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B. Nandi Ganguly, P. Sarkar. Interaction of positronium with Co^{+2} and Cu^{+2} ions in aqueous chloride and sulphate media. Journal de Physique IV Proceedings, 1993, 03 (C4), pp.C4-139-C4-142. 10.1051/jp4:1993418 . jpa-00251461

HAL Id: jpa-00251461

<https://hal.science/jpa-00251461>

Submitted on 1 Jan 1993

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Interaction of positronium with Co^{+2} and Cu^{+2} ions in aqueous chloride and sulphate media

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ABSTRACT

The interactions of positronium in aqueous solutions of Co^{+2} and Cu^{+2} ions at 297⁰K in the presence of chloride and sulphate ions were studied at varying concentrations of the ions using LS and DBARL techniques. In the case of Co^{+2} , the results suggest a spin conversion reaction, while for Cu^{+2} , there is predominantly an oxidation reaction with a small contribution of spin conversion. In both cases the reaction rate constants were calculated. The Different behaviours of Co^{+2} and Cu^{+2} ions are discernable from the results. A different trend in the variation of the DBARL narrow component with concentration is observed for Cu^{+2} ions in Cl^- and SO_4^{2-} media.

1. INTRODUCTION

Positronium (Ps) can undergo chemical reactions like complex formation, oxidation [1] and spin conversion reactions with paramagnetic solutes [2]. In the present work, Co^{+2} and Cu^{+2} ions have been chosen as solutes to study the effect of spin conversion in the former and the combined effect of oxidation and spin conversion in latter case.

A comparative study of the reactions of Co^{+2} and Cu^{+2} in Cl^- and SO_4^{2-} media to explore the difference in the positronium formation, lifetime quenching characteristics etc., has been made with the help of lifetime spectroscopy (LS) as well as from Doppler broadening of annihilation radiation (DBARL) studies.

2. EXPERIMENTAL AND DATA ANALYSIS

The CoCl_2 , CuCl_2 and CoSO_4 , CuSO_4 salts were procured from E. Merck (India) Ltd., and millipore water was used as solvent. The solutions were contained in special reaction vials and flushed thoroughly with pure argon gas. The positron source used was ^{22}Na ($\sim 4 \mu\text{Ci}$), sandwiched between two mylar films. The positron lifetime distribution was measured with a conventional slow-fast coincidence lifetime spectrometer with plastic scintillators giving resolution of 260 ps for the prompt ^{60}Co γ -rays. The DBARL study was done using a 40 cc HPGe detector with a resolution of 1.1 keV at 475 keV (γ -line from ^{102}Rh). Gamma lines of ^{133}Ba and ^{207}Bi were used for energy calibration of the DBARL system and the channel constant was fixed at 60 eV per channel.

Analysis of the lifetime distribution was done using the standard computer programs POSITRONFIT and RESOLUTION [3]. The measurements have been mainly confined to the determinations of the long-lived component τ_3 (decay

constant, $\lambda_3 = 1/\tau_3$) and its intensity.

For DBARL measurements, the observed experimental spectra were deconvoluted using the method of Dannefaer and Kerr [4] coupled with a random search technique. After deconvolution, a two-gaussian fit to the spectrum is made and from the two gaussians thus obtained, the narrow component was isolated. Fig. 1 shows the measured distribution the deconvoluted spectrum and the two fitted gaussians for CuSO_4 in 0.2M solution as a representative DBARL data analysis.

3. RESULTS AND DISCUSSION

The variations of the long lifetime, $\tau_3 = 1/\lambda_3$ with respect to solute concentration, for Co^{+2} and Cu^{+2} in presence of Cl^- and SO_4^{2-} ions in aqueous solutions are shown in figs. 2(a) and (b) respectively. The trends of λ_3 vs. concentrations for Co^{+2} and for Cu^{+2} ions show a similar quenching effect and an almost linear rising trend in SO_4^{2-} medium. However, a different trend in Cl^- medium is evident from figs. 2(a) and 2(b). The slopes of the curves are steeper especially in the case of Cu^{+2} with a levelling off at concentrations above 0.06M.

