SOLID STATE PHOTOCHEMISTRY OF URANYL FORMATE MONOHYDRATE

B. CLAUDEL, M. FEVE, J. P. PUAUX and H. SAUTEREAU

Laboratoire de Cinétique et Génie Chimiques, 404 INSA, 20 avenue A. Einstein, F. 69621 Villeurbanne (France)

Summary

The solid state photodecomposition of $UO_2(HCOO)_2 \cdot H_2O$ has been investigated at 298 K with monochromatic irradiation at 366 nm. An original set-up has been built in order to monitor continuously the intensities of absorbed light and of fluorescence. It is shown that the first electronically excited state is responsible both for photoluminescence and for photodecomposition. The intermediary species uranium(V) and $HCOO^{\cdot}$ have been detected. Quantum yield measurements allow identification of U^V as a primary product, the final product U^{IV} being formed in a later stage. A dark reaction yielding U^{IV} from U^V is observed. Finally, a mechanism is proposed in order to interpret the experimental findings.

Introduction

The solid state photochemistry of inorganic compounds is still largely in its infancy [1]. However, it is a field which raises a growing interest, especially owing to its applicability to non-conventional photography [2]. Uranyl salts photochemistry appears to be especially attractive because on the one hand the photochemistry of uranyl ions in solution has been extensively investigated [1, 3 - 5] and on the other hand the fluorescence of these compounds [6] allows additional information on the kinetics and mechanisms of these reactions to be obtained. To the best of our knowledge the only compounds of uranyl known to be light sensitive in the solid state are formates: $NaUO_2(HCOO)_3 \cdot H_2O$ [7], $(NH_4)_2UO_2(HCOO)_4$ [8] and $UO_2(HCOO)_2 \cdot H_2O$. It is noteworthy that within this family of formates anhydrous $UO_2(HCOO)_2$ [9] and $UO_2(OH)(HCOO) \cdot H_2O$ [10] have been recognized as non-photosensitive, so that a thorough investigation of their structural and electronic properties could give a clue to their sensitivity (or absence of sensitivity) to light.

Earlier research in this laboratory has allowed us to determine the crystal lattice [11] and structure [12] of $UO_2(HCOO)_2 \cdot H_2O$, to identify the

gaseous products of photolysis as CO_2 and H_2O [13, 14], and to provide evidence for the intermediate formation of uranium(V) [15], uranium(IV) being the ultimate photoreduction stage of U^{VI} [16]. The purpose of the present paper is to elucidate the mechanism of this passage from U^{VI} to U^{IV} through U^{V}.

Experimental

Starting material

Uranyl formate monohydrate is prepared according to the method already described [17]. In order to eliminate the effect of grain size on the quantum yield measurements [18] and to ensure the best possible reproducibility, we used exclusively solid grains, the diameters of which were between 125 and 160 μm. When this salt is kept under vacuum in the dark it remains unaltered for weeks.

Quantum yield determination

The precision of quantum yield determinations poses particular problems in solid state photodecompositions; on the one hand the number of einsteins absorbed is not often accurately known and on the other hand photoproducts are generally more absorbing than the initial solid and this decreases the quantum yield. For these reasons we designed the set-up sketched in Fig. 1.
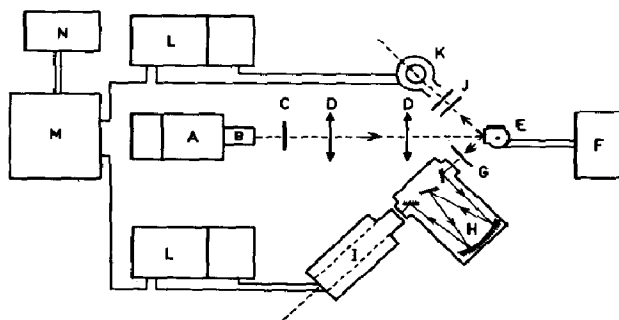

Fig. 1. Experimental set-up: A, Bausch and Lomb monochromator; B, condenser; C, filter MTO H 397a; D, D', condensing lenses; E, cell C; F, temperature regulator; G, filter Kodak W2B; H, monochromator Huet M25; I, photomultiplier XP 1002; J, filters Kodak No. 96 and MTO H 325a; K, photomultiplier IP 28; L, L', high voltage source and photometer; M, recorder; N, integrator.

