Electronic Spectra and Magnetic Circular Dichroism of the Uranyl Ion. Part II.[1] The Effect of Reduced Symmetry on the Spectra

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We have examined the absorption and m.c.d. spectra of the dinitrate, trinitrate, and tetranitrate complexes of the uranyl ion and have interpreted the results in terms of an axial symmetry perturbation on the $D_{\infty h}$ states characterised in Part I. It is found that this gives a consistent account of the m.c.d. spectra at liquid-helium temperatures. We have also investigated the striking changes in structure observed in the absorption spectrum of the dinitrate complex in various solvents and have obtained quantitative estimates of reduction in symmetry from changes in the excited state moment.

IN Part I [1] we discussed the absorption and m.c.d. spectra of $(NBu_4)UO_2(NO_3)_3$ as a solution in poly(methyl methacrylate) at liquid-helium temperature. This uranyl compound has bands in the region 20 000—35 000 cm^{-1} due to the $UO_2(NO_3)_3^-$ ion, and exhibits a very highly structured spectrum. The spectra were analysed by considering the uranyl ion as a linear $D_{\infty h}$ ion perturbed by the lower symmetry imposed by the equatorial ligands. This approach accounted well for the absorption and m.c.d. spectra. Summarising our assignments, we divide the spectrum into two main regions.

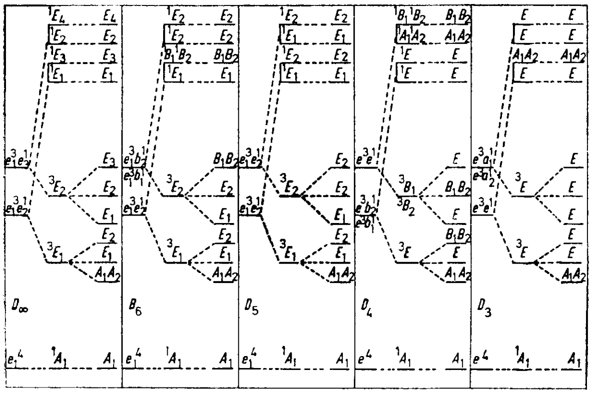

FIGURE 1 Changes in the orbital and state designations resulting from reduction of symmetry in the UO_2^{2+} ion

(i) 20 000—28 000 cm^{-1} ($\varepsilon_{max.}$ ca. 50).—This region we assigned as being due to transitions from the totally symmetric ground state to electronic levels arising from two triplet states $^3E_{1g}$, $^3E_{2g}$ (from $f \longrightarrow f$ type transitions). These are close in energy, and therefore interact strongly through spin–orbit coupling. We were able to fit the spectrum accurately with an energy parameter for the separation of the two triplet states of 3800 cm^{-1}, and a spin–orbit constant of 1700 cm^{-1}.

(ii) 28 000—35 000 cm^{-1} ($\varepsilon_{max.}$ ca. 500). This region we assigned as due to transitions to levels arising from an odd-parity triplet state (from an $f \longrightarrow d$ type excitation).

In this paper we use these assignments as a basis for the spectra of a number of uranyl compounds, and we present data on molecules of this type having a variety of symmetries. The spectra are of samples at liquid-helium temperature and in solution at room temperature, and we have interpreted these spectra in terms of a linear UO_2^{2+} ion which is perturbed by the symmetry of the axial ligands.

Figure 1 shows the energy-level scheme suggested in Part I for the energy region under consideration. Also Figure 1 displays the changes of orbitals and states as a function of symmetry for the D_n groups. For convenience all transitions in the text are referred to the $D_{\infty h}$ designation, unless otherwise stated.

EXPERIMENTAL

Although maximum information would be obtained from a study of single crystals containing the uranyl ion we have been unable to grow large uniaxial samples. We have therefore examined the compounds where possible in polymer matrices at *ca.* 10 K. These have the advantage of showing no birefringence effects due to imperfect alignment of crystalline strain. The disadvantage is that multiple site effects broaden the lines even at low temperature and we do not see the very large number of lines observed by Dieke and Duncan.[2] However, the main electronic features are well displayed in this host lattice and we concentrate on these rather than the site- and phonon-induced sidebands.

