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THE KINETICS OF THE SPIN-CONVERSION OF POSITRONIUM MEASURED BY $\beta^+\gamma\Delta E$ AGE-MOMENTUM CORRELATION

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Age-momentum correlation (AMOC) measurements provide time-resolved information on the momentum distribution of annihilating electron-positron pairs through correlated determination of Doppler broadening (ΔE) of the 511 keV annihilation radiation line and positron age. In the $\beta^+\gamma\Delta E$ AMOC technique implemented at the Stuttgart pelletron accelerator the start signals for the age measurements are generated when the relativistic positrons pass through a fast plastic scintillator, which has a detection efficiency close to unity. Beam-based $\beta^+\gamma\Delta E$ AMOC measurements thus combine high $\beta^+\gamma\Delta E$ triple-coincidence rates with low background. From a practical point of view this constitutes a major progress compared to conventional (source-based) $\gamma\gamma\Delta E$ AMOC measurements. The AMOC technique permits direct access to a wide variety of time-dependent processes, among them the reaction kinetics in positronium chemistry. As an example, we present a $\beta^+\gamma\Delta E$ AMOC investigation of the kinetics of a spin-conversion reaction of positronium in methanol induced by the presence of a nitrosyl free-radical paramagnetic solute (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, HTEMPO). The AMOC measurements allowed the time-resolved observation of the spin-conversion process, which had been investigated before by uncorrelated positron lifetime and Doppler-broadening measurements. It is found that within the concentration range investigated (≤ 0.1 mol/l) the spin-conversion reaction rate at room temperature depends linearly on the HTEMPO concentration with a reaction-rate constant $k_{\text{conv}} = (22.5 \pm 0.5) \times 10^9$ l mol⁻¹ s⁻¹.

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1. Introduction

The two quantities which characterize the annihilation of a positron in condensed matter are the momentum p of the annihilating electron-positron pair and the positron age t , defined as the time between the implantation and the annihilation of the positron. Since both annihilation quanta of the dominating 2- γ annihilation transmit equivalent information, one quantum can be used to determine the age of the annihilating positron and the other to measure the momentum of the annihilating electron-positron pair. This leads to the so-called age-momentum correlation (AMOC) technique. In addition, it gives us the information provided by separate lifetime and momentum measurements, the AMOC technique allows us to study changes in the measured momentum distribution of the annihilating electron-positron pairs as a function of the positron age. This additional information may help us to identify the positron states that are formed in complex systems.

The distribution of the momentum transverse to the direction of the observed annihilation quanta can be determined with high resolution by measuring the angular correlation between the two 511 keV γ -quanta of the annihilation radiation (ACAR). For a recent attempt to use the potentially high momentum resolution of ACAR in AMOC measurements see [1] (so far, however, time resolution (FWHM 3 ns) and triple-coincidence count rate (0.6 s^{-1}) are far from that achieved in the set-up used in the present work). Despite of the unique momentum resolution of ACAR spectroscopy, in the interest of high triple-coincidence rates it has become standard to use one of the two annihilation γ -quanta to obtain the Doppler broadening (ΔE) of the 511 keV line by means of a germanium detector [2], which provides information on the longitudinal momentum distribution of the annihilating electron-positron pairs. A further increase in the triple-coincidence rate has been achieved in a beam-based AMOC set-up at the Max-Planck-Institut für Metallforschung in Stuttgart [3]. At the Stuttgart laboratory, relativistic positrons from a pelletron accelerator [4] are available. This allows one to detect the start signal for the lifetime measurement with unity efficiency from the positrons passing through a scintillator, almost without disturbing the velocity distribution of the transmitted relativistic positrons. The technique combines a high triple-coincidence rate ($\approx 100 \text{ s}^{-1}$ at a beam-intensity of $3 \times 10^4 \text{ e}^+ \text{ s}^{-1}$) with a good suppression of pile-up events. These, together with a low background ($\leq 0.01\%$) and deep implantation of the high-energy (4–6 MeV) positrons into the sample, constitute substantial advantages of positron annihilation spectroscopy based on a relativistic beam over the conventional source-based techniques. The triple coincidence rate can be enhanced by about one order of magnitude when the present rather weak ($3 \times 10^8 \text{ Bq}$) ^{22}Na positron source in the high voltage terminal of the accelerator is replaced by a stronger ($3.7 \times 10^9 \text{ Bq}$) ^{22}Na positron source. Reports on beam performance, applications, and recent developments have been published elsewhere [3–9].

