Muon Coulomb Capture in Aqueous Solutions and the Controversy between the Large–Mesonic-Molecule Model and the Transfer Model

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Muonic x-ray spectra from aqueous solutions of alkali halides have been measured and compared with spectra from the respective solid salts. In the solutions the higher members of the Lyman series are enhanced. From this and from $p+\pi^- \rightarrow n+\pi^0$ data on hydrogen-containing compounds it is concluded that transfer involving $p\mu$ or $p\pi$ atoms, respectively, is responsible for the hydrogen effects while mechanisms involving mesonic-molecular orbitals are ruled out.

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Large "chemical effects" for condensed targets containing chemically bonded hydrogen atoms have been observed both in muonic x-ray spectra and in pionic charge-exchange reactions. In the case of muonic x-ray spectra these are characterized by a general enhancement of higher Lyman series transitions in relation to the $2p \rightarrow 1s$ transition, compared to compounds which do not contain hydrogen. In the case of (negative) pions they are characterized by a strongly Z-dependent suppression of the charge-exchange reaction $p+\pi^- \rightarrow n+\pi^0$ in a hydrogen-containing condensed compound, where Z is the atomic number of the higher-Z element in the compound. It was not clear up to now whether these effects are due to mesonic transfer or to formation of mesonic-molecular orbitals. In this Letter we describe a crucial experiment which decisively shows that transfer is the operating mechanism.

The hydrogen enhancement effect in muonic x-ray spectra was first observed by Daniel *et al.*[1] by comparing polyethylene with graphite and water with metal oxides. It was later confirmed in a large number of cases.[2,3] The effects are large, up to a factor of 2.

Related to the above hydrogen enhancement effect in chemical compounds is an enhancement effect in gaseous mixtures which contain molecular hydrogen. Here higher members of the muonic Lyman series are enhanced[4–6] compared to the $2p \rightarrow 1s$ transition, even more strongly than for the hydrogen compounds in the condensed state.

The suppression of charge exchange in chemical compounds was first observed by Panofsky *et al.*[7] The Z dependence was subsequently estimated by Petrukhin and Prokoshkin[8] to be $Z^{3.5}$. Later similar results were obtained in a great number of cases.[9]

The enhancement of the higher members of the muonic Lyman x-ray series generally results from a more pronounced population of low-angular-momentum, high-n atomic states, where n is the principal quantum number, as is shown by comparison with corresponding calculations of muonic x-ray cascades.[2,5,6,10] There remains, however, the question of the mechanism by which the bonded hydrogen atoms affect this population.

According to our present understanding the majority of negative muons in matter are first slowed down to kinetic energies of the order of the valence-electron binding energy and then undergo Coulomb capture,[11–16] replacing a loosely bound electron. The characteristic feature of the large–mesonic-molecule model advanced by Gershtein *et al.*[16] is that this electron is an electron engaged in molecular binding; thus the first bound state of the muon is a molecular state centered on both the hydrogen and a higher-Z atom. From this molecular state there is easy access to lower-lying atomic states of the higher-Z atom with low angular momentum. Thus the large–mesonic-molecule model can explain the hydrogen enhancement effect in hydrogen-containing compounds, at least qualitatively. However, no direct experimental evidence for the model exists.

The Coulomb capture of negative pions is generally thought to be similar to that of negative muons (cf., for example, Ref. 12). Since pions from molecular states in a hydrogen-containing compound can easily annihilate at the higher-Z nucleus of the molecule, the large–mesonic-molecule model also can explain the charge-exchange suppression, at least qualitatively. Again, however, there is no evidence that the mechanism of suppression really includes a mesonic-molecular state.

The enhancement effect in gas mixtures containing hydrogen clearly cannot be explained by large mesonic molecules. Here all evidence from cascade calculations[5,6,17] and transfer calculations[17] speaks for transfer as the reason for the population of low-angular-momentum states. The general idea is that first a neutral $p\mu$ system of very low kinetic energy is formed which penetrates the higher-Z atom; then the muon is transferred. This is the transfer model.

The transfer model evidently can also explain the hydrogen enhancement effect and the charge-exchange suppression in hydrogen-containing compounds. Although the $p\pi$ system (and, by the way, also the $p\mu$ system) will be slow because of the low energy of the pion before Coulomb capture, it can live long enough to travel in a compound to a neighboring higher-Z atom, at least in an excited state. After Coulomb capture of the pion in hydrogen the $p\pi$ will have about the same momentum as the incoming pion, and hence a velocity of the order of $\alpha c \times (m_e m_\pi)^{1/2}/(m_\pi + m_p)$, where α is the fine-structure constant, c is the velocity of light, and m_e, m_π, and m_p are the rest masses of the electron, the pion, and the proton, respectively. The mean travel length for the ground state, with a mean life[18] of only 1.1×10^{-15} s, is then of the order of 1.7×10^{-11} m, a distance somewhat smaller than a typical bond length. For a $p\pi$ system in an excited state, however, the lifetime is longer by one or several orders of magnitude, making transfer possible.