This arrangement (i) ensures good reproducibility by always irradiating the same amount of powder evenly distributed on the same area, (ii) allows the continuous monitoring of surface reflectivity, and hence the determination of the number of einsteins effectively absorbed, and (iii) allows the continuous measurement of fluorescence intensity linked to the extent of photoreduction. The radiation source consists of a Bausch and Lomb monochromator fitted with either a mercury or a xenon lamp [19]. The solid sample is con-
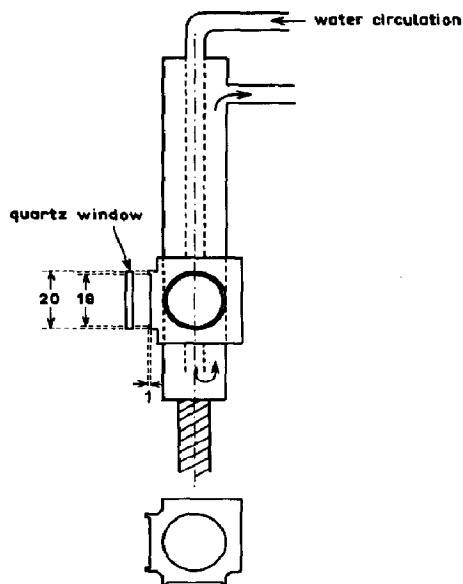
Fig. 2. Cell C.

tained in one of the cavities of cell C (Fig. 2) (exposed area S = 2.54 cm^2) and is held with a quartz plate. The other cavity contains MgO, which is used as a reference material for the reflectivity measurement. A right-angle rotation of cell C allows the exposure of either cavity to the incident light. Water circulation inside the cell maintains the sample temperature at a fixed value.

Fluorescence spectra and their evolution in time are obtained with the analyzing device already described, the spectral response of which has been determined with the help of an iodine lamp calibrated by the Laboratoire National d'Essais. A photomultiplier IP 28 equipped with the appropriate filters monitors variations in reflectivity.

Potassium ferrioxalate actinometry [20, 21] is used in order to determine the incident intensity. The solution is contained in a quartz cell, the entrance window of which has the same thickness as that of the quartz plate covering the sample. At 366 nm the incident intensity is of the order of 10^{-6} einstein min^{-1}. The measurement of reflectivity coefficients R_λ allows the calculation of the intensity absorbed by the sample. Uranium(V) is determined by polarography in perchloric acid [15] and uranium(IV) is determined by spectrophotometry at 620 nm in a 40% solution of H_3PO_4 [22] (ϵ = 33 l mol^{-1} cm^{-1}). When uranium(V) is present, this procedure gives the sum of the U^V and U^{VI} concentrations [16].

Results and discussion

Photoluminescence

Absorption of a photon leads to an excited state which may revert to the ground state through several competitive transitions. In the case of uranyl salts

a fraction of the excess energy is re-emitted as luminescence [3, 6]. The photoluminescence spectrum of $UO_2(HCOO)_2 \cdot H_2O$ has been recorded at 298 K and 77 K [19]. The various lines have been assigned to transitions from the first electronically excited state (20 300 cm^{-1} above the zero-phonon ground level) to different vibrational levels of the ground state. Several investigations [6, 23, 24] have shown that this photoluminescence is a fluorescence in spite of the relatively long lifetime of the excited state (10^{-4} s at 298 K). The first excited state will be considered in the following to be a singlet (S_1^0) state, although the question of its multiplicity is still under discussion [25 - 28].

Photoreactive state

In order to establish the excited state responsible for photodecomposition, the influence of the exciting wavelength on the extent of photoreduction has been investigated, the number of incident photons remaining constant. The results are shown in Fig. 3, where it can be seen that radiation of wavelength shorter than 490 nm is actinic. The corresponding wavenumber ($\approx$ 20 400 cm^{-1}) is close to that of the transition leading to the first electronically excited state as determined by fluorescence [19] and by absorption [29].
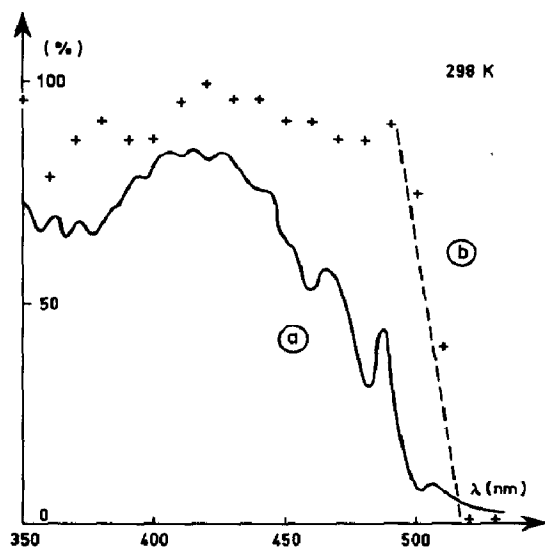

Fig. 3. (a) Absorption spectrum of $(UO_2)(HCOO)_2 \cdot H_2O$ and (b) reaction extent vs. wavelength at 298 K.

