chemically bound electrons ( $\tau_1 = 0.2-0.4$  ns). Usually, the experimental decay curves are evaluated in terms of three components

$$N(t) = \sum_{k=0}^2 I_k e^{-t/\tau_k} \quad (4)$$

with  $\tau_k$  lifetimes and  $I_k$  corresponding intensities. In the case of simple pick-off quenching (no chemical reaction of positronium involved)

$$I_2 = 3I_0 \quad (5)$$

and for the Ps formation probability

$$P = 4I_2/3. \quad (6)$$

The width of the angular distribution of annihilation  $\gamma$ -quanta is related to the momentum of the annihilating  $e^+e^-$  system. When Ps is formed a characteristic narrow component appears in the angular correlation spectrum superposed on the broad component due to free annihilation and, probably, pick-off quenching<sup>4/</sup>. In addition to the angular correlation method information on the momentum of the  $e^+e^-$  system can be obtained by precisely measuring the energy distribution of the annihilation photons (the Doppler-broadening method).

Since 1974 there are two models for the mechanism of Ps formation: the Ore model and the spur-reaction model. The Ore model is based on the assumption that Ps forms in the collisions of energetic positrons with atomic electrons<sup>5/</sup> that is in the process



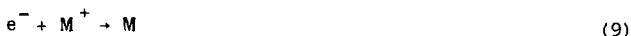
The Ps atoms formed in reaction (7) have kinetic energies between 0 and 6.8 eV, the Ps binding energy, thus a significant part of them is "hot" and may enter chemical reactions forbidden for thermal Ps atoms<sup>5/</sup>. In this case the long-lived component of the lifetime spectrum is contributed by the pick-off annihilation of thermal Ps only, while

the short components contain, in addition to the fast p-Ps decay and free annihilation, the annihilation from hot Ps reactions as well<sup>/8/</sup>. By the Ore mechanism a decrease in  $I_2$  at  $\tau_2 = \text{const}$  can be explained in (i) a faster slowing-down of positrons, (ii) a less effective slowing down of Ps atoms, or (iii) a more intensive hot Ps reaction with some constituent. For noble gases the Ore model gives a quantitative description of Ps formation and explains quite reasonably the nonformation of Ps in perfect ionic crystals and metals.

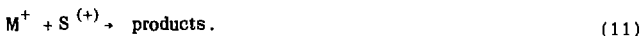
According to the spur-reaction model proposed by O.E.Mo-gensen<sup>/7/</sup> Ps is formed as a result of the reaction between the positron and an excess electron produced by the positron itself in its ionization spur (Fig.1). As spurs are transient clusters of reactive species (electrons, positive ions, radicals, etc.) in the terminal spur the Ps formation



competes with other processes such as recombination



or electron and positive ion scavenging

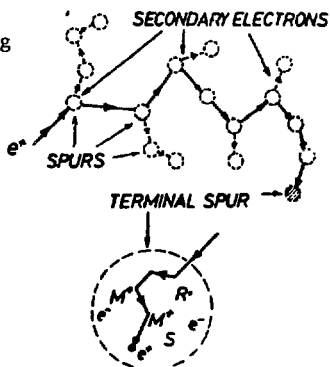


Thus by the predictions of the spur model adding of an electron or positive-ion scavengers  $S^{(-)}$  or  $S^{(+)}$  to the system reduces (inhibits) or enhances the Ps formation, respectively.

The use of the spur model of Ps formation is based upon the results of radiation chemistry research<sup>/7/</sup>. The spurs are characterized by numerous experimental quantities as  $G_f$ , the number of free electrons per 100 eV energy loss of the primary particle<sup>/7/</sup>;  $G_e$ , the number of electrons avoiding the initial recombination by trapping in defects or solvating<sup>/8/</sup>;  $b$ , the range of the secondary electrons which determines the mean spur size;  $\mu$ , the excess electron mobility;  $V_0$ , the excess electron work function in the solvent<sup>/8/</sup>.

