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Application of ^{19}F NMR Spectroscopy to the Study of Equilibrium Dynamics of Uranyl(2+)–Fluoride Complexes

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One- and two-dimensional magnetization-transfer ^{19}F NMR methods were applied in a quantitative study of the fluoride exchange for uranyl(2+)–fluoride complexes in aqueous solution. The applicability of these techniques and the classical lineshape analysis is discussed, and the quality of the results (rate constants and relaxation rates) obtained by the three methods is compared.

KEY WORDS NMR, ^{19}F NMR Magnetization transfer 2D-EXSY Uranyl(2+)–fluoride complexes Ligand exchange

INTRODUCTION

The equilibrium and dynamic properties of several uranyl compounds have been extensively studied during the last decade, owing to their importance in the nuclear energy industry and in the isolation of uranium isotopes.[1,2] The linear dioxouranium(VI) ion, UO_2^{2+}, forms very stable complexes with ligands containing hard donor atoms. The reaction with the simplest ligand of this type, namely fluoride, can be described by the following equation:

$$UO_2(H_2O)_5^{2+} + nF^- = UO_2(H_2O)_{5-n}F_n^{2-n} + nH_2O \qquad n = 1\text{–}5 \quad (1)$$

The equilibrium constants for the species $UO_2F_n^{2-n}$, $n = 1$–4, have been previously determined using different experimental methods.[1] In two recent studies of the UO_2^{2+}–F^- system by ^{19}F NMR, the formation of the previously not detected species $UO_2F_5^{3-}$ was observed.[3,4] On the basis of these results $UO_2F_5^{3-}$ seems to be the limiting complex, and probably it has the same pentagonal bipyramidal structure with five fluoride ligands in the equatorial plane as that previously found in the solid state.[5] The ^{19}F NMR chemical shift differences between the various fluoride sites are very large, at least in comparison with those encountered in ^1H NMR. This fact and the very high sensitivity of ^{19}F NMR spectroscopy offered an attractive possibility to study the equilibrium dynamics in the UO_2^{2+}–F^- system by several NMR techniques,[6] namely by inversion-transfer experiments, two-dimensional exchange spectroscopy (2D-EXSY) and the classical lineshape analysis.

The choice of the optimum experimental technique in dynamic NMR spectroscopy is usually dictated by the characteristics of the exchange system. Still, the experimental conditions (temperature, magnetic field, NMR nucleus, solution composition, etc.) can in many cases be altered in such a way that a certain technique can be applied that provides maximum information on the chemical exchange and/or has the highest accuracy. In several cases, different techniques applied on the same exchange system can give complementary information. Thus, in order to make an optimum choice of the technique, it is important to know the limitations and the accuracy of the potential techniques applied on the studied system.

Modifications of the saturation-transfer technique, first described by Forsén and Hoffman,[7] are becoming powerful tools for obtaining kinetic information for systems undergoing chemical exchange at equilibrium. In systems which are in slow exchange on the chemical shift time-scale, where the longitudinal relaxation rates ($1/T_1$) are of the same order of magnitude or slower than the exchange rates (fast or intermediate exchange on the T_1 time-scale), it is possible to evaluate the rate constants between two or more sites by a selective inversion of one signal. After a period τ, a non-selective $(\pi/2)_x$ pulse generates observable magnetization of the inverted and the non-inverted species. The intensities of these signals depend on the longitudinal relaxation rate of the exchanging species, on the exchange rates between the sites and on the variable τ value. The time dependence of the signal intensities can be calculated on the basis of the Bloch–McConnel equations modified for the transfer of magnetization by chemical exchange:[6,8,9]

$$\frac{d[M_{i(t)} - M_{i(\infty)}]}{dt} = R[M_{i(t)} - M_{i(\infty)}] \qquad (2)$$

where $M_{i(t)}$ is the z-magnetization of the ith site at time t, $M_{i(\infty)}$ is the equilibrium magnetization at the ith site and R is the so-called rate matrix. After diagonalization of R by means of $R = X\Lambda X^{-1}$, where X is the eigenvector matrix, X^{-1} is its inverse and Λ is the diagonal eigenvalue matrix, the final solution can be written as

$$M_{i(t)} = M_{i(\infty)} + \sum_{j=1}^{n} c_{ij} \exp(-\lambda_j t) \qquad (3)$$

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where

$$c_{ij} = X_{ij} \sum_{k=1}^{n} (X^{-1})_{jk}[M_{k(0)} - M_{k(\infty)}] \quad (4)$$

where λ_j are elements of Λ and $M_{i(0)}$ is the initial magnetization of the site i. Then a series of experiments with different τ values may give sufficient information to determine the relaxation rates and the exchange rates independently by a non-linear fitting procedure.