2. Analysis of AMOC Spectra

Positrons implanted into a sample are assumed to annihilate in different states i which may be characterized by their annihilation rate constants λ_i and their momentum distributions $P_i(p)$. Denoting the time-dependent population of a certain state with $n_i(t)$, we may write the two-dimensional AMOC spectrum $F(t, p)$ as

$$F(t, p) = \sum_i P_i(p) \lambda_i n_i(t). \quad (1)$$

The measured distributions are the convolutions of $P_i(p)$ and $\lambda_i n_i(t)$ with the instrumental resolutions. From these distributions we may derive time-dependent lineshape parameters, e.g. the S_i parameter:

$$S_i(t) = \frac{\sum_i S_i \lambda_i n_i(t)}{\sum_i \lambda_i n_i(t)}, \quad (2)$$

where the lineshape parameters of the individual positron states, S_i , are assumed to be time independent. Experimentally, the $S_i(t)$ parameter of an AMOC spectrum is determined by the number of counts in the centroid of the Doppler broadened 511 keV line at the age t normalized to the whole content of this line.

If in Eq. (2) the populations $n_i(t)$ are replaced by the occupation probabilities N_i , which are defined as

$$N_i = \frac{\int_0^\infty n_i(t) dt}{\sum_i \int_0^\infty n_i(t) dt}, \quad (3)$$

we obtain the time-averaged lineshape parameter

$$\bar{S} = \frac{\sum_i S_i \lambda_i N_i}{\sum_i \lambda_i N_i} \quad (4)$$

familiar from the conventional Doppler-broadening measurements.

Time-dependent lineshape parameters such as the S_i parameter can be measured with good statistical significance. S_i has the advantage to be linear in the parameters S_i of the individual components, in contrast to parameters measuring the width of the Doppler broadening of the annihilation radiation line, e.g., the variance. In the latter case, assumptions on the form of the momentum distributions of the individual positron states would have to be made in order to express the total width of the annihilation radiation line as a function of the widths of the individual momentum distributions.

We illustrate the preceding discussion by the example of positronium formation in methanol. Figure 1 shows the two-dimensional age-momentum correlation spectrum measured on pure methanol at room temperature. The coincidence counts are plotted versus the positron age and the energy of one of the two annihilation quanta. Cuts along planes of constant energy represent lifetime spectra with different longitudinal momenta of the annihilating electron-positron pair, cuts along planes of constant time energy spectra at different positron ages. The S_i parameters which are evaluated from the energy spectra measured at the positron ages t are plotted versus the positron age in Fig. 2. The measured time-dependence

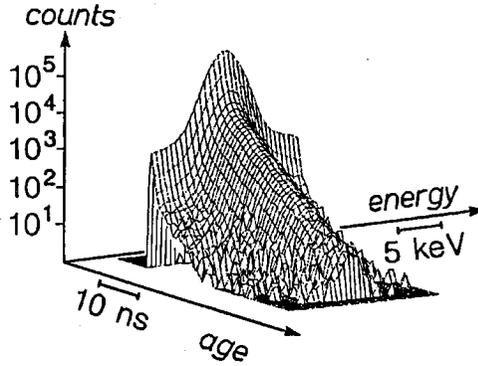


Fig. 1. Two-dimensional age-momentum correlation spectrum measured on pure methanol at room temperature.