As Tao has shown the two models of Ps formation do not exclude each other. In any substance Ps atoms may be formed

Fig.1. Formation of spurs along the positron ionization track.  
 $e^-$  - electron,  $e^+$  - positron,  
 $M^+$  - solvent ion,  $R'$  - radical,  
 $S$  - scavenger<sup>4/</sup>.



by both mechanisms concurrently<sup>10/</sup>. For determining which of them dominates in a system one has to study the dependence of Ps formation probability on hot atom reaction and spur reaction properties. In gases the spur mechanism cannot be important because of the low density and great electron mobility, in ionic solids and metals Ps is not formed and in molecular solids the formation of positronium is under question<sup>8/</sup>. Therefore, the Ps research has been performed mainly in liquids<sup>6-12/</sup>. Below we make an attempt to illustrate the effectiveness of the models in interpreting some features of Ps formation in solutions.

In pure polar solvents such as water or alcohols the liquid-solid phase transition leads to a two-fold increase in Ps formation probability<sup>7,8'</sup> while the liquid - glass-state transition does not affect  $I_2$ <sup>8/</sup>. The enhancement at solidification can be explained by an increase in the free volume available for Ps in the host lattice<sup>1/</sup>. In terms of the spur model this transition effect was interpreted as a result of a much slower solvation of excess electrons and as an exception to the rule, naphthalene (liquid:  $I_2 = 29\%$ , solid:  $9\%$ ), by electron - solvent molecule reaction<sup>77'</sup>. Later, in liquid, solid, and glassy alcohols a correlation has been found between  $I_2$  and  $G_e$ , which is the number of electrons, avoiding the initial recombination<sup>8'</sup>.

Certain compounds when added to a solution facilitate a strong reduction in  $I_2$  at a constant  $r_2$ . As shown above, in terms of the Ore model this can be explained by inhibition of Ps formation or by hot Ps reactions with the solute<sup>11</sup>. On the other hand, according to the spur model the



Ps formation may be inhibited by electron or positron scavenging only. As the hot atom reactions have threshold energies the reduction should level off at higher solute concentrations while such a "limited" inhibition effect does not conform with the ideas of the spur model<sup>11/</sup>. Nevertheless, some compounds cause "full" inhibition; and others, a "limited" one.

Inhibition studies in organic fluids revealed a most striking feature in Ps chemistry, the antiinhibition effect<sup>8/</sup>. There are active electron acceptors which cause no inhibition in a solvent but, on the contrary, can remove or reduce the inhibition induced by other solutes. For example, 0.06 mole iodobenzene reduces I<sub>2</sub> in benzene from 38% to 18% (inhibition) and adding 0.6 mole C<sub>6</sub>F<sub>6</sub> to the solution leads to an increase in I<sub>2</sub> to 34% that is C<sub>6</sub>F<sub>6</sub> restores the Ps formation probability reduced by C<sub>6</sub>H<sub>5</sub>I<sup>8/</sup>. The antiinhibition effect cannot be explained by hot atom processes<sup>8,11/</sup> but it is readily understandable in terms of the spur model<sup>8/</sup>. All the antiinhibitors such as CS<sub>2</sub>, CO<sub>2</sub>, C<sub>6</sub>F<sub>6</sub>, or naphtalene scavenge excess electrons forming molecular ions in reaction (10). In these ions the electron is bound loosely (electron affinity  $\epsilon \leq 1.5$  eV<sup>8/</sup>) and so may be given to the positron to form Ps. On the other hand, inhibitors attach spur electrons in a dissociative way,



forming a stable radical X<sup>-</sup>. Reactions (10) and (12) may have similar cross sections and compete in scavenging the excess electrons.

In certain aliphatic hydrocarbons CS<sub>2</sub> behaves as an inhibitor at small concentrations and as an antiinhibitor at greater ones<sup>9/</sup>. CS<sub>2</sub> has an electron affinity too low to inhibit Ps formation by electron scavenging so its inhibition effect prevails by reducing the mobility of spur electrons. (There is an empirical correlation between excess electron mobility and Ps formation probability<sup>9/</sup>). At higher CS<sub>2</sub> concentrations, however, the electron tunnelling between neighbouring CS<sub>2</sub> molecules probably enhances the electron mobility and hence the Ps formation<sup>9/</sup>. Similar effects have been observed in aqueous solutions of alkali halides, KSCN, and Na<sub>2</sub>S<sup>12/</sup> and interpreted by inhibition combined with enhancement of Ps formation due to "positive hole" (in the given case OH) scavenging.