In order to distinguish between the two alternatives, large–mesonic-molecule model or transfer model, a crucial experiment was performed. The basic idea is to choose systems where the hydrogen atom is close to a higher-Z atom but not chemically bound. Here the large–mesonic-molecule model would not predict any hydrogen-related effect but the transfer model would. We measured muonic x-ray spectra from ions in a dilute aqueous solution and from crystalline targets. In this way we ensured almost equal spectral flux densities of the muons (i.e., the number of muons per unit energy and time entering a small sphere divided by the cross section of the sphere) for all kinds of atoms in the target, as first pointed out by Knight *et al.*[19] for the solutions; the same applies to our crystalline ionic reference targets not containing hydrogen—the alkali halides.[20]

Our aqueous and crystalline samples were contained in thin polyethylene holders with interior dimensions $0.6\times5\times7$ cm^3. Accordingly, all corrections for self-absorption of the muonic x rays observed were negligible. The sodium chloride was supplied by E. Merck and Company, Darmstadt, Germany. The magnesium chloride (water free) was prepared in our Institute. The muonic x-ray spectra were recorded at the muon channel I of the Swiss Institute for Nuclear Research (SIN), Villigen, Switzerland. A Ge(Li) spectrometer with a 42-cm^3 sensitive volume was employed. The stopping telescope and coincidence electronics have been described elsewhere.[10]

The muonic Lyman intensity patterns observed for both the crystalline samples and $4M$ solutions of sodium and magnesium chlorides are provided in Tables I and II. Here the intensity of the higher members for a given element is given as a ratio to the intensity of the K_α x ray:

$$R_{n\to1} = I_{n\to1}/I_{2\to1}.$$

In passing we point to the close similarity of the K-series intensities recorded for the chloride ion in the solids and the distinct but similar chlorine spectrum recorded for the solutions.

Apparently a major increase of the relative intensity

TABLE I. Experimental K-series intensity patterns from sodium chloride in aqueous solution or crystalline state (in percent of 2 → 1; errors in parentheses).

Transition	Na intensity	Cl intensity
	$4M$ NaCl	
2 → 1	100	100
3 → 1	12.3(6)	9.4(6)
4 → 1	10.2(6)	5.4(5)
5 → 1	6.9(5)	4.6(4)
6 → 1	3.4(5)	4.2(4)
7 → 1	1.4(5)	2.6(4)
8 → 1		2.0(4)
	NaCl crystal	
2 → 1	100	100
3 → 1	9.55(12)	8.11(13)
4 → 1	6.19(10)	3.27(9)
5 → 1	4.18(9)	3.13(9)
6 → 1	1.85(7)	2.53(8)
7 → 1	0.66(19)	1.45(7)
8 → 1		0.79(6)
9 → 1		0.65(6)
10 → 1		0.53(5)
11 → 1		0.19(5)

TABLE II. Experimental K-series intensity patterns from magnesium chloride in aqueous solution or crystalline state (in percent of 2 → 1; errors in parentheses).

Transition	Mg intensity	Cl intensity
	$4M$ $MgCl_2$	
2 → 1	100	100
3 → 1	10.8(6)	9.7(3)
4 → 1	7.9(6)	4.5(2)
5 → 1	5.8(6)	5.0(3)
6 → 1	3.7(5)	3.9(3)
7 → 1		2.7(3)
	$MgCl_2$ crystal	
2 → 1	100	100
3 → 1	8.75(9)	8.04(13)
4 → 1	5.61(17)	3.36(8)
5 → 1	4.14(19)	3.14(8)
6 → 1	2.61(17)	2.51(8)
7 → 1	1.78(16)	1.46(6)
8 → 1		0.68(5)

of the high members for a given K x-ray series occurs in the aqueous solutions for *both* the cation and anion.[21] To permit comparison of this effect for all the ions in solution we calculate enhancement ratios for the K x-ray series of a given element:

$$E_{n\rightarrow 1} = (R_{n\rightarrow 1})_{\text{solution}}/(R_{n\rightarrow 1})_{\text{solid}}.$$

These enhancement ratios are displayed in Table III and Fig. 1. Clearly similar enhancements are observed for both the anions and cations, the effect for both ions approaching a factor of 2 for the higher members of the K x-ray series.