The samples were mounted in the bore of a superconducting magnet, and the m.c.d. spectra recorded on a c.d. spectrometer originally built at the National Physical Laboratory and modified in these laboratories. The electronic absorption spectra were recorded on a Cary 14

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[1] Part I, P. Brint and A. J. McCaffery, *Mol. Phys.*, 1973, **25**, 311.

[2] G. H. Dieke and A. B. F. Duncan, 'Spectroscopic Properties of Uranium Compounds,' McGraw-Hill, New York, 1949.

spectrometer, and also on the modified N.P.L. equipment in absorption mode.

The solution spectra were recorded by use of the same equipment, with a room-temperature insert fitted to the magnet. The solution chemistry of the uranyl ion is extensive and complex. Where relevant this is discussed in the text and a comprehensive review of uranyl ion chemistry is contained in the article by Comyns.[3]

$UO_2(NO_3)_2,2H_2O$ was commercial and $(Et_4N)_2UO_2(NO_3)_4$ was prepared by Dieke and Duncan's method.[2]

DISCUSSION

In this work we have data relevant to two different aspects of the chemistry and spectroscopy of the uranyl ion and we discuss these in turn. First there is the problem of the shifting and splitting of $D_{\infty h}$ states as we change the equatorial co-ordination (and consequent symmetry). In relation to this we have absorption and m.c.d. results on a number of complexes in plastic matrices at low temperatures. The second problem is the marked change in the spectra of the nitrate complex with solvent and the results discussed are of uranyl nitrate in a number of different solvents.

Low-temperature Spectra.—The structure of crystalline uranyl nitrate hexahydrate consists of a linear (or nearly so) uranyl ion co-ordinated to two bidentate nitrate oxygens and to two water oxygens[4] *trans* to one another. The same structure is found for the dihydrate.[5] A feature of this structure is the very small O–N–O nitrate chelate angle of 49° in this eight-co-ordinate system. Conductivity measurements[6] suggest that this structure persists when the nitrate is dissolved in organic solvents and indeed it is known that the important process of dissolution of the uranyl ion in organic solvents requires the presence of small amounts of water.[2] We can assume therefore that the species in solution in non-co-ordinating or weakly co-ordinating solvents probably consists of this same diaquo-complex or, alternatively, is a solvated species in which solvent molecules are bonded in place of the water ligands. The symmetry of these two possibilities is the same, D_{2h} or D_2.

The spectrum of the dinitrate species in poly(methyl methacrylate) at 10 K is shown in Figures 2 and 3. Much structure is observed at low temperature though this is not as detailed as were the spectra of the trinitrate[1] and we attribute this to the lower symmetry of the complex. Transitions to the approximately degenerate $A_1A_2(^3E_1)$ levels are not separated but appear as one band at *ca.* 20 747 cm^{-1}. That there are two transitions under this broad origin can be demonstrated since we find that vibrational progressions in the

$$A_1(^1A_{1g}) \longrightarrow \underset{\sim 20\,747}{A_1A_2} \quad \underset{21\,575}{A_1 + 1\nu_1}, \; \underset{21\,739}{A_2 + 1\nu_2} \quad \underset{22\,287}{A_1 + 2\nu_1}, \; \underset{22\,442}{A_2 + 2\nu_4}$$

SCHEME 1

symmetric stretch built on these two are not coincident in energy (Scheme 1). Since the bands are not well resolved beyond $\nu = 2$, the progressions cannot be traced to as high a vibrational quantum number as was possible in the trinitrate spectrum.[1] However, we have analysed the spectral data and we are able to pick out, with the