2D-EXSY is another emerging implementation of magnetization transfer between exchanging sites.[10–20] The method has been applied mainly in ^{1}H NMR spectroscopy for organic and biological molecules, but recently also inorganic chemistry problems have been investigated using ^{119}Sn NMR,[18] ^{195}Pt NMR,[12] ^{51}V NMR,[14] ^{9}Li NMR,[15] ^{77}Se NMR,[19a] ^{31}P NMR[19b] and ^{13}C and ^{205}Tl NMR.[20] The basic pulse sequence for 2D-EXSY is identical with that for NOESY.[21] During the mixing time (τ_m) the individually frequency-labelled z-magnetization components are in exchange with the different frequency components involved in the chemical processes providing kinetic information for the Fourier transformation in both dimensions. Therefore, the choice of suitable mixing time is very important.[6] It has been shown that in many cases all rate constants in the studied system can be determined with a certain accuracy from the intensity of both the cross and the diagonal peaks of a single 2D spectrum using the following equation:[13]

$$-R = \frac{1}{\tau_m} \ln A = \frac{1}{\tau_m} X(\ln D)X^{-1} \quad (5)$$

where A is a matrix whose elements contain the normalized peak intensities of a 2D experiment measured with a given mixing time (τ_m). The rate matrix (R) can be calculated directly from A, by the eigenvalue matrix procedure mentioned above.

When the exchange is fast enough to affect the lineshape, the desired kinetic information can be obtained by analysis of the exchange-broadened spectra.[22] In the intermediate region, when the number of peaks equals the number of species and the lineshapes are Lorentzian, the measured line widths for each of the signals can be written as

$$\Delta\nu_{1/2} = 1/(\pi T_2^{exp}) \quad (6)$$

where $\Delta\nu_{1/2}$ is the measured linewidth and $1/T_2^{exp}$ is a sum of contributions from the transverse relaxation time, the inhomogeneity of the magnetic field and the chemical exchange. The measured linewidths of the ith species exchanging with n other species, can be written as

$$\pi\Delta\nu_{1/2}(i) = \pi\Delta\nu^0_{1/2}(i) + \sum_{j=1}^{n} k_{i,j} \quad (7)$$

where $\Delta\nu^0_{1/2}(i)$ is the non-exchange linewidth for the ith species and k_{ij} is the pseudo-first-order rate constant for the chemical exchange process from the ith to the jth site. Introducing the microscopic reversibility ($k_{ij}p_i = k_{ji}p_j$), the rates can be calculated from the measured linewidths. However, when the number of exchanging sites is large and/or spin–spin coupling is present, it is preferable to use density matrix formalism[22] in the treatment of the lineshape data.

As a part of an ongoing study of the uranyl(VI)–fluoride system, it was the aim of this work to study the applicability of the methods mentioned above for the quantitative determination of the rate constants of ligand-exchange processes in uranyl(2+)–fluoride complexes in aqueous solution. The kinetic and mechanistic discussion of this chemical system will be presented in a forthcoming publication.

EXPERIMENTAL

A uranium(VI) perchlorate stock solution[23] prepared from $UO_2(NO_3)_2 \cdot H_2O$ (Merck) and an NaF stock solution (from recrystallized NaF) were used for preparing the investigated aqueous solutions. The ionic medium was kept constant with $NaClO_4$ so that $[ClO_4^-] = 1$ M.