Therefore, the necessary and sufficient condition for the photodecomposition to take place is that the level S_1^0 be reached. The dissociation of the uranyl group (which needs about 29 500 cm^{-1}) [30] is not required to account for our observations. The fact that the first singlet state S_1^0 is responsible both for the photoreaction and for photoluminescence makes it important to measure the quantum yields of these competing processes.

Quantum yield of fluorescence

The absolute determinations of fluorescence yield being very difficult [31], the relative method described by Bourcet [32] has been used at 298 K with sodium salicylate as reference material. This quantum yield Φ is found to be independent of the wavelength of the exciting light [3] and is equal to 0.45×10^{-3} for $UO_2(HCOO)_2 \cdot H_2O$ and 6.3×10^{-3} for anhydrous $UO_2(HCOO)_2$, these values being very small compared with those of other uranyl salts [25].

Thus, fluorescence appears as a de-excitation process of secondary importance, but specific to U^{VI} since the compounds of U^V and U^{IV} are not luminescent [3]. Fluorescence is therefore a means of monitoring the extent of photodecomposition. Figure 4 shows the decrease of fluorescence intensity as a function of time during the photoreaction. This decrease is identical for all fluorescence bands, which confirms that these bands come from the same excited state. This state is also responsible for photodecomposition.
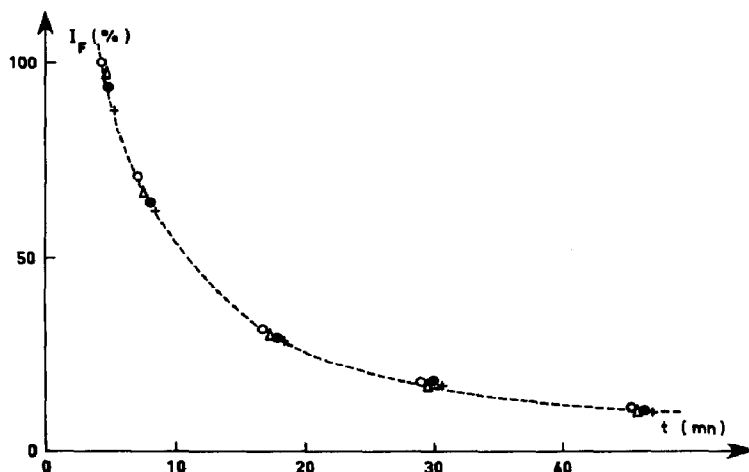

Fig. 4. Decay of fluorescence bands of $UO_2(HCOO)_2$, H_2O during photodecomposition at 298 K: ○ 492.5 nm, △ 512.5 nm, ● 535 nm, + 560 nm.

Reaction intermediates
    Formate radicals HCOO·

Uranyl formate monhydrate irradiated at 298 and 77 K is examined in a Varian E3 ESR spectrometer. The spectrum exhibits an anisotropic signal ($g_1 = 2.0036$, $g_2 = 2.0021$, $g_3 = 1.9975$) which is assigned not to U^V ($5 f^1$) [33 - 36], but to HCOO· radicals [37, 38] which have also been detected during uranyl ion photoreduction by formic acid in aqueous media [1, 3, 38].

    Uranium(V)

It has been shown earlier [15] that U^V is formed in the irradiated solid.

Determination of photoreaction quantum yield

We shall call "effective quantum yield" the ratio of the number n of moles of product formed to the number $\mathcal{N}_a$ of einsteins absorbed by the initial reactant U^{VI};

$$\varphi_{\text{eff}} = \frac{n(U^V)}{\mathcal{N}_a(U^{VI})} \qquad \psi_{\text{eff}} = \frac{n(U^{IV})}{\mathcal{N}_a(U^{VI})}$$

The apparent quantum yield, however, is referred to the total number of einsteins $\mathcal{N}_a$ absorbed by the whole sample:

$$\varphi_{\text{app}} = \frac{n(U^V)}{\mathcal{N}_a} \qquad \psi = \frac{n(U^{VI})}{\mathcal{N}_a}$$

with

$$\mathcal{N}_a = \mathcal{N}_a(U^{VI}) + \mathcal{N}_a(U^V) + \mathcal{N}_a(U^{IV})$$

