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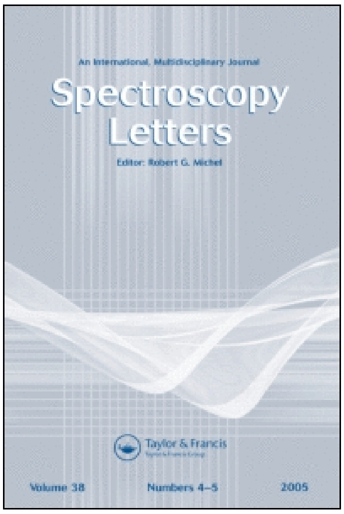

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A RAMAN Spectroscopic Investigation of Alloxan and Alloxan Monohydrate

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A RAMAN SPECTROSCOPIC INVESTIGATION OF ALLOXAN AND ALLOXAN MONOHYDRATE

Key Words: Anhydrous alloxan, Alloxan monohydrate,
Raman and Infrared spectroscopy.

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ABSTRACT

The present Raman investigation of anhydrous alloxan and the misnamed alloxan monohydrate suggests that some of the assignments previously made on basis of the IR spectrum of the anhydrous compound must be changed, i.e., the ones related to the NH stretching and ring breathing modes. The hydrogen bonding network in the crystal of the so called alloxan monohydrate, although extensive, is not strong enough to cause substantial frequency shifts in the NH and CO stretching modes.

INTRODUCTION

Alloxan [2,4,5,6(1H,3H)-pyrimidinetetrone] (I) was the first member of the pyrimidine family to be

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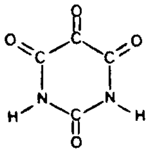
identified [1], and most of Chemistry textbooks mention that its more common form is the monohydrate, a white solid, from wich the yellow anhydrous compound can be obtained by heating in vacuum. Alloxan monohydrate is a misname since X-ray investigations [1] have shown that the compound is not in the 2,4,5,6-tetraketo form with a water molecule, but is in fact in the 2,4,6-triketo-5,5-dihydroxypyrimidine configuration (II).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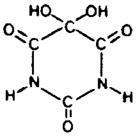
II

The so called monohydrate has been used as the starting material for the synthesis of several cyclic urea derivatives, and also as a powerful diabetis inducer in pharmacological studies [2]. It is now well known by X-ray investigation [3] that in anhydrous alloxan the molecule is planar with C_{2v} symmetry, while in the so called hydrate both NH and CO groups participate in the intermolecular hydrogen bonding, the molecule losing its planarity [1]. As far as spectroscopic investigations are concerned the situation is much less satisfactory since only anhydrous alloxan was investigated by infrared spectroscopy [4], while Raman spectroscopy has been employed only to investigate the saturated aqueous solution about 50 years ago [5,6]. We then decided to investigate anhydrous alloxan, the so called monohydrate and its saturated aqueous solution, aiming to complement the available IR data and consequentely deepen our knowledge on the structures of such species.

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EXPERIMENTAL

Alloxan monohydrate was prepared according to the directions of the literature [7] and the anhydrous material obtained from the so called hydrate by heating at ca. 180°C in vacuum for several hours. The chemical composition of both compounds was confirmed by chemical analysis. The Raman spectrum of the anhydrous alloxan was obtained with the sample contained in a sealed glass capillary that was rotated to prevent local heating of the sample. In the case of the hydrate a rotating disc was employed to support the sample since in this case local heating could eventually lead to the anhydrous compound. The Raman spectrum of the saturated solution was obtained using a conventional cell for liquids. The spectra were obtained using a Jarrel-Ash 25-300 double monochromator spectrometer fitted with photon counting detection, excitation being provided by the 514.5 nm line of an Ar^+ laser or the 647.1 nm line of a Kr^+ laser of Spectra-Physics model 165. The IR spectrum of the so called hydrate was obtained with use of the KBr pellet technique in a Perkin-Elmer 1700 FTIR spectrophotometer.