^{19}F NMR spectra were recorded at 376.5 MHz on a Bruker AM400 spectrometer in the unlocked mode at 268 K. Samples under investigation were kept in PTFE inserts (HF reacts with glass) within the standard 5 mm sample tubes. The probe temperature was kept constant using a Bruker Eurotherm variable-temperature control unit and was measured with a calibrated Pt-100 resistance thermometer. NMR parameters were chosen in order to record quantitative spectra; typical values for routine spectra were: pulse width 8 μs (90° pulse width = 10.7 μs) and relaxation delay 2 s, spectral width 100 000 Hz (covered by 32 K data points). The spectra are referenced to the chemical shift (0 ppm) of a 0.01 M NaF solution in 1 M $NaClO_4$ (pH ≈ 12). Inversion-transfer spectra were measured for 22 delay values (τ) ranging from 0.0006 to 2.5 s. The selective inversion was achieved using a DANTE pulse train[24] which consisted of twelve 2 μs pin pulses with a 30 μs delay between the pulses. The relaxation delay was 3 s and the number of scans was 512 at each τ value.

2D-EXSY spectra were measured by using the standard NOESY pulse program. The data were collected in phase-sensitive mode (TPPI)[21] using a 3 s relaxation delay and a mixing time of 3 ms. The spectral window was 83 000 Hz; 256 experiments, each consisting of 128 scans, were collected in 2K data points. After the application of a shifted sine-bell apodization function in the f_1 and a Gaussian weighting function in the f_2 dimension, the Fourier transformation was performed in 2K × 2K points, which gave satisfactory resolution in both dimensions. Quantitative evaluation of the 2D-EXSY spectra was performed by means of the 2D WIN-NMR software[25] using volume integrals of the peaks.

RESULTS AND DISCUSSION

The linewidths of the different fluorine sites indicate that there is chemical exchange between the species. The exchange rate is faster for the higher complexes ($n = 4$, 5). At room temperature these signals are very broad and their shapes depend on the composition of the solution; they can coalesce for certain solution composi-

tions. On decreasing the total concentration of UO_2^{2+} and/or the temperature, the exchange rates turn from intermediate to slow on the ^{19}F NMR chemical shift time-scale, but remain fast enough on the T_1 time-scale, offering the possibility of using magnetization-transfer experiments as mentioned above.

The total concentrations of UO_2^{2+} and F^- and the pH of the solution for the different experiments were chosen using the equilibrium constants determined for the same ionic medium by Ahrland and Kullberg,[26] so that the resulting ^{19}F NMR spectrum consisted of three signals with approximately equal intensities, corresponding to UO_2F^+, UO_2F_2 and HF/F^- sites, respectively. A typical spectrum is shown in Fig. 1(a) for a solution containing 5 mM UO_2^{2+} and 10 mM total fluoride concentration at pH 1.7 and at $-5\,^{\circ}C$. The signals of UO_2F^+ (*ca* 30% of the total fluoride concentration), UO_2F_2 (*ca* 35%) and HF/F^- (32% for HF and 2% for F^-) appear at 161.09, 140.56 and -38.34 ppm, respectively, on the scale referenced to the chemical shift of the free F^- ligand (0 ppm). The half-widths of these signals, 98 Hz for UO_2F^+, 210 Hz for UO_2F_2 and 81 Hz for HF/F^-, indicate that the exchange between the species remains relatively fast even at $-5\,^{\circ}C$. Our preliminary investigations of the $HF–F^-$ system showed that there is fast exchange between HF and F^- on the chemical shift time-scale, and the line broadening of their coalesced signal is negligible compared with the broadening caused by the exchange with the uranyl fluoride complexes.

The large chemical shift differences between the three peaks in the spectrum [cf. Fig. 1(a)] provided an excellent possibility for the selective excitation of the different sites by DANTE pulse train in inversion-transfer experiments. Because of the fast chemical exchange and the fast relaxation rates, the only problem was to keep the duration of the 180° DANTE pulse as short as possible with sufficient selectivity. It was achieved by twelve 2 μs pulses using a 30 μs delay between them, which resulted in 2600 Hz (6.9 ppm) 'selectivity'. The excitation side bands were situated $\pm n \times 33\,000$ Hz (88 ppm) from the selected signal and thus had no effect on the other signals. Owing to the large chemical shift differences between the signals of the different complexes, this relatively low selectivity of the DANTE (at least compared with that usual in ^1H NMR) was satisfactory in the present case. This pulse train inverted the signals with an efficiency of 55–65%, depending on the chosen species. It was due not only to the imperfection of the DANTE, but also to the chemical exchange and relaxation in the course of the DANTE sequence. The initial magnetizations were treated as unknown parameters and refined simultaneously with the other unknowns in the least-squares procedures (see below). An example of the magnetization courses, after a selective inversion of the HF/F^- signal, is shown in Fig. 2.