The evolution in time of species U^V and U^{IV} under irradiation is shown in Fig. 5 where it can be seen that uranium(V) appears at the very start of the illumination, whereas the formation of uranium(IV) is delayed. The slopes at the origin of these curves give the values

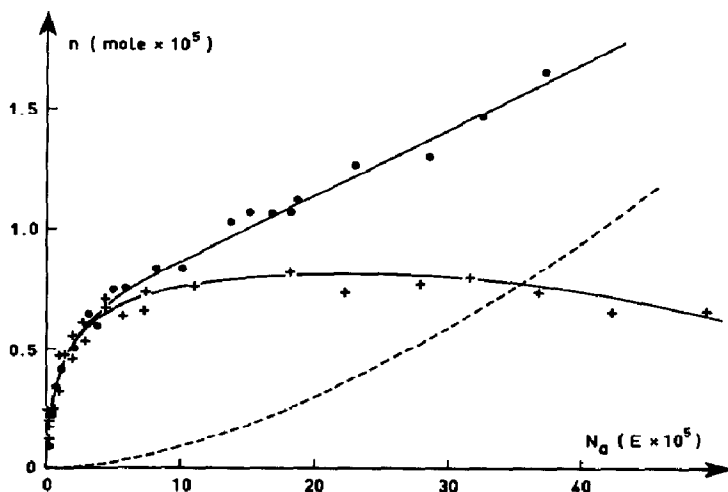$$\varphi_{\text{eff}} = 0.83 \pm 0.13 \qquad \psi_{\text{eff}} = 0$$

Fig. 5. Evolution of species U^V and U^{IV} produced during photodecomposition at 298 K: $n(U^{VI})$ (initial) = 0.951 × 10^{-3} mol; λ_{ex} = 366 nm; ● $n(U^{IV}) + n(U^V)$, + $n(U^V)$, --- $n(U^{IV})$.

Figure 6 shows the evolution in time of the apparent quantum yields. Uranium(V) appears as a primary product of photodecomposition. The final product uranium(IV) is formed in a subsequent non-photochemical stage [16]. Figure 7 shows that the reflectivity at 640 nm which is characteristic of U^{IV} decreases with time after illumination has stopped which proves the formation of U^{IV} in the dark.
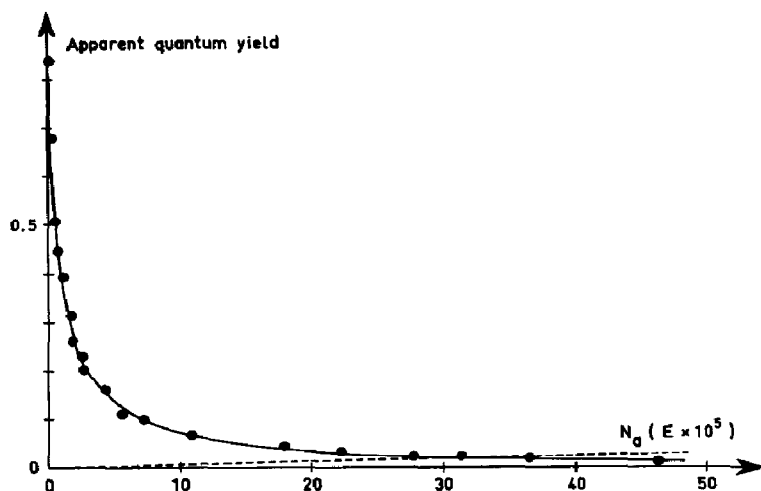
Fig. 6. Apparent quantum yields *vs.* absorbed einsteins at 298 K; λ_{ex} = 366 nm; ● φ_{app}, ---- ψ_{app}.
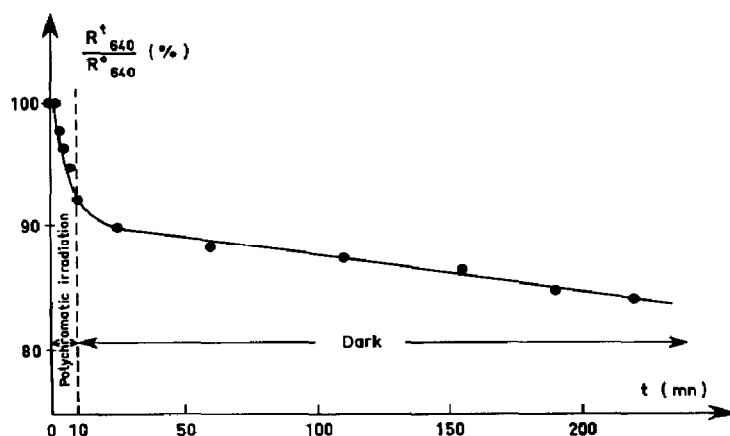

Fig. 7. Reflectivity at 640 nm during irradiation and in the dark at 298 K.