Thus we have two models of Ps formation: the Ore model with hot Ps reactions and the spur reaction model. The former gives an adequate description of Ps formation in gases and explains its nonformation in crystalline solids. In fluids, however, the spur model has won a great popularity although the simultaneous proceeding of both formation processes cannot be excluded.

#### MUONIUM

The positive muons are produced in the decay of positive pions in flight having complete polarization. In the muon decay reaction (1) the positrons are emitted preferentially in the direction of the muon spin<sup>2,4,6/</sup>. When polarized muons are stopped in matter the direction and magnitude of their polarization can be measured by observing their asymmetric decay as they precess in a transverse magnetic field. The muon spin rotation ( $\mu$ SR) technique involves stopping polarized muons in the sample and counting decay positrons in a given direction as a function of the time spent by the muons in the medium. The spin precession in the magnetic field results in characteristic oscillations in the  $\mu$ SR spectrum.

Three types of muonic species can be identified from their precession signals<sup>13/</sup>:

(i) Free muons in diamagnetic environment give rise to nuclear Larmor precession at 13.55 kHz/G. This diamagnetic signal occurs for all liquids.

(ii) In low magnetic fields ( $<10$  G) one half of the free Mu atoms precesses at the frequency 1.4 MHz/G, the frequency of the other half is too high to resolve. Muonium has been identified in various substances.

(iii) Using high magnetic fields (about 1 kG) several muonic radicals have been observed due to their characteristic "splitted Mu" frequencies<sup>2,14/</sup>.

According to the generally accepted model Mu is formed in an energetic state and may enter epithermal reactions before thermalization. In solutions of bromine and iodine in hexane, for example, more than 10% of Mu atoms were attributed to forming diamagnetic compounds in epithermal reactions<sup>6/</sup>. There are indications, however, that Mu atoms may be formed in spur processes as well<sup>2,13,15/</sup>. Percival et al.<sup>13/</sup> have observed the inhibition of Mu formation by adding electron scavengers to water. On the basis of the spur model of Mu formation several predictions were made by Mogensen<sup>15/</sup>. Thus the spur reaction model has come into action in muonium chemistry, too.

## PIONIC HYDROGEN

Pionic hydrogen atom ( $p\pi^-$ ) forms when negative pions are stopped in a sample containing hydrogen as a result of Coulomb capture of the pion on an atomic orbit around the proton. The neutral and very small  $p\pi^-$  atom leaves the molecule in a highly excited state, having a considerable kinetic energy, and collides with other atoms. The  $p\pi^-$  atom never reaches its ground state as the pion capture by proton takes place from the levels  $N \geq 4$ <sup>16/</sup>. In collisions the pion can be transferred to a heavier atom  $Z$ ,



with subsequent nuclear capture of the pion in nucleus  $Z$ .

The event of the capture of a stopped pion in proton can be easily detected by the nuclear charge-exchange reaction (3). According to the model of "large mesic molecules"<sup>16/</sup> an electron of the bound hydrogen atom should be replaced by the pion to form  $p\pi^-$ . As is shown by the earlier measurements of V.I.Petrukhin et al. summarized in reviews<sup>4,16-18/</sup> the W probability that in a system containing hydrogen the pion is captured in proton is closely related to the properties of the chemical bound of hydro-

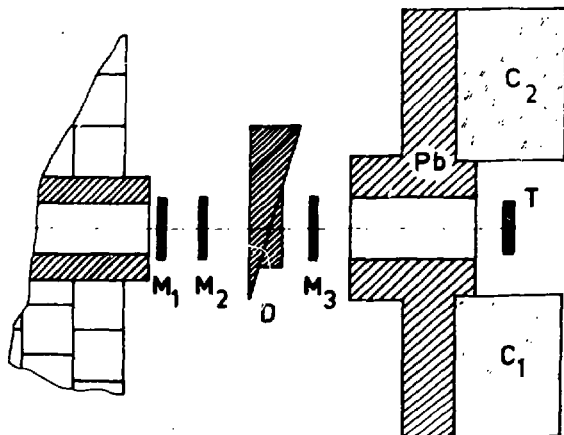


Fig.2. The experimental set-up of pionic hydrogen measurements.  $M_1, M_2, M_3$ - scintillation counters monitoring the pion beam,  $D$ - beam moderator (degrader),  $T$  - target,  $C_1, C_2$ - total-absorption Čerenkov detectors<sup>18/</sup>.