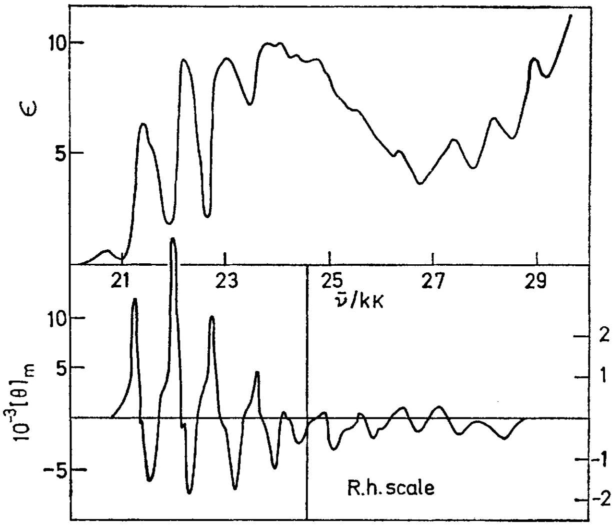

FIGURE 2 Absorption and m.c.d. spectra of the low-energy region ($^3E_{1g}$, $^3E_{2g}$) of $UO_2(NO_3)_2,2H_2O$ in poly(methyl methacrylate) at 10 K. $[\theta]_m$ is in units of deg. dl dm^{-1} gauss^{-1} mol^{-1} with phase conversions as for natural optical activity; ε is the molar extinction coefficient in l mol^{-1} cm^{-1}

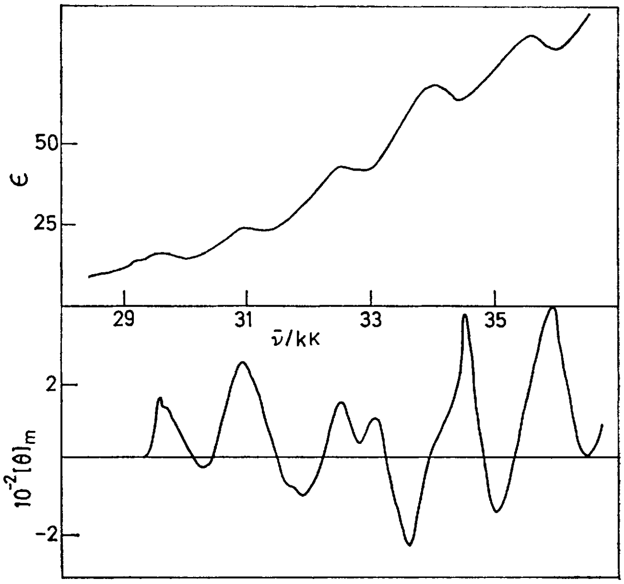

FIGURE 3 Absorption and m.c.d. spectra of the high-energy region ($^3E_{1u}$) of $UO_2[NO_3]_2,2H_2O$ in poly(methyl methacrylate) at 10 K. Units as in Figure 2

aid of the m.c.d. spectrum, the origins of six electronic transitions. The high-energy region also shows a structured absorption and m.c.d. spectrum similar to that observed in the trinitrate. It is poorly resolved by comparison with the trinitrate but the similarity of

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[3] A. E. Comyns, *Chem. Rev.*, 1960, **60**, 115.

[4] D. Hall, A. D. Rae, and T. N. Waters, *Acta Cryst.*, 1965, **19**, 389.

[5] N. K. Dalley, M. H. Mueller, and S. H. Simonsen, *Inorg. Chem.*, 1971, **10**, 323.

[6] W. E. Keder, J. L. Ryan, and A. S. Wilson, *J. Inorg. Nuclear Chem.*, 1961, **20**, 106.

band shape and position led us to conclude that it is due to the same type of transition as in the trinitrate.

Some indication of the effective symmetry of the dinitrate species is obtained from the m.c.d. spectra. It is fairly clear on inspection that the m.c.d. of the dinitrate is not very different from that of the trinitrate given in ref. 1. Some bands and shoulders have increased somewhat in intensity leading to a general decrease in sharpness of the spectrum but the salient features of the $A_1(^1A_{1g}) \longrightarrow E_1(^3E_1)$ Faraday A term can still be discerned. This suggests that the low-symmetry equatorial perturbation is small, *i.e.*, somewhat less than the bandwidth of the A term of 300—400 cm^{-1}. The effective overall symmetry of this species is high enough that the angular momentum of the $E_1(^3E_1)$ state is not destroyed and is probably that of the co-ordination sphere, namely D_6. However this applies only for our particular criterion, though agreeing with i.r. analyses,[7] and the ' effective ' symmetry of the complex will in general be a function of the physical technique employed in its study. The increase in line-widths and general broadening compared with the trinitrate spectra indicate an increase in the number of totally symmetric modes in the complex, resulting from the reduction of degenerate modes. Each of these may form a progression built upon real or false origins. The m.c.d. and absorption spectra indicate some small reduction in symmetry compared with the trinitrate without giving precise data on the exact symmetry.