The relaxation rates of individual species, with the exception of HF and F^-, could not be measured directly, so they were treated as unknown parameters in the fitting procedure of the inversion-transfer data to Eqn (3) (time dependence of the observed signal intensities). Since the importance of a complementary set of magnetization-transfer experiments has been emphasized for two-site exchange,[8] we carried out three series of experiments inverting all of the signals (i.e. one at the time). On the basis of our results we can demonstrate the necessity for the complementary experiments. The rate constants evaluated by separate analysis of each of the three individual experiments and also by simultaneous analysis of all of the experiments, are given in Table 1. As can be seen, the accuracy of the calculated exchange rates and relaxation rates increases dramatically in the cases of simultaneous analysis of several data sets. Comparison of the last two rows of the 1D part of Table 1 shows that treating the relaxation rate of HF as an adjustable parameter has no significant effect on the obtained values of the other parameters.

[A more exact value of relaxation rate of the HF/F^- signal ($1/T_1$) can be calculated from the following

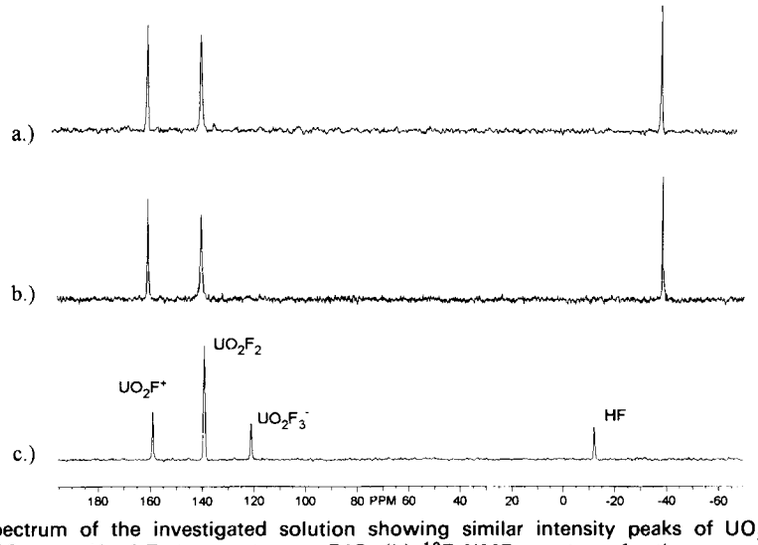


Figure 1. (a) ^{19}F NMR spectrum of the investigated solution showing similar intensity peaks of UO_2F^+, UO_2F_2 and HF/F^- sites. $[UO_2^{2+}]_{tot} = 5$ mM; $[F]_{tot} = 10$ mM; pH = 1.7; temperature = $-5\,^{\circ}C$. (b) ^{19}F NMR spectrum for the same solution obtained by computer simulation using the established kinetic parameters and a noise level similar to that in (a). (c) ^{19}F NMR spectrum of the investigated solution at pH = 3. Temperature = $-5\,^{\circ}C$.

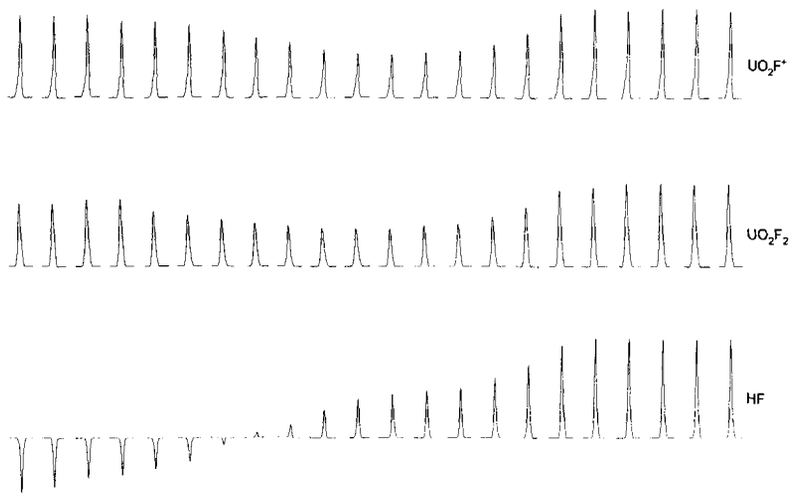


Figure 2. An example of magnetization time courses for UO_2F^+, UO_2F_2, and HF/F^- after a selective inversion of the HF/F^- signal, as a function of the interval τ between the end of the inversion pulse train and the observation pulse (horizontal and vertical units are arbitrary, and the same for the three courses).