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RESULTS AND DISCUSSION

The Raman spectra of anhydrous alloxan and alloxan monohydrate are displayed in Figure 1, and the IR spectrum of the monohydrate is shown in Figure 2. Raman and IR frequency values of the investigated compounds are listed in Table 1, together with a tentative assignment. According to the X-ray data [3], in anhydrous alloxan, the molecule has a C_{2V} symmetry what implies that its normal vibrations can be classified according to the representation: $11A_1 + 3A_2 + 10B_1 +$

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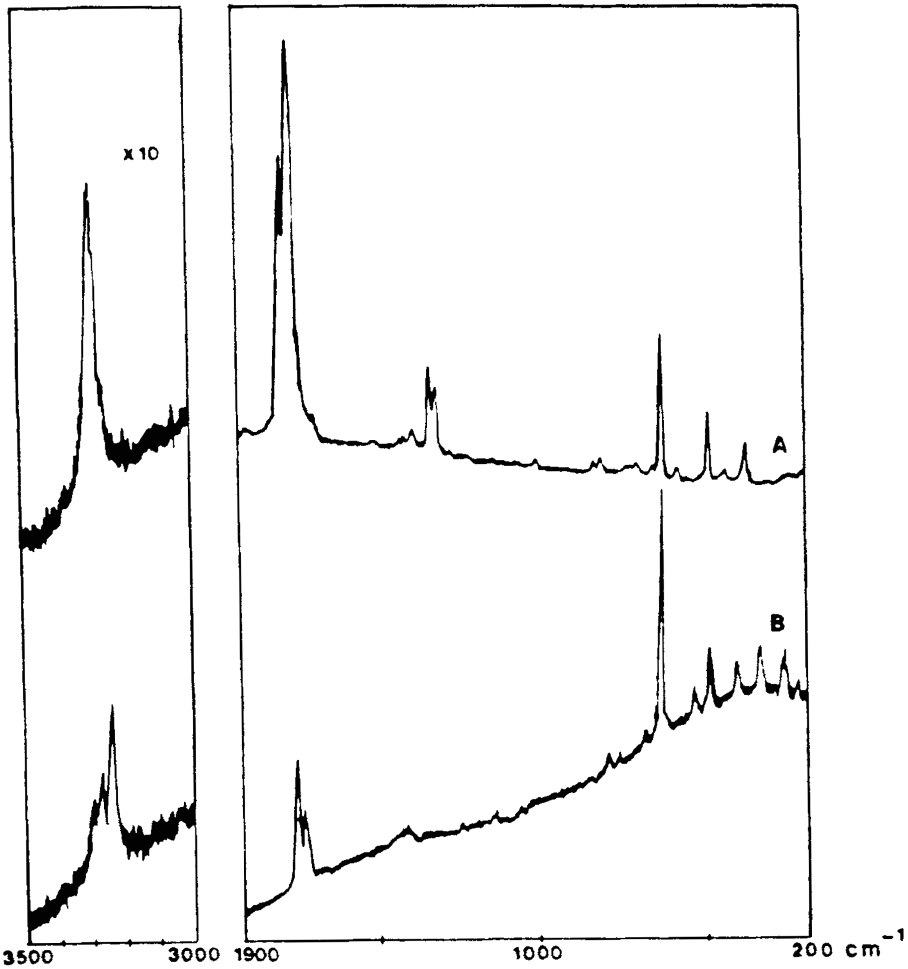

FIG. 1 - Raman spectra in the solid state of anhydrous alloxan (A, 514.5 nm excitation) and alloxan monohydrate (B, 647.1 nm excitation).

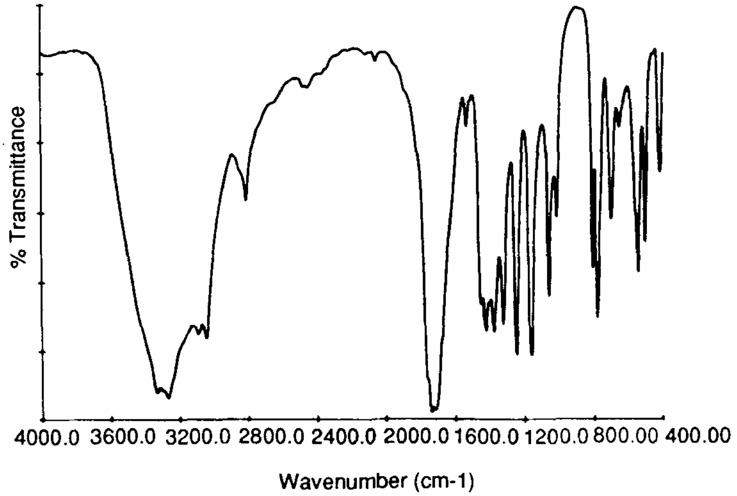

FIG. 2 - Infrared spectrum of alloxan monohydrate in KBr pellet.