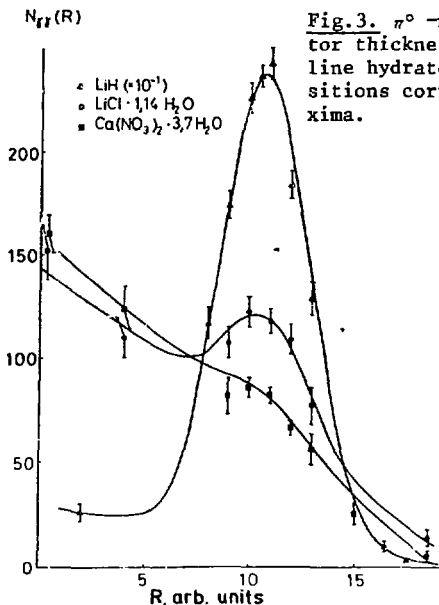


Fig. 3.  $\pi^0$ -meson yields vs. moderator thickness in LiH and crystalline hydrate targets. The peak positions correspond to pion-stop maxima.

gen, particularly to the electronic density in a bound hydrogen atom.

The measurements to be reported here were performed in the 80 MeV negative pion beam of the JINR synchrocyclotron. The experimental set-up is shown in Fig. 2<sup>18/</sup>. The fast pions are slowed down in scintillation counters  $M_1$ ,  $M_2$  and  $M_3$  and a plexiglass moderator of variable thickness and get into the target where a part of them is stopped. The photons from the  $\pi^0$  decay are detected by two total-absorption Čerenkov counters. Altering the thickness  $R$  of the moderator the  $\pi^0$ -yields from reaction (3)  $N_{\pi^0}(R)$  can be measured as a function of the pion beam energy. For hydrogenous targets  $N_{\pi^0}(R)$  consists of a peak corresponding to the maximal number of pion stoppages and a more-or-less linear background (Fig. 3) while for hydrogen-free samples the peak is absent (Fig. 4). The probability of the charge-exchange reaction of stopped pions with composite nuclei (except  $^3\text{He}$ ) is strongly suppressed; by our new data it is smaller than

$6 \cdot 10^{-6}$  for carbon and  $(1-3) \cdot 10^{-5}$  for Al, V, Cu, Zr, Sn, Ta, and Pb<sup>19/</sup>. The method of mathematical evaluation of the experimental  $N_{\pi^0}(R)$  spectra is described in<sup>20/</sup>.

The atomic capture and transfer of pions have been studied in gas mixtures of hydrogen<sup>21/</sup> and methane, ethane, ethylene<sup>22/</sup> with noble gases. The dependence of the rate of the transfer reaction (13) on the concentration and the atomic number of the noble gas could be approximated by the same function; the transfer rates, however, were twice higher in the case of  $H_2$  than of  $CH_4$ ,  $C_2H_6$ , and  $C_2H_4$ . This difference can be interpreted with different conditions of formation of  $p\pi^-$  atoms in hydrogen and hydrocarbons. The pionic hydrogen atoms are formed in less excited states at the disintegration of mesic molecule  $CH_4\pi^-$ , etc., than at that of  $H_2\pi^-$ . This implies a reduction in the transfer cross-section and an increase in the pion capture rate by