relationship:

$$1/T_1 = p_{HF}/T_1^{HF} + p_{F^-}/T_1^{F^-} \quad (8)$$

where T_1^{HF} and $T_1^{F^-}$ are the individual relaxation times and p_{HF} and p_{F^-} are the relative populations of the HF and F^- signal, respectively. The values of T_1^{HF} and $T_1^{F^-}$ were determined, respectively, in a 0.1 M aqueous solution of NaF in 1 M $HClO_4$ and in 0.1 M solution of NaF in water, and are $T_1^{HF} = 0.60$ s and $T_1^{F^-} = 1.30$ s. The relative populations of HF and F^- at pH = 1.7 can be calculated from the equilibrium data:[26] $p_{HF} = 0.946$ and $p_{F^-} = 0.054$. From Eqn (8), we calculate $1/T_1 = 1.62\ s^{-1}$, not significantly different from the value of $1.67\ s^{-1}$ determined for HF alone.] The plot of peak integrals of the species against the variable delay (τ) in an experiment when the HF signal was inverted, and also the least-squares fitted curves, are shown in Fig. 3.

In order to compare the applicability of the one-dimensional inversion-transfer experiment with its two-dimensional implementation, we also measured a 2D-EXSY spectrum of the same solution for a quantitative evaluation (see Fig. 4). To the best of our knowledge, this is the first 2D-EXSY ^{19}F NMR spectrum to be published. A mixing time of 3 ms, estimated from the results of the inversion-transfer experiments detailed above, was enough to produce well defined cross peaks between all of the sites, reflecting the chemical exchange processes between the different species. (Repetition of

Table 1. Comparison of the fluoride exchange rate constants and ^{19}F NMR relaxation rates for the different fluoro species, as calculated from the inversion-transfer and 2D-EXSY experiments ($[UO_2^{2+}]_{tot} = 5$ mM, $[F^-]_{tot} = 10$ mM, pH = 1.7, temperature = −5 °C), with one standard deviation given in parentheses (except for the 2D experiment)

Experiment	$k(UO_2F_2, UO_2F^+)$ (s^{-1})	$k(HF, UO_2F^+)$ (s^{-1})	$k(HF, UO_2F_2)$ (s^{-1})	$1/T_1(UO_2F^+)$ (s^{-1})	$1/T_1(UO_2F_2)$ (s^{-1})	$1/T_1(HF)$ (s^{-1})
I(*HF*)[a]	365 (266)	25 (39)	158 (41)	11 (12)	10 (11)	1.67[f]
II(*UO_2F^+*)[a]	234 (39)	14 (27)	178 (71)	29 (5)	2 (5)	1.67
III(*UO_2F_2*)[a]	243 (24)	46 (65)	153 (16)	26 (1)	0[e]	1.67
I + II[b]	213 (18)	42 (8)	137 (11)	19 (5)	6 (4)	1.67
I + II + III[c]	**226 (11)**	**35 (5)**	**148 (7)**	**21 (3)**	**4 (3)**	**1.67**
I + II + III[d]	227 (11)	35 (6)	148 (7)	21 (3)	3 (4)	2 (2)
2D-EXSY[g]	238 (±26)	40 (±7)	155 (±19)	—	—	—

[a] Analysis of only one inversion-transfer experiment of the three experiments in the complementary set (the inverted species are given in italics).
[b] Simultaneous analysis of two inversion-transfer experiments in the complementary set.
[c] Simultaneous analysis of all of the inversion-transfer experiments in the complementary set. These values were used during the calculations for the exchange rates between $UO_2F_3^-$ and the other sites (see text).
[d] Simultaneous analysis of all of the inversion-transfer experiments treating the relaxation rate ($1/T_1$) of HF as an unknown parameter.
[e] This value was fixed at zero in the course of analysis, otherwise a negative value was obtained.
[f] The $1/T_1$ of HF was determined in an independent experiment.
[g] Numbers in parentheses are the estimated maximum errors from the integration procedure (see text).