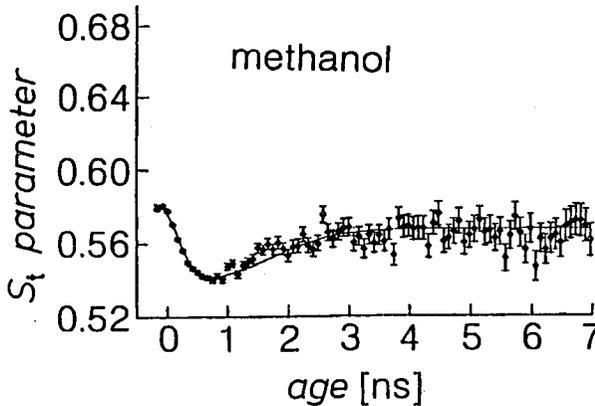


Fig. 2. Time-dependent lineshape parameter S_t versus positron age in pure methanol at room temperature. The solid line represents a fit of Eqs. (2, 5) to the data with the parameters given in Table.

of the S_t parameter can be fitted by Eq. (2) if we assume exponential decays of three positron states i according to

$$n_i(t) = n_i(0)e^{-\lambda_i t}. \quad (5)$$

We identify the three different positron states as *parapositronium* (p -Ps), *orthopositronium* (o -Ps), and free positrons. The parameters S_i , λ_i , and the normalized initial population $\tilde{n}_i(0) = n_i(0)/\sum_i n_i(0)$ obtained from a quantitative fit to the data are given in Table. The value of the S_t parameter observed at positron ages higher than 3 ns (Fig. 2) is essentially that of the "pick-off" annihilation of long-lived o -Ps, denoted by $S_{o\text{-Ps}}$, since at these times practically all of the positrons in short-lived positron states, viz. p -Ps and free positrons, have died out. The intrinsic three- γ annihilation of o -Ps with its very small decay constant

TABLE

Parameters obtained from a fit of Eqs. (2, 5) to the measured time-dependent S_i parameter values of pure methanol at room temperature (Fig. 2).

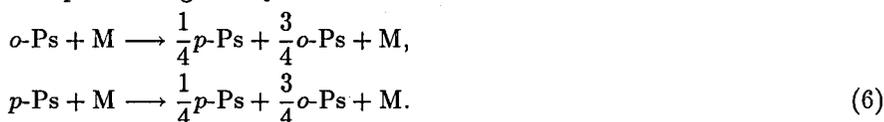
	Parapositronium $i = p\text{-Ps}$	Orthopositronium $i = o\text{-Ps}$	Free positron $i = e^+$
S_i	0.75	0.57	0.54
λ_i	$8.0 \times 10^9 \text{ s}^{-1}$	$2.8 \times 10^8 \text{ s}^{-1}$	$2.2 \times 10^9 \text{ s}^{-1}$
$\tilde{n}_i(0)$	6.7%	20.1%	73.2%

($\lambda_{3\gamma} = 7.1 \times 10^6 \text{ s}^{-1}$) can be neglected compared to the much more frequent two- γ "pick-off" annihilation of the bound positron with a "foreign" molecular electron of opposite spin ($\lambda_{o\text{-Ps}} = 2.8 \times 10^8 \text{ s}^{-1}$). The decrease in the S_i parameter in the time interval between 0.5 ns and 1 ns (Fig. 2) is due to the annihilation of free positrons, which becomes dominant over $o\text{-Ps}$ annihilation. The S_{e^+} parameter of the annihilation of free positrons turns out to be smaller than the $S_{o\text{-Ps}}$ parameter of the "pick-off" annihilation. A higher overlap of the free positron wave function with high-momentum inner-shell electrons of the methanol molecules, compared to that of the more localized wave function of the more massive positronium atom might account for this. At ages lower than 0.5 ns the contribution of $p\text{-Ps}$ annihilation causes an increase in the $S_i(t)$ magnitude, since the annihilation of $p\text{-Ps}$ gives not only the shortest lifetime of all three positron states but also the narrowest momentum distribution.

3. The spin-conversion reaction

Positronium chemistry studies chemical reactions of positronium, by far the lightest atom. Chemical reactions of positronium, e.g., oxidation ($\text{Ps} + \text{M} \rightarrow e^+ + \text{M}^-$), may lead to changed electronic surroundings of the positron and therefore to a change in the lifetime and momentum distributions. This permits to investigate chemical reactions by means of positron annihilation spectroscopy (see, e.g., [10]).