The various positronium reactions and their annihilation can be dealt with the help of the kinetic equations as described in [5]. The reaction rates that are dependent on the solute concentration are described by a linear relationship $\lambda_x = K_x [M]$, where subscript x stands for the appropriate reaction, K_x is the reaction rate constant for that reaction and $[M]$ is the molar solute concentration. Using this relation, K_{conv} is computed to be $\sim 2.00 \text{ M}^{-1} (\text{ns})^{-1}$ in SO_4^{2-} medium and $\sim 1.8 \text{ M}^{-1} (\text{ns})^{-1}$ in Cl^- medium. This agrees with the values given in reference [6]. It can be inferred that the interaction of positronium with Co^{+2} ion in the aqueous medium is a purely cationic effect, the Cl^- and the SO_4^{2-} ions have little influence on K_{conv} . However, these values will be 4 times higher if we consider $\lambda_{\text{conv}} = (K_{\text{conv}}/4)[M]$ as discussed in [6].

The other important observed feature is that the intensity of the narrow component due to p-Ps formation (obtained after deconvolution) increases with the increase in the Co^{+2} concentration (see fig. 3(a), 3(b)). This can be attributed to the spin conversion effect, more so, if we consider increasing inhibition of Ps formation with solute concentration.

In the case of Cu^{+2} ions, the variations of λ_3 values show a very different trend in Cl^- and SO_4^{2-} medium (fig. 2(a), 2(b)). The saturation effect in Cl^- medium can be due to incomplete dissociation of the salt. The increase in λ_3 in the Cu^{+2} system is also accompanied by a marked fall in the intensity of the narrow component in both the media, due to predominating oxidation reaction and inhibition of Ps formation [8]. Neglecting the conversion effect the reaction rate constants of Ps with Cu^{+2} is evaluated to be $2.46 \text{ M}^{-1} (\text{ns})^{-1}$ and $2.7 \text{ M}^{-1} (\text{ns})^{-1}$ for Cl^- and SO_4^{2-} media respectively. These values agree with those of references [8] and [9].

Fig.1. The measured and deconvoluted spectra of 0.2M CuSO_4 solution at room temperature.

Fig. 2a Variation of the decay constant λ_3 with the concentration of CoCl_2 and CuCl_2 solutions at room temperature.

The conversion effect [10] can be dealt with separately from the DBARL data. The deconvoluted narrow component intensity (due to p-Ps) shows a small initial increase due to conversion effect but at higher concentrations (above 0.04M) strong oxidation and inhibition reactions mask the conversion effect. This experimental result yields a conversion rate constant $1.5 \text{ M}^{-1} \text{ ns}^{-1}$. However, from the experimental results of the p-Ps component intensity in Cl^- medium in the case of Cu^{+2} no meaningful data could be extracted. The initial decrease (fig. 3(a)) in I_N may be attributed to the undissociated salt and towards the higher concentration, the decay of the bound states formed contribute to the narrow component.

4. CONCLUSIONS

(i) The Co^{+2} ions show a purely conversion effect in SO_4^{2-} and Cl^- media.

(ii) Cu^{+2} ions in the solution are responsible for both oxidation and a small contribution towards conversion effect.

(iii) The bound state formation of e^+ and Cl^- ion in solution tend to affect the observations. A better cationic effect could be observable in SO_4^{2-} medium.

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Fig. 2b Variation of the decay constant λ_3 with the concentration of CoSO_4 and CuSO_4 solutions at room temperature.

Fig. 3a Variation of I_N (%) of the narrow component with the concentration of CoCl_2 and CuCl_2 solutions at room temperature.

Fig. 3b. Variation of I_N (%) of the narrow component with the concentration of CoSO_4 and CuSO_4 solutions at room temperature.

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