The trinitrate was dealt with in Part I and provides the theoretical basis for this present work. Some new light is thrown on this ion by our present work particularly on the transition assigned as $A_1(^1A_{1g}) \longrightarrow A_2(^3E_1)$. In Part I we suggested the progression listed as built on this electronic origin could alternatively be interpreted as due to a progression involving an active O–U–O *bend* vibration built up on the $A_1(^1A_{1g}) \longrightarrow E_1(^3E_1)$ origin. The former of these arguments now seems the more reasonable in the light of present work since we resolve progressions built on both A_1 and A_2 origins in the dinitrate spectrum. This is an important point since it now appears that the general loss of structure in uranyl complexes, which is characteristic of reduction in symmetry of the complex and is paralleled by a loss of angular momentum in the excited states, is due to an increase in the number of vibronic progressions rather than an increase in the activity of the bend vibration.

The spectra of the tetranitrate $(Et_4N)_2UO_2(NO_3)_4$ are shown in Figure 4 and exhibit less structure than those of the di- and tri-nitrates. We assume this compound to have D_{4h} symmetry since its solution absorption spectrum is identical to that of $(NH_4)_2UO_2Cl_4$ [8] which is known to have D_{4h} symmetry in the solid state. However this requires a ten-co-ordinate structure in the case of the tetranitrate or else some reduction in symmetry. The main transition $A_1(^1A_{1g}) \longrightarrow E_1(^3E_1)$ shows a well developed A-term progression with $A/D = 0{\cdot}4\beta$.

Other low-temperature spectra were run on $UO_2(ac)_2$ [(ac) = acetate^{2-}] and $UO_2F_5{}^{3-}$ but in neither of these were reliable data obtained owing to broadness in the former case and lack of solubility in the second. Both, however, showed the high-energy structure in their spectra first seen in the trinitrate indicating that these are genuine uranyl spectra and not to be associated solely with the nitrate ions.

Solution Spectra.—Previous workers [9] have noticed that the absorption spectrum of uranyl dinitrate is very sensitive to the nature of the solvent. The spectrum passes from a weak, unstructured band system in methanol to the intensified and sharp spectrum observed in nitromethane or in acetonitrile. In addition there is the remarkable intensification and loss of structure found in the pyridine spectrum (see Figures 5—8). Broadening of structure in this manner might reasonably be associated with reduction of symmetry of the molecule since this would increase the number of symmetric vibrational modes and also increase the density of background states above the lowest band origin. To test this we have measured the m.c.d. of uranyl dinitrate in a variety of solvents since any reduction in the overall symmetry should be observed in reduced excited state angular momentum and smaller A/D values. The spectra (Figures 5—8) represent a wider range of solvents the results of which are shown in the Table. In several cases the D values were obtained by curve-fitting and thus the accuracy is reduced.

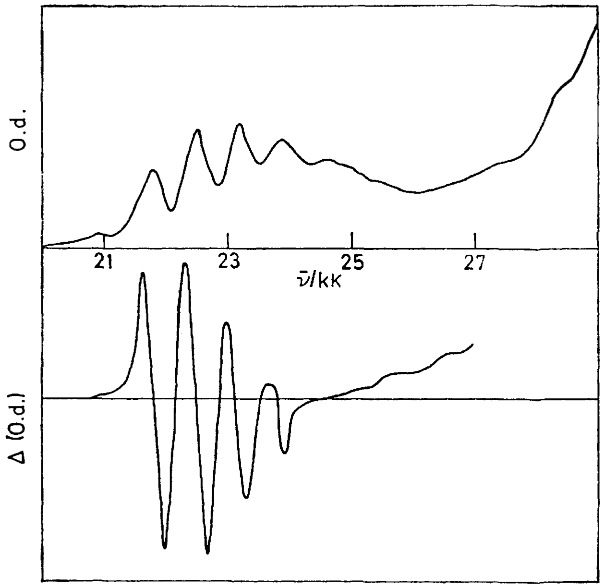

FIGURE 4 Absorption and m.c.d. spectra of $(Et_4N)_2UO_2(NO_3)_4$ in poly(methyl methacrylate) at 10 K. Arbitrary units

From the Table and the spectra we discern a distinct reduction in the excited-state angular momentum as we pass from aprotic to protic solvents. This corresponds to the loss in the structure of the absorption

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[7] S. P. McGlynn, J. K. Smith, and W. C. Neely, *J. Chem. Phys.*, 1961, **35**, 105.