This paper is concerned with the so-called spin-conversion reactions of positronium. Spin-conversion reactions are a special class of chemical reactions of positronium with paramagnetic molecules that change the spin-state of positronium. The reaction equation is given by



The spin-conversion reaction tends to counteract the depletion of the $p\text{-Ps}$ population and to retain the initial ratio 3:1 between $p\text{-Ps}$ and $o\text{-Ps}$. This leads to formation of short-lived $p\text{-Ps}$ at the cost of $o\text{-Ps}$ population, which in general possesses even in condensed matter a high mean lifetime $\lambda_{o\text{-Ps}}^{-1}$ compared to that of

the *p*-Ps ensemble. Therefore, when spin-conversion takes place, the decay of *p*-Ps is observed even at high positron ages, when the initially formed *p*-Ps have died out.

The spin-conversion reaction of positronium with the nitrosyl free-radical paramagnetic solute HTEMPO (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, structure formula, see Fig. 3) dissolved in a polar solvent, e.g., methanol, has been investigated in detail by means of uncorrelated Doppler broadening and positron lifetime spectroscopy (see [11, 12] and references therein).

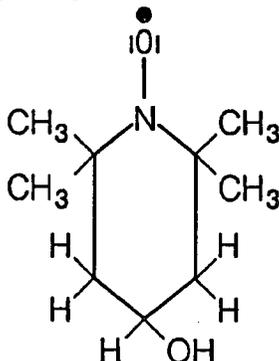


Fig. 3. Structure formula of HTEMPO.

The beam-based $\beta^+\gamma\Delta E$ age-momentum correlation technique has been applied to study this reaction with concentrations of 0.005 mol/l, 0.01 mol/l, 0.05 mol/l, and 0.1 mol/l HTEMPO dissolved in methanol. The measurement on pure methanol described before was performed during the same beam time and under the same experimental conditions. All samples were carefully degassed and then transferred into cylindrical glass vessels under argon pressure in order to avoid oxidation of positronium. The 4 MeV positrons were implanted through a 0.2 mm thin glass window. Owing to the size of the vessels (3 cm in diameter, 3 cm long) almost all positrons annihilated inside the liquid.

The experimentally determined $S_t(t)$ curves at the different measured concentrations of HTEMPO are shown in Fig. 4. The decay of *p*-Ps formed in the spin-conversion reaction with the HTEMPO radical is supposed to result in a drastic increase of the $S_t(t)$ magnitude at high positron ages, compared to the pure solvent methanol (see, e.g., Fig. 4a), where only *o*-Ps decay is present in the later time ranges. The values of the lineshape parameter S_t (Fig. 4a-d) at positron ages exceeding 3 ns are determined by the ratio of the annihilation of *o*-Ps and spin-converted *p*-Ps and thus by the HTEMPO concentration. In the limit of an infinite spin-conversion reaction rate K_{conv} the thermal equilibrium distribution 3:1 of *o*-Ps and *p*-Ps at the time of positron implantation is maintained. For this asymptotic case the S_t parameter, calculated with the values for S_i and λ_i given in Table, is

$$S_t(t) = \text{const} = \frac{\lambda_{p\text{-Ps}} S_{p\text{-Ps}} + 3\lambda_{o\text{-Ps}} S_{o\text{-Ps}}}{\lambda_{p\text{-Ps}} + 3\lambda_{o\text{-Ps}}} = 0.73. \quad (7)$$