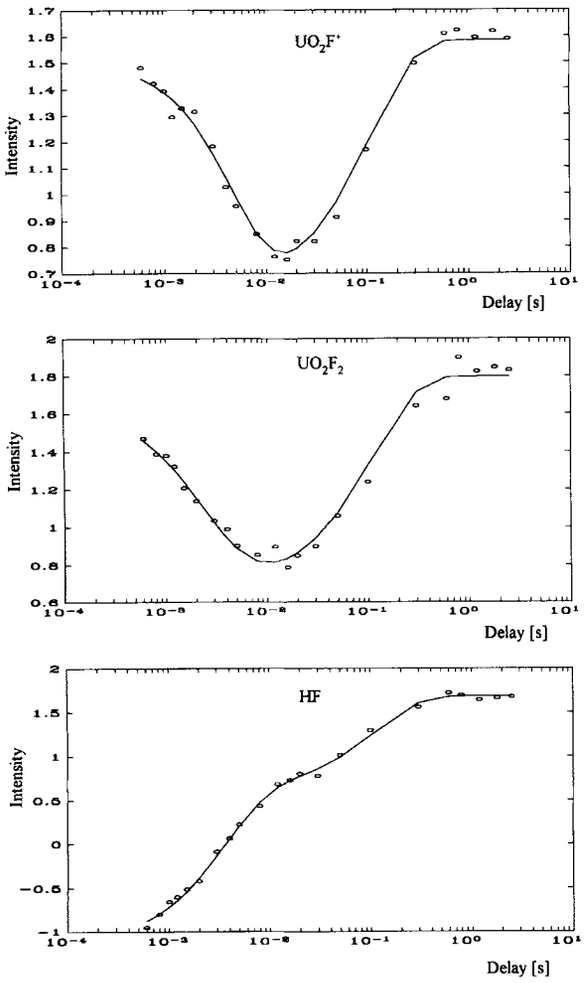


Figure 3. Plots of peak intensity (arbitrary units) for UO_2F^+, UO_2F_2 and HF/F^- against variable delay τ, after selective inversion of the HF/F^- signal (cf. Fig. 2). The solid lines are generated by a simultaneous analysis of all the inversion-transfer experiments detailed in the text.

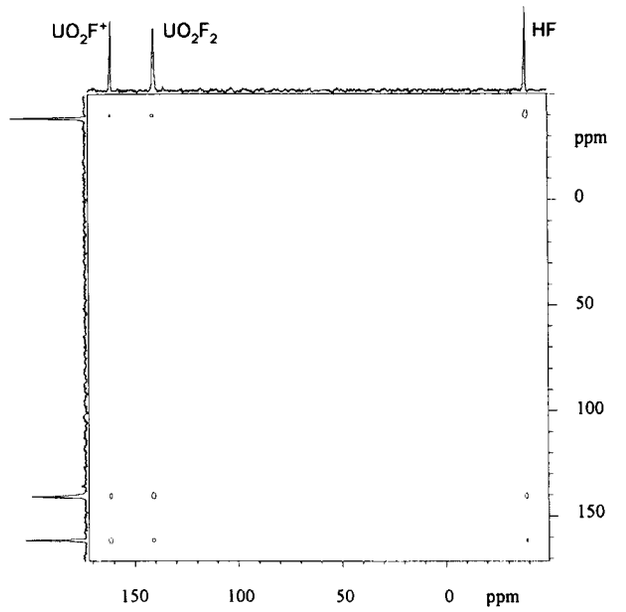
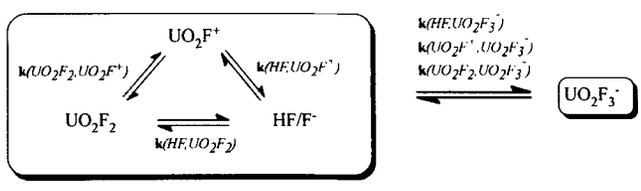


Figure 4. 2D-EXSY ^{19}F NMR spectrum of the investigated solution. Temperature = −5 °C; τ_m = 3 ms; 256 incremented experiments, each consisting of 128 scans and collected in 2K data points; relaxation delay = 3 s. Fourier transformation was performed in 2K × 2K data points. This spectrum, in connection with the zero-mixing-time experiment, was used for the determination of the rate matrix.