The decline of the fluorescence due to U^{VI} has been used to monitor the photoreaction kinetics. Figure 8 shows that the latter are independent of the exciting wavelength at short irradiation times.

Proposed mechanism

The following reaction sequence is proposed:

$$UO_2^{2+} \xrightarrow{h\nu \,>\, h\nu_0} (UO_2^{2+})^* \,(S_n) \tag{1}$$

$$(UO_2^{2+})^* \,(S_n) \rightarrow (UO_2^{2+})^* \,(S_1) \tag{2}$$

$$(UO_2^{2+})^* \,(S_1) \rightarrow (UO_2^{2+}) \,(S_0) + h\nu_F \qquad \Phi = 4.5 \times 10^{-4} \tag{3}$$

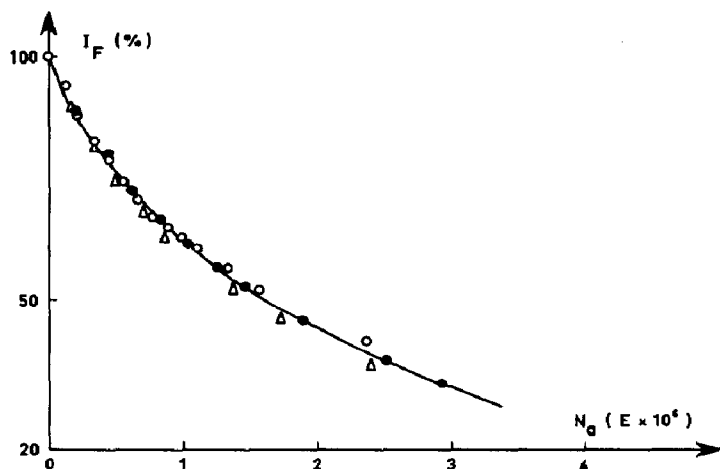$$(UO_2^{2+})^* \,(S_1) + HCOO^- \rightarrow UO_2^+ + HCOO^{\,\cdot} \qquad \varphi_{eff} = 0.83 \pm 0.13 \tag{4}$$

Fig. 8. Influence of exciting wavelength on the decline of fluorescence at 298 K. Exciting wavelength: ● 366 nm, △ 404.7 nm, ○ 435.8 nm.

$$HCOO^{\cdot} \quad \rightarrow \quad CO_2 + H^{\cdot} \tag{5}$$

$$UO_2^+ + H^{\cdot} \quad \rightarrow \quad UO_2H^+ \tag{6}$$

Reaction (1) is the photo-excitation of the uranyl ion, which requires frequencies higher than the threshold value ν_0. Uranyl in the excited state S_n returns to the level S_1 by the internal conversion (2). From this state S_1 it may revert to the ground state either by undergoing fluorescence or by undergoing decomposition according to reaction (4). Reaction (5) follows reaction (4); this would explain the immediate appearance of CO_2 [38, 39]. Reaction (6) accounts for the passage from U^V to U^{IV} in the dark. The cation UO_2H^+ (or $UO(OH)^+$) is that of the salt $UO(OH)(HCOO) \cdot H_2O$, which has already been reported as the solid end product [13]. The delayed evolution of water could be due to dehydration of this salt.

Conclusion

Our experimental results on the photodecomposition of $UO_2(HCOO)_2 \cdot H_2O$ have led us to propose a reaction path which differs from the mechanism of thermolysis of this solid, which was also studied in our laboratory [40]. This is ascribed to the fact that the action of light can induce intermediates different from those resulting from the increase of thermal motion. Further studies are required in order to understand the differences in photoreactivity already mentioned for the uranyl formate compounds.