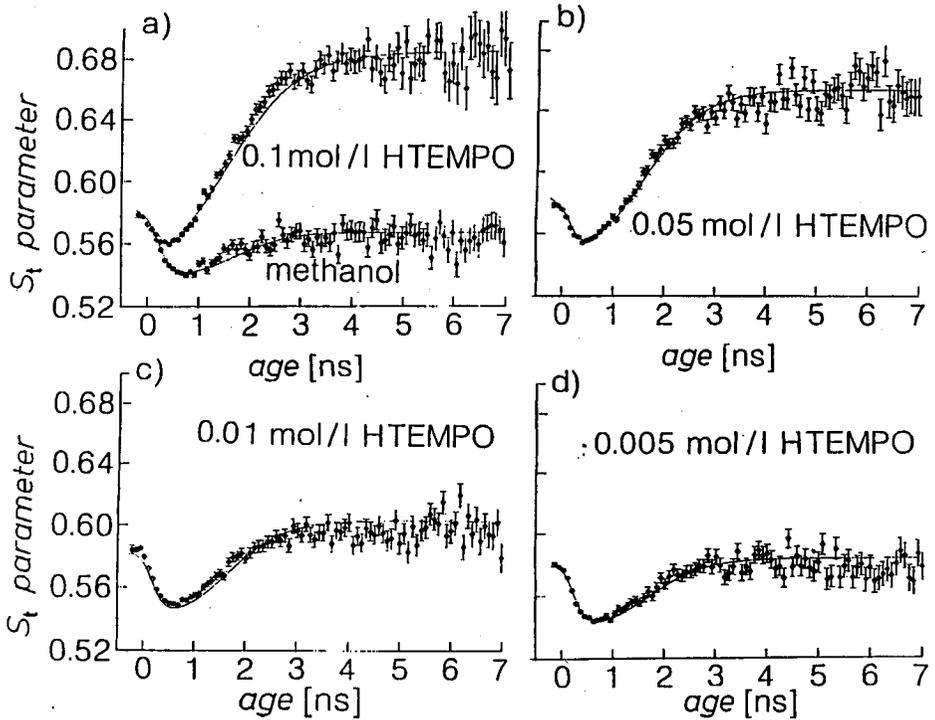


Fig. 4. Time-dependent lineshape parameter S_t versus positron age for different concentrations of HTEMPO dissolved in methanol measured at room temperature. The lines represent fits of (2) based on the solutions (13) of the rate equations (8) to the data points.

Besides spin-conversion with HTEMPO molecules, also oxidation and complex formation reaction of positronium with reaction rates K_{ox} and K_{comp} could be induced in the solution. The time-dependence of the S_t parameter (2) is determined by Dixon-Trainer type [13] rate equations for the populations n_{p-Ps} and n_{o-Ps} of the two positronium spin-states extended by rate equations for the populations of the free positron state n_{e^+} and of positronium complexes* n_{comp} :

$$\begin{aligned} \frac{dn_{p-Ps}}{dt} &= -\Lambda_1 n_{p-Ps} + \frac{1}{4} K_{conv} n_{o-Ps}, \\ \frac{dn_{o-Ps}}{dt} &= \frac{3}{4} K_{conv} n_{p-Ps} - \Lambda_2 n_{o-Ps}, \\ \frac{dn_{e^+}}{dt} &= K_{ox} (n_{p-Ps} + n_{o-Ps}) - \lambda_{e^+} n_{e^+}, \end{aligned}$$

*In the following rate equation concerning complex formation only non-reversible reactions are considered.

$$\frac{dn_{\text{comp}}}{dt} = K_{\text{comp}}(n_{p-\text{Ps}} + n_{o-\text{Ps}}) - \lambda_{\text{comp}}n_{e^+}; \quad (8)$$

where

$$A_1 = K_{\text{ox}} + K_{\text{comp}} + \frac{3}{4}K_{\text{conv}} + \lambda_{p-\text{Ps}} \quad (9)$$

and

$$A_2 = K_{\text{ox}} + K_{\text{comp}} + \frac{1}{4}K_{\text{conv}} + \lambda_{o-\text{Ps}}.$$

The solution of the characteristic equation of the Laplace transform of (8) yields

$$s_{1,2} = \frac{-\alpha \pm \gamma}{2}, \quad s_3 = -\lambda_{e^+}, \quad \text{and} \quad s_4 = -\lambda_{\text{comp}}, \quad (10)$$

$$\text{where } \alpha = A_1 + A_2 \quad \text{and} \quad \gamma = \sqrt{(A_1 - A_2)^2 + \frac{3}{4}K_{\text{conv}}^2}. \quad (11)$$