the experiment with a mixing time of 10 ms resulted in a less useful spectrum from the quantitative point of view, since τ_m was too long compared with the fast chemical exchange processes. The intensities of the cross and diagonal peaks became comparable, losing their information on the exchange rates.) The normalization of the intensity matrix was achieved by using the diagonal peaks of an additional experiment with $\tau_m = 0$. In the course of the quantitative evaluation of these experiments, we used volume integrals of the three-dimensional peaks. Repeating the integration procedure many times we were able to reproduce the integral values within approximately $\pm 10\%$, which constituted the main source of error in these experiments. Introduction of the extreme values from the integration procedure into the intensity matrix allowed us to estimate the largest possible error in the elements of the rate matrix, 10–20% (see Table 1).

The calculated rate constants are in very good agreement, within the experimental error, with those obtained from the inversion-transfer experiments. However, the uncertainty of the rate constants is relatively high, at least compared with the absolute values of the relaxation rates, so the latter could not be determined from the diagonal peaks of the rate matrix (see Table 1).

Finally, we tried to compare the rate constants calculated from the 1D and 2D magnetization-transfer experiments with those which could be calculated from the linewidth of the signals. However, considering the investigated system as a three-site exchange, we encountered some difficulties. For example, using the measured linewidths in the three-site exchange variant of Eqn (7), we obtained negative rates for one of the exchange processes. If we introduced the rate constants established from previous experiments into the same set of three linear equations, large differences were found between the measured and the calculated linewidths, especially in the case of UO_2F_2. The conflict of the parameters could be resolved assuming the presence of a fourth, 'hidden' exchange partner (see Scheme 1). Calculations on the basis of the equilibrium data[26] showed the existence of the third complex, $UO_2F_3^-$, in a concentration



Scheme 1. Exchange processes for the investigated system. The exchange rates for $UO_2F_3^-$, as a 'hidden' exchange partner, were calculated by using the linewidths of UO_2F_2, UO_2F^+, and HF/F^- and rate constants obtained by the magnetization transfer experiments (see details in the text).

lower than 2.5% of the total fluoride at the applied pH. It can be proved that the effect caused by an exchange partner in the magnetization-transfer experiments is negligible, if it is present in a very low concentration and if its relaxation rate is not very large compared with that of the other sites. In the light of these facts, Eqn (7) can be written for a four-site exchange system as follows:

$$\pi\Delta\nu_{1/2(HF)} = k(HF, UO_2F^+) + k(HF, UO_2F_2) + k(HF, UO_2F_3^-) \quad (9)$$

$$\pi\Delta\nu_{1/2\,(UO_2F^+)} = k(UO_2F^+, HF) + k(UO_2F^+, UO_2F_2) + k(UO_2F^+, UO_2F_3^-) \quad (10)$$

$$\pi\Delta\nu_{1/2\,(UO_2F2)} = k(UO_2F_2, HF) + k(UO_2F_2, UO_2F^+) + k(UO_2F_2, UO_2F_3^-) \quad (11)$$

$$\pi\Delta\nu_{1/2(UO_2F_3^-)} = k(UO_2F_3^-, HF) + k(UO_2F_3^-, UO_2F^+) + k(UO_2F_3^-, UO_2F_2) \quad (12)$$

Introducing the microscopic reversibility [for example, $p_{UO_2F}{\cdot}k(UO_2F^+, UO_2F_2) = p_{UO_2F_2}k(UO_2F_2, UO_2F^+)$, where p_{HF}, $p_{UO_2F^+}$, $p_{UO_2F_2}$ and $p_{UO_2F_3^-}$ are known], and using the measured linewidths for HF, UO_2F^+ and UO_2F_2, and also the rate constants obtained the magnetization-transfer experiments, the number of unknown parameters could be reduced to four. These are the exchange rates between $UO_2F_3^-$ and the other sites (cf. Scheme 1), and the linewidth of the $UO_2F_3^-$ signal. The calculated values (using the bold-type rate constants in Table 1) are $k(HF, UO_2F_3^-) = 64\ s^{-1}$, $k(UO_2F^+, UO_2F_3^-) = 52\ s^{-1}$, $k(UO_2F_2, UO_2F_3^-) = 339\ s^{-1}$ and $\Delta\nu_{1/2(UO_2F_3^-)} = 1026$ Hz. The invisibility of this broad signal at *ca* 122 ppm[3] was demonstrated by a model spectrum which was simulated using the established parameters, at a similar signal-to-noise ratio [Fig. 1(b)]. However, when the pH of the investigated sample was increased to *ca* 3, the signal of this hidden partner became observable in the spectrum, in agreement with the equilibrium constants [see Fig. 1(c)].