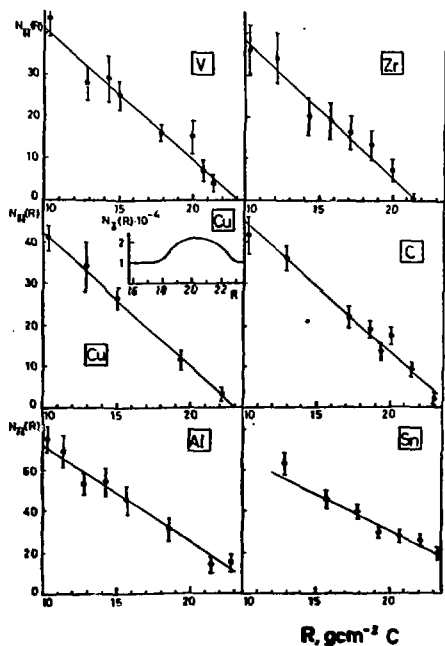


Fig.4.  $\pi^0$  -meson yields vs. moderator thickness in various elements. For copper the yields of single photons are also presented indicating the location of pion-stop maximum<sup>19/</sup>.

the collisions of the hot  $p\pi^-$  atoms with other protons, competing with the transfer process<sup>/22/</sup>.

Below the electronic structure studies will be described, performed last years for pure water<sup>/23/</sup> and aquacomplexes<sup>/24/</sup> by our group in Dubna.

A special feature of hydrogen is its ability to form hydrogen bonds  $Z-H...X$  when atom  $X$  has a lone electron pair and can play the role of electron donor<sup>/25/</sup>. The H-bond formation is accompanied by changes in the physico-chemical properties of the system; by those changes, however, the character of alteration in electron density near the proton when H-bond forms cannot be unambiguously determined<sup>/23/</sup>.

Among the compounds with hydrogen bonds water is the most frequented one. There are indications that the bonds  $O-H...O$  of water break at heating. In terms of the bond-breaking model of Haggis et al.<sup>/26/</sup> the structure of water can be characterized by parameter  $f_T$  - the concentration of broken H-bonds at temperature  $T$ . In ice all the protons are bound in H-bonds,  $f_{T<0} = 0$ , in liquid water at melting point  $f_0 = 9\%$  and it increases with increasing temperature up to  $f_T = 100\%$  at  $T \geq 374^\circ C$ , the critical temperature of water.

In the course of our experiments we have measured the relative change  $p_T$  of probability  $W$  of pion capture in water hydrogen as a function of temperature  $T$  in comparison with  $25^\circ C$  (Fig.5).

$$p_T = (W_T - W_{25}) / W_{25} \quad (14)$$

The experimental details have been described in<sup>/23/</sup>. To avoid systematic errors  $W_T$  and  $W_{25}$  were obtained in each case by measurements under the same geometric conditions.

On the basis of the bond-breaking model, probability  $W$  in water can be approximated by a sum of the contributions of hydrogen atoms in H-bonds and out of them:

$$W_T = W_{in}(1 - f_T) + W_{out} f_T \quad (15)$$

Using relation (15) in (14) we obtain

$$p_T = \frac{f_T - f_{25}}{f_{25} + (Q-1)^{-1}} \quad (16)$$

where  $Q = W_{out} / W_{in}$  and the  $f_T$  values are taken from<sup>/26/</sup>. Parameter  $Q$  can be estimated by equation

$$Q = W(T \geq 374^\circ C) / W(T < 0) = 2.0 \pm 0.1 \quad (17)$$

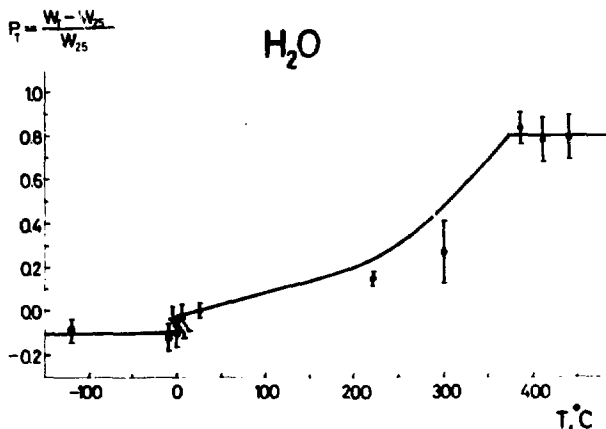


Fig.5. The temperature dependence of the relative change  $P_T$  of the probability  $W$  that a pion stopped in water is captured by a proton. ■ - ice, ○ - liquid water, ● - supercritical fluid<sup>'25'</sup>. The solid curve corresponds to equation (16) with  $f_T$  values taken from<sup>'26'</sup> and  $Q = 2$ .