[8] P. Brint and A. J. McCaffery, unpublished observations.

[9] E. Rabinowitch and R. L. Belford, ' Spectroscopy and Photochemistry of Uranyl Compounds,' Pergamon, Oxford, 1964.

spectra particularly in the 'magnetic' series of bands $A_1 \longrightarrow E_1^a(^3E_1)$.[1] Thus the poly(methyl methacrylate), nitromethane, and acetonitrile spectra have high A/D values (0·55—0·62) and well developed structure represented by the poly(methyl methacrylate) spectrum

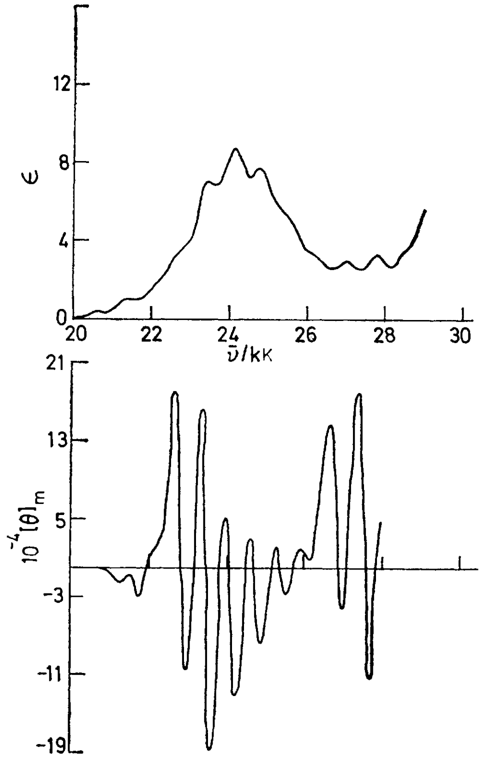

Figure 5 Absorption and m.c.d. spectra of $UO_2(NO_3)_2,2H_2O$ in acetone at 290 K. Units as in Figure 2

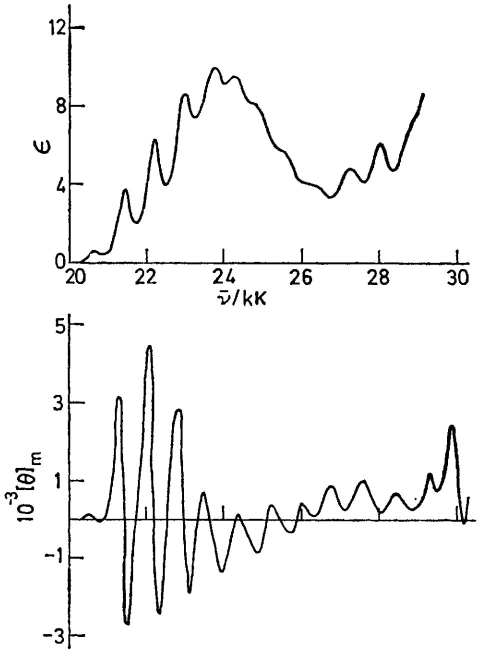

Figure 6 Absorption and m.c.d. spectra of $UO_2(NO_3)_2,2H_2O$ in water at 290 K. Units as in Figure 2

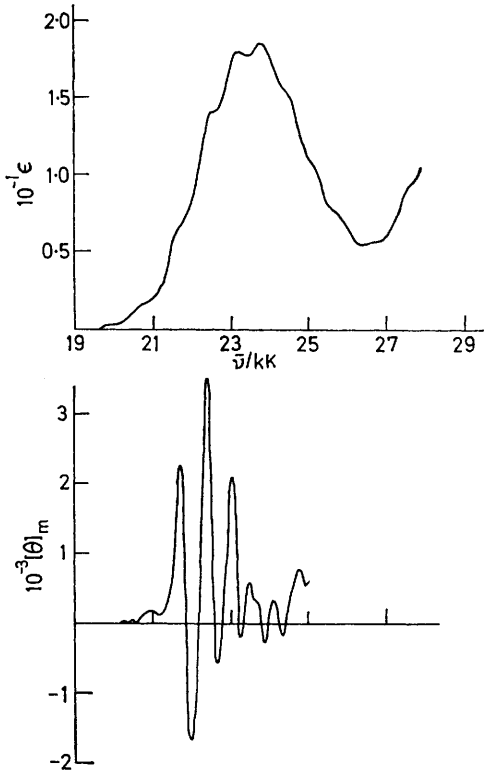

Figure 7 Absorption and m.c.d. spectra of $UO_2(NO_3)_2,2H_2O$ in methanol at 290 K. Units as in Figure 2