Our results for the aqueous ionic solutions require a discussion taking hydration into account. The structures of hydrated anions and cations differ markedly in the orientation of the polar water molecules immediately coordinated around each ion. Hydrogen atoms lie closest to the negative anions; oxygen atoms are closest to the positive cations. A recent theoretical investigation of lithium-fluoride-water systems[22] indicates that about four hydrogen atoms surround the fluoride ion at a distance of 2.0 Å; seven hydrogen atoms surround each lithium ion at a distance of 3.2 Å. Conversely about four oxygen atoms surround each lithium ion at a distance of 2.5 Å; also four oxygen atoms surround each fluoride ion at a distance of 3.1 Å.

The noteworthy feature of our data is that the *positive* cations in solution, $\mathrm{Na}^{+}_{\mathrm{aq}}$ and $\mathrm{Mg}^{+2}_{\mathrm{aq}}$, show the marked enhancement characteristic of the hydrogen-atom-transfer mechanism to approximately the same extent as for the *negative* anion, $\mathrm{Cl}^{-}_{\mathrm{aq}}$. This occurs even though (a) the hydrogen atom of each of the solvating water molecules is bound to the oxygen atoms and (b) these water molecules are oriented so that the hydrogen atoms lie at the greatest distance from the center of the cations, thus ruling out even the possibility of an H-μ-cation molecule.

TABLE III. K-series enhancement ratios observed for the aqueous solutions (errors in parentheses).

Transition	Na	Cl
$3\rightarrow 1$	1.29(6)	1.16(7)
$4\rightarrow 1$	1.64(10)	1.68(15)
$5\rightarrow 1$	1.64(12)	1.47(15)
$6\rightarrow 1$	1.84(27)	1.64(17)
$7\rightarrow 1$	2.12(93)	1.79(28)
$8\rightarrow 1$		2.52(52)
	Mg	Cl
$3\rightarrow 1$	1.23(7)	1.21(4)
$4\rightarrow 1$	1.41(11)	1.34(8)
$5\rightarrow 1$	1.40(15)	1.49(8)
$6\rightarrow 1$	1.40(22)	1.56(13)
$7\rightarrow 1$		1.86(20)

Our experimental results lead us to conclude that transport of the muon after capture is occurring *throughout* the solvated ion complex by means of a neutral mesonic hydrogen atom. Such a transport and subsequent transfer mechanism then becomes available to *any* higher-Z atom in a complex ion or molecule containing bound hydrogen atoms. In accord with the known suppression of the pion charge-exchange process, this transport mechanism should involve mesonic hydrogen systems in excited states, in accord with the experimentally determined mean time of $(2.3 \pm 0.6)\times 10^{-12}$ s that a negative pion needs in liquid hydrogen to go from $\leq 0.006c$ to nuclear capture.[23] Such dimensionally large mesonic hydrogen atoms, in turn, would be readily subject to distortion and meson transfer on encountering the Coulomb field of any proximate higher-Z nucleus.

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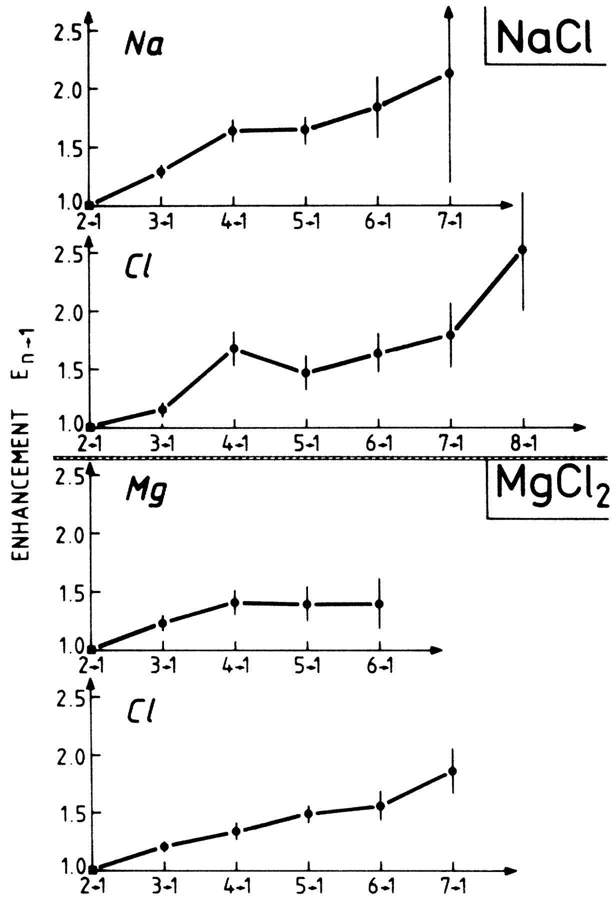

FIG. 1. Enhancement $E_{n\rightarrow 1}$ for various transitions in the elements stated. The solid lines are only to guide the eye.

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