References

1   V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, New York, 1970.
2   J. Kosar, Light Sensitive Systems, Wiley-Interscience, New York, 1965.
3   E. Rabinowitch and R. L. Belford, Spectroscopy and Photochemistry of Uranyl Compounds, Pergamon Press, Oxford, 1964.
4   H. D. Burrows and T. J. Kemp, Chem. Soc. Rev., 3 (1974) 139.
5   M. Feve, Ph.D. Dissertation, Université Claude Bernard, Lyon, 1974, no. 242.
6   G. H. Dieke, Spectroscopic Properties of Uranium Compounds, McGraw-Hill, New York, 1949.
7   B. Claudel, B. Mentzen, A. Navarro and H. Sautereau, J. Inorg. Nucl. Chem., 38 (1976) 759.
8   E. R. Russel and M. L. Hyder, Inorg. Nucl. Chem. Lett., 12 (1976) 247.
9   A. Navarro, Ann. Chim. (Paris), 6 (1971) 349.
10 M. Bideau, R. Bressat, B. Mentzen and A. Navarro, C. R. Acad. Sci., Ser. C, 271 (1970) 225.
11 B. Claudel, B. Mentzen, A. Navarro and J. P. Puaux, C. R. Acad. Sci., Ser. C, 274 (1972) 1417.
12 B. F. Mentzen, J. P. Puaux and H. Loiseleur, Acta Crystallogr., in the press.
13 R. Bressat, B. Claudel, A. Navarro and J. P. Puaux, 6th Int. Conf. on Photochemistry, Bordeaux, 1971.
14 B. Claudel, J. P. Puaux and A. Renouprez, C. R. Acad. Sci., Ser. C, 282 (1976) 571.
15 B. Claudel, M. Feve, J. P. Puaux and H. Sautereau, C. R. Acad. Sci., Ser. C, 280 (1975) 169.
16 H. Sautereau, Ph.D. Dissertation, INSA and Université Claude Bernard, Lyon, 1976, no. I.DE-76-008.
17 B. Sahoo, S. Panda and D. Patnaik, J. Indian Chem. Soc. 37 (1960) 594.
18 H. E. Spencer and M. W. Schmidt, J. Phys. Chem. 75 (1971) 2986.
19 B. Claudel and H. Sautereau, Spectrochim. Acta, Part A, 29 (1973) 1687.
20 C. A. Parker, Proc. R. Soc. London, Ser. A, 220 (1953) 104.
21 C. G. Hatchard and C. A. Parker, Proc. R. Soc. London, Ser. A, 235 (1956) 518.
22 C. J. Rodden, Analytical Chemistry of the Manhattan Project, McGraw-Hill, New York, 1950, p. 77.
23 R. Delorme and F. Perrin, J. Phys. Radium, 10 (1929) 177.
24 L. A. Hall and G. H. Dieke, J. Opt. Soc. Am., 47 (1957) 1092.
25 S. P. MacGlynn and J. K. Smith, J. Mol. Spectrosc., 6 (1961) 164.
26 J. T. Bell and R. E. Biggers, J. Mol. Spectrosc., 18 (1965) 247; 22 (1967) 262; 25 (1968) 312.
27 A. P. Abramov and N. A. Tolstoi, Opt. Spektrosk., 37 (1974) 360.
28 C. K. Jorgensen and R. Reisfeld, Chem. Phys. Lett., 35 (1975) 441.
29 C. Gorller-Walrand and S. de Jaegere, J. Chim. Phys., 69 (1972) 726.
30 S. de Jaegere and C. Gorller-Walrand, Spectrochim. Acta, Part A, 25 (1969) 559.
31 J. N. Demas and G. A. Crosby, J. Phys. Chem. 75 (1971) 991.
32 J. C. Bourcet, Ph.D. Dissertation, Université Claude Bernard Lyon, 1974, no. 256.
33 J. Selbin and J. D. Ortego, Chem. Rev., 69 (1969) 657.
34 P. Rigny and P. Plurien, J. Phys. Chem. Solids, 28 (1967) 2589.
35 W. Low, Paramagnetic Resonance in Solids, Academic Press, New York, 1960.
36 W. B. Lewis, H. G. Hecht and M. D. Eastman, Inorg. Chem., 12 (1973) 1634.
37 C. W. Chantry, A. Horsfield, J. R. Morton and D. H. Whiffen, Mol. Phys., 5 (1962) 589.
38 D. Greatorex, R. J. Hill, T. J. Kemp and T. J. Stone, J. Chem. Soc. Faraday Trans. 1, 68 (1972) 2059.
39 J. K. Kochi, R. A. Sheldon and S. S. Lande, Tetrahedron, 25 (1969) 1197.
40 M. Bideau, Ph.D. Dissertation, INSA and Université Claude Bernard, Lyon, 1976, no. 1-DE-76-015.