With the initial conditions

$$n_{o-\text{Ps}}(0) = 3n_{p-\text{Ps}}(0) \quad \text{and} \quad n_{\text{comp}}(0) = 0, \quad (12)$$

inverse Laplace transformation gives us for the time-dependent populations of the three positron states

$$\begin{aligned} n_{p-\text{Ps}}(t) &= n_{p-\text{Ps}}(0) \frac{\exp(-\frac{\alpha}{2}t) \cosh \frac{\gamma}{2}t}{s_1 - s_2} \\ &\quad \times \left[(K_{\text{conv}} + \lambda_{o-\text{Ps}} - \lambda_{p-\text{Ps}}) \tanh \frac{\gamma}{2}t + \gamma \right], \\ n_{o-\text{Ps}}(t) &= 3n_{p-\text{Ps}}(0) \frac{\exp(-\frac{\alpha}{2}t) \cosh \frac{\gamma}{2}t}{s_1 - s_2} \\ &\quad \times \left[(K_{\text{conv}} + \lambda_{p-\text{Ps}} - \lambda_{o-\text{Ps}}) \tanh \frac{\gamma}{2}t + \gamma \right], \\ n_{e^+}(t) &= n_{p-\text{Ps}}(0) \left[\frac{As_1^2 + Bs_3 + C}{(s_1 - s_2)(s_1 - s_3)} \exp(s_1t) \right. \\ &\quad \left. + \frac{As_2^2 + Bs_3 + C}{(s_2 - s_1)(s_2 - s_3)} \exp(s_2t) + \frac{As_3^2 + Bs_3 + C}{(s_3 - s_1)(s_3 - s_2)} \exp(s_3t) \right], \\ n_{\text{comp}}(t) &= n_{p-\text{Ps}}(0) \left[\frac{4K_{\text{comp}}s_1 + D}{(s_1 - s_2)(s_1 - s_4)} \exp(s_1t) \right. \\ &\quad \left. + \frac{4K_{\text{comp}}s_2 + D}{(s_2 - s_1)(s_2 - s_4)} \exp(s_2t) + \frac{4K_{\text{comp}}s_4 + D}{(s_4 - s_1)(s_4 - s_2)} \exp(s_4t) \right] \quad (13) \end{aligned}$$

with the coefficients A , B , and C (depending on the ratio $x = n_{e^+}(0)/(n_{p-\text{Ps}}(0) + n_{o-\text{Ps}}(0))$ between the positron and positronium population at the time of positron implantation) and the coefficient D according to

$$A = 4x,$$

$$B = 4x(A_1 + A_2) + 4K_{\text{ox}},$$

$$C = 4x \left(A_1 A_2 - \frac{3}{16} K_{\text{conv}}^2 \right) + \left(\frac{3}{2} K_{\text{conv}} + 3A_1 + A_2 \right) K_{\text{ox}},$$

$$D = \frac{3}{2} K_{\text{conv}} K_{\text{comp}} + 3A_1 K_{\text{comp}} + A_3 K_{\text{comp}}. \quad (14)$$

The full lines shown in Fig. 4a–d represent fits of Eq. (2), based on the solutions (13) of the rate equations (8), with the parameters S_i and λ_i obtained for pure methanol (Table) to the experimental $S_i(t)$ curves, which were measured for different concentrations C_S of the HTEMPO radical. It has been possible to obtain a consistent set of fits to the data for all measured concentrations of HTEMPO with the reaction rates K_{comp} and K_{ox} set to zero, so that the reaction rate K_{conv} has been the only varied parameter. All other parameters have been kept at the values determined from the fit to the $S_i(t)$ -curve of the pure solvent (see Table). From the fits to the $S_i(t)$ -curves of the solutions, the reaction rate K_{conv} of the spin-conversion process is obtained for the different HTEMPO concentrations C_S . At low positron age ($t \rightarrow 0$) all $S_i(t)$ curves measured coincide within the experimental errors. This indicates that within the concentration range investigated the HTEMPO radical does not significantly inhibit positronium formation. Figure 5

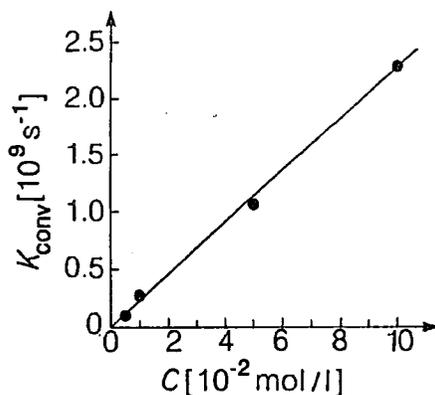


Fig. 5. Reaction rate K_{conv} of the spin-conversion reaction of positronium with HTEMPO dissolved in methanol versus the concentration C_S of HTEMPO.