In terms of the model of large mesic molecules this effect shows that the formation of the hydrogen bond involves a substantial reduction in the electron density of hydrogen atoms, i.e., in the covalency of bond O-H. This conclusion is in agreement with the theoretical estimations<sup>'25'</sup> that the formation of a  $(H_2O)_2$  dimer with one hydrogen bond leads to a decrease of electron density about  $(0.03-0.04)e^-$  on the proton involved. The liquid water has a fused-ice structure forming large polymers which results, virtually, in a further reduction of the mean electron density in the bound hydrogen atoms.

In aquacomplexes the water molecules are bound to the cations by ion-dipole forces and coordination interaction and, possibly, to the anions by hydrogen bonds. The coordination involves an electron transfer from the ligands to the central cation<sup>'27'</sup>. The probability  $W$  of pion capture in water hydrogen has been measured by us for 31 aquacomplexes and suppressions were observed in  $W$  as compared to free water molecules. Calculating the suppression values

we took into consideration that a part of the pions are absorbed in the salt atoms of the complex. By the suppression values  $\epsilon$  the complexes studied can be divided into four groups<sup>/24/</sup>. Group 1 consists of compounds of alkali cations with weak suppressions ( $\epsilon \approx 3$ ). Group 2 is composed of the chlorides and sulphates of di- and trivalent cations as  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  ( $\epsilon \approx 5$ ). In Group 3 ( $\epsilon \approx 10$ ) the complexes with nitrate and perchlorate anions have been included (e.g.,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ) while Group 4 ( $\epsilon \approx 20$ ) contains two complexes with  $\text{Cu}^{2+}$  cations and  $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ .

According to the model of large mesic molecules the suppressions observed should be connected with a reduction of the electronic density in the hydrogen atoms of water molecules. In the alkali metal complexes (Group 1) the water molecules are bound via ion-dipole forces weakly affecting the electronic structure of the ligands. For the other groups the suppression is due to, mainly, coordination by the cations<sup>/27/</sup>. The difference between Groups 2 and 3, however, indicates the effects of the anion probably through hydrogen bonds. This is clearly illustrated by comparing suppressions  $\epsilon$  for series of analogous complexes of type  $\text{MX} \cdot n\text{H}_2\text{O}$  (Table 3). The high  $\epsilon$  values obtained in Group 4 for copper hydrates can be possibly explained by the ability of copper to form particularly stable complexes<sup>/27/</sup>. As to  $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$  its two cations  $\text{Cr}^{3+}$  coordinate six ligands which means twice greater cation charge per water molecule than in the complexes of Group 3.

T a b l e 3

Suppressions of the probability of pion capture by protons of water molecules coordinated in complexes  $\text{MX} \cdot n\text{H}_2\text{O}$

M	n	$X = (\text{Cl}^-)_2$	$X = \text{SO}_4^{2-}$	$X = (\text{NO}_3^-)_2$	$X = (\text{ClO}_4^-)_2$
$\text{Ca}^{2+}$	2	$5.0 \pm 1.3$	$4.4 \pm 1.3$	-	-
$\text{Ca}^{2+}$	4	$5.1 \pm 0.9$	-	$17.3 \pm 7.3$	-
$\text{Mg}^{2+}$	6	-	$5.1 \pm 0.4$	$9.3 \pm 1.5$	$13.1 \pm 4.4$
$\text{Fe}^{2+}$	6	-	$5.6 \pm 0.5$	-	$13.6 \pm 3.5$
$\text{Co}^{2+}$	6	$4.7 \pm 0.6$	$5.2 \pm 0.9$	$8.6 \pm 1.9$	-
$\text{Ni}^{2+}$	6	$3.8 \pm 0.4$	$5.6 \pm 0.9$	$17.4 \pm 3.6$	-



## CONCLUSIONS

There are several similarities in positronium and muonium researches. The nuclei in these atoms are replaced by positive particles, they can enter chemical reactions as light hydrogen isotopes. In gases, apparently, they are formed by picking up atomic electrons, in liquids, however, a considerable part of them forms probably in spur reactions. The spur reaction model has helped the positronium investigators to ask new questions and find new effects and has made a great contribution to developing an interaction with radiation chemistry research.