CONCLUSION

Exchange phenomena can be studied on both T_1 and T_2 NMR time-scales. Owing to the different effects caused on each of the scales, different chemical information can be obtained. It seems worthwhile to investigate the dynamics of an exchanging system on both time-scales, especially if presence of an invisible exchange partner can be expected. The exchange processes which take place on the time-scale of magnetization-transfer experiments can be investigated with 1D inversion-transfer method, in addition to 2D exchange spectroscopy. We have found that the agreement between the results obtained using the two techniques is remarkably good (cf. Table 1, bold-type row for 1D). The accuracies of the rate constants obtained from the two types of data are comparable, assuming that the maximum error estimated for the 2D results corresponds to about two standard deviations obtained for the 1D results (cf. Table 1). In the present case, where the T_1 relaxation rates are small compared with the exchange rate constants, the former could not be determined from the 2D-EXSY data, but could be obtained from the 1D experiments. This is probably due to the different algorithm used for the evaluation of the data [cf. Eqns (2)–(4) and (5)]. In order to achieve good accuracy in the inversion-transfer method, it is desirable to perform complementary experiments, inverting the NMR signals of all of the present exchanging sites. This is certainly a drawback, especially in systems containing a large number of exchanging sites. This method is less sensitive to the errors in integration (within reasonable limits), owing to the fitting procedure.

In the course of the quantitative evaluation of a 2D-EXSY experiment, although the errors could arise from several sources discussed in detail in the literature,[12] we found that precise integration of both the diagonal and the cross peaks obtained for a single mixing time has fundamental importance and the uncertainty in the integrals constitutes the main source of error in the calculated rate constants. In 2D experiments for nuclei with large chemical shift ranges the digital resolution is often a matter of compromise, since the desired large number of experimental points is in conflict with the limited computer disk space and the experiment time. When the digital resolution is satisfactory, the accuracy of the integration can be improved by using more sophisticated NMR processing software and calculating volume integrals. Another difficulty for 2D-EXSY experiments is the choice of the optimum mixing time, which implies an *a priori* knowledge of the exchange rates in the investigated system. In the present case the inversion-transfer experiments provided kinetic data which allowed an estimation of a suitable mixing time. (It should also be noted that a single 2D EXSY spectrum contains sufficient information only on the exchange rates that have approximately the same order of magnitude as the inverse of the applied mixing time. This means that if in the same chemical system much slower or much faster exchange reactions take place, they have to be studied in separate experiments with different τ_m values.) The accuracy of the rate constants obtained from the 2D-EXSY is comparable to those from the experiments, but the time efficiency of the 2D-method increases with increasing inversion-transfer number of exchanging sites. In the present case, the (1D and 2D) magnetization-transfer experiments, which require the chemical system to be in slow exchange regime on the chemical shift time-scale, cannot replace the lineshape analysis for the determination of the activation parameters, since at higher temperatures the NMR peaks overlap and coalesce. An additional limitation of the 1D technique, as applied in this work, is the DANTE excitation: since the exchange processes are relatively fast compared with the DANTE pulse

train and therefore even at $-5\,^{\circ}C$ significant exchange occurs during the pulse preparation, the 1D magnetization-transfer technique with DANTE soft pulses cannot be extended to much higher temperature.

In a case with several exchanging sites, the classical lineshape analysis is hardly feasible if only one solution composition is studied, because the spectra cannot be uniquely fitted to four or more independent rate constants. Still, a series of solutions with varying composition can easily be investigated using a relatively short experimental time. Consequently, this will be the method of choice for the continued study of the dynamics in the uranyl(VI)–fluoride system, and the magnetization-transfer methods will only be used in special cases as a source of complementary information.

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