shows a plot of the reaction rates K_{conv} versus C_S . From the observed linear concentration dependence of the reaction rate at room temperature a value of

$$k_{\text{conv}} = K_{\text{conv}}/C_S = (22.5 \pm 0.5) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1} \quad (C_S \leq 0.1 \text{ mol/l})$$

for the reaction-rate constant of the spin-conversion reaction of positronium induced by HTEMPO dissolved in methanol is deduced for the investigated concentration range.

4. Conclusions

The beam-based $\beta^+\gamma\Delta E$ AMOC facility at the Max-Planck-Institut für Metallforschung in Stuttgart has been used in a time-resolved study of the spin-conversion reaction of positronium with a nitrosyl free-radical (HTEMPO) dissolved in

methanol. A significant increase of the time-dependent line-shape parameter S_t at high positron ages has been observed with increasing HTEMPO concentration as it was predicted on the basis of separate Doppler-broadening and lifetime measurements [11, 12]. The description of the time-dependence of the Doppler broadening with a Dixon–Trainor type model for the spin-conversion reaction gives excellent agreement with the observations. In the HTEMPO concentration range investigated ($C_S \leq 0.1$ mol/l) a spin-conversion reaction rate-constant

$$k_{\text{conv}} = (22.5 \pm 0.5) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1} \quad (15)$$

was found at room temperature. This is in fairly good agreement with the previous result ($k_{\text{conv}} = (19.2 \pm 0.5) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) obtained from uncorrelated lifetime and Doppler-broadening measurements [11]. The power of age-momentum correlation measurements for the study of complex reactions in positronium chemistry has been clearly demonstrated.

References

- [1] H. Saito, Y. Nogashima, T. Hyodo, *Mater. Sci. Forum* **105–110**, 1967 (1992).
- [2] I.K. McKenzie, B.T.A. McKee, *Appl. Phys* **10**, 245 (1976).
- [3] H. Stoll, M. Koch, K. Maier, J. Major, *Nucl. Instrum. Methods Phys. Res. B* **56/57**, 582 (1991).
- [4] W. Bauer, J. Briggmann, H.D. Carstanjen, S. Connell, W. Decker, J. Diehl, K. Maier, J. Major, H.-E. Schaefer, A. Seeger, H. Stoll, E. Widmann, *Nucl. Instrum. Methods Phys. Res. B* **50**, 300 (1990).
- [5] H. Stoll, P. Wesolowski, M. Koch, J. Major, A. Seeger, *Mater. Sci. Forum* **105–110**, 1989 (1992).
- [6] K. Maier, J. Major, A. Seeger, H. Stoll, P. Wesolowski, M. Koch, *Mater. Sci. Forum* **105–110**, 1935 (1992).
- [7] M. Koch, K. Maier, A. Seeger, J.P.F. Sellschop, E. Sideras-Haddad, H. Stoll, S.H. Connell, *Mater. Sci. Forum* **105–110**, 671 (1992).
- [8] T. Grund, K. Maier, A. Seeger, *Mater. Sci. Forum* **105–110**, 1879 (1992).
- [9] P. Wesolowski, K. Maier, J. Major, H. Stoll, T. Grund, M. Koch, *Nucl. Instrum. Methods Phys. Res. B* **68**, 468 (1992).
- [10] V.I. Goldański, V.P. Shantarovich, in: *Modern Physics in Chemistry*, Eds. E. Fluck, V.I. Goldański, Academic Press, New York, London 1974, p. 269.
- [11] I. Billard, J.Ch. Abbé, G. Duplâtre, *J. Phys. Chem.* **88**, 2071 (1991).
- [12] W.F. Magalhães, J.C. Abbé, G. Duplâtre, *Struct. Chem.* **2**, 39 (1991).
- [13] W. Dixon, L. Trainor, *Phys. Rev.* **79**, 13 (1955).