While positronium and muonium investigations relate to the chemical environment in a system, the  $p\pi^-$  atom is an extremely sensitive tool for obtaining information on the bond properties of hydrogen in various compounds. This has been demonstrated by the study of the effects of hydrogen bond and coordination on the electron density of hydrogen in water. Thus positronium and muonium inform us on a macroscopic or intermolecular level while  $p\pi^-$  does it on an intramolecular one.

The author is indebted to Dr. Béla Lévy for stimulating discussions and to Drs. V.I.Petrukhin, V.N.Pokrovsky, and I.A.Yutlandov for critical remarks concerning this paper.

## REFERENCES

1. West R.N. Advan. Phys., 1973, 22, p.263.
2. Brewer J.H., Crowe K.M. Ann. Rev. Nucl. Part. Sci., 1978, 28, p.239.
3. Lambrecht R.M., BNL 50510, 1975.
4. Lévy B. At. Energy Rev., 1979, 17, p.403.
5. Tao S.J., Green J.H. J. Chem. Soc. A., 1968, p.408.
6. Ache H.J. In: Hot Atom Chem. Status Rep., IAEA, Vienna, 1975, p.81.
7. Mogensen O.E. J. Chem. Phys., 1974, 60, p.998.
8. Molin Yu.N., Anisimov O.A. Advan. Chem., in press.
9. Jansen P., Mogensen O.E. Chem. Phys., 1977, 25, p.75.
10. Tao S.J. Appl. Phys., 1976, 10, p.67.
11. Djermouni B., Ache H.J. J. Phys. Chem., 1978, 82, p.2378.
12. Duplatre G., et al. Radiat. Phys. Chem., 1978, 11, p.199.
13. Percival P.W., Roduner E., Fischer H. Chem. Phys., 1978, 32, p.353.
14. Roduner E., et al. Chem. Phys. Lett., 1978, 57, p.37.
15. Mogensen O.E. Hyperfine Interactions., in press.
16. Ponomarev L.I. Ann. Rev. Nucl. Sci., 1973, 23, p.395.

17. Schneuwly H. In: Exotic Atoms (G.Fiorentini and G.Torelli, eds.), Pisa, 1977, p.255.
18. Petrukhin V.I. In: Proc. 4th Int.Conf.High Energy Phys. Nucl.Struct. (Dubna, 1971), JINR, D1-6349, Dubna, 1972, p.431 (In Russian).
19. Horváth D. JINR, 14-12343, Dubna, 1979. (In Russian).
20. Horváth D. JINR, 10-12229, Dubna, 1979. (In Russian).
21. Petrukhin V.I., Suvorov V.M. Zh.Eksp.Teor.Fiz., 1976, 70, p.1145. (In Russian).
22. Bystritsky V.M., et al. In: Mesons in Matter, Proc. Int. Symp. on Meson Chemistry and Mesomolecular Processes in Matter, Dubna, 1977, p.223. JINR, D1,2,14-10908, Dubna, 1977. (In Russian).
23. Kachalkin A.K., et al. Zh.Eksp.Teor.Fiz., 1979, 77, p.26 (In Russian).
24. Dézsi I., et al. JINR, P14-11237, Dubna, 1979.
25. Schuster P. In: The Hydrogen Bond (P.Schuster, G.Zundel, and C.Sandorfy, eds.), North-Holland, Amsterdam, 1976, Vol.1, p.15.
26. Haggis G.H., Hasted J.B., Buchanan T.J. J.Chem.Phys., 1952, 20, p.1452.
27. Grinberg A.A. "Introduction to the Chemistry of Coordination Compounds", Moscow, "Khimiya", 1966. (In Russian).

Received by Publishing Department  
on October 2 1979.