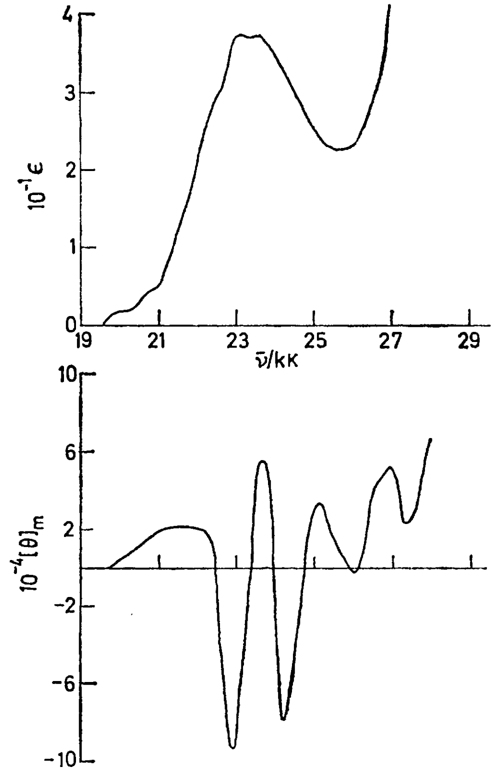

Figure 8 Absorption and m.c.d. spectra of $UO_2(NO_3)_2,2H_2O$ in pyridine at 290 K. Units as in Figure 2

(Figure 2). This is in accord with the deduction from the dinitrate spectra in poly(methyl methacrylate) earlier that this represents the eight-co-ordinate species in organic solvents with two nitrate and two water ligands. The effective symmetry is quite high though not as high as in the trinitrate[1] which has $A/D = 0{\cdot}90$ for the ' magnetic ' series and whose spectrum can be attained by the addition of excess of nitrate ion to the dinitrate species in solution.[9] Further reduction in symmetry ($A/D = 0{\cdot}42$) and loss in structure is found in acetone (Figure 5). Here presumably symmetry reduction arises by replacement of some of the ligands by acetone and broadening occurs through the increase in number of slightly different species. The trend continues with the water and methanol spectra (Figures 6 and 7). The ' magnetic ' series structure becomes much less pronounced and the A/D values drop markedly, particularly in methanol solution. Although the m.c.d. is still sharp even in the latter spectrum, its magnitude has dropped and the absorption intensity is beginning to rise. Here presumably unsymmetric co-ordination of solvent molecules begins to mix in parity-allowed excited states. Finally the pyridine solution spectrum (Figure 8) indicates almost complete loss of symmetry and structure. This presumably results from a number of co-ordinated pyridine molecules in equatorial positions. Note that throughout these spectral changes the band positions shift by relatively small amounts, the absorption peak staying mainly around 23 000—24 000 cm^{-1}. This clearly justifies the original assumption of a strong axial ligand field perturbed by a much weaker equatorial co-ordination which affects the ' spread ' of the components of the two triplets and is manifest in the structure of the bands. It is clear though that a study of the m.c.d. in conjunction with the absorption spectrum may lead to valuable information concerning equatorial co-ordination and that these sharp spectra could be used as a probe into the fine details of bonding problems.

A/D Values for the ' magnetic ' series bands [$A_1 \longrightarrow E_1^{a}(^3E_{1g})$] for uranyl nitrate $UO_2(NO_3)_2,2H_2O$ *

Solvent	T/K	A/D [a]
Poly(methyl methacrylate)	10	0·62
Nitromethane	290	0·60
Acetonitrile	290	0·55
Acetone	290	0·42
Water	290	0·29
Ethanol	290	0·18
Methanol	290	0·09
Dimethylformamide	290	0·05

[a] Obtained from moments analysis.

* For $(Et_4N)_2UO_2(NO_3)_4$ in poly(methyl methacrylate) at 10 K, A/D = *ca.* 0·4.

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