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$6B_2$. In the Raman spectrum all the species are expected to be active, whereas in the IR spectrum all but the B_2 species are expected to be active. In fact, in the reported IR spectrum all the modes have been observed, what has been ascribed to the breaking of the selection rules in the solid [4]. In the present work the Raman bands that were observed correlate quite well with their IR counterparts. In the NH stretching region one finds some apparent discrepancy between the Raman and IR values, making the correlation less straightforward. So, in the Raman spectrum a weak band at 3290 cm^{-1} and a shoulder at 3240 cm^{-1} are observed, while in the IR spectrum two intense bands at 3351 and 3340 cm^{-1} were previously assigned to the assymetric and symmetric NH streching modes, respectively [4]. As a matter of fact, in that paper the authors also report

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TABLE 1

Raman and IR frequency values (in cm^{-1}) observed for anhydrous alloxan and for alloxan monohydrate, with the respective assignments.

Alloxan hydrate		Alloxan anhydrous		Assignment*
Raman	IR	Raman	IR*	
241 w				
274 w				
346 m		372 vw	370 s	CO o.p. bend (B_2)
420 wm	420 w	436 vw	428 s	CO i.p. bend, ν ring, ring bend (B_1)
503 m	502 w	484 wm	483 s	ring i.p. bend, νring, CO i.p. bend (B_1)
558 w	543 w	578 m		
648 s(p)	653 wm	623 ms	623 w	ring breathing(A_1)**
	699 wm	693 vw	699 m	CO o.p. bend (B_2) **
772 vw	779 w	725 vw	720 w	NH o.p. bend (A_2)
801 vw	807 w	805 vw	809 vw	CO i.p. bend (A_2)
1060 vw	1059 w		1062 s	CO i.p. bend, νring (A_1)
1145 vw	1161 vw		1162 m	CO i.p. bend, νring (B_1)
1240 vw	1246 vw	1270 vw	1263 s	νring (A_1)
		1332 wm	1330 s	νring (B_1)
1407 vw	1399 w	1388 vw	1392 s	νring (B_1)
1426 vw	1421 w	1416 vw	1428 s	NH i.p. bend (A_1,B_1)
		1679 vw	1686 sh	νCO (A_1)
1709 sh	1715 vs		1706 s	νCO (A_1)
1723 m(p)	1736 vs	1730 sh		νCO (A_1)
1749 s(p)	1759 vs	1749 s	1745 vs	νCO (A_1)
		1770 ms	1781 s	νCO (A_1)
		1868 vw		
3236 sh		3240 sh		
3251 w	3267 vs	3290 vw		νNH (B_1)**
3282 vw	3297 vs		3340 s	
3308 vw	3330 vs		3351 s	νNH (A_1)**

(*) Reference 4; (**) this work.

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the presence in the IR of very weak bands at ca. 3290 and ca. 3240 cm^{-1}, that by virtue of their intensities were assigned to combinations. It seems that the presence of such bands in the Raman spectrum makes their assignment as combinations very unlike. The forementioned observations can be explained if one assumes that the strong IR bands at 3351 and 3340 cm^{-1} are assigned to the assymmetric stretching mode, split in the solid state, while the Raman bands at 3290 and 3240 cm^{-1}, that show up very weakly in the IR, are assigned to the symmetric stretching mode, also split in the solid state. Unfortunately all the tentatives to dissolve anhydrous alloxan in suitable organic solvents as to investigate the NH stretching region in solution were not successful, and in fact even in the saturated solutions, only the most intense Raman bands are observed. In the case of the so called monohydrate, in the IR the NH stretching region is swamped by the very broad and intense absorption characteristic of an extensive hydrogen bonded framework that involves both N-H and C=O groups of different molecules [1], while in the Raman spectrum of the hydrate additional bands are observed in this region, as a consequence of the hydrogen bonding in the framework of the molecule. According to Table 1 we can see that there is, in general, only small frequency shifts in comparing anhydrous alloxan and the hydrate, what is somewhat surprising, since the extensive hydrogen bonding in the latter and the absence of hydrogen bonding in the former should lead to appreciable frequency shifts, particurlaly for the NH and CO stretching modes. We are then lead to the conclusion that the hydrogen bonding in the hydrate, although extensive, since all the NH, CO and OH groups participate, cannot be significantly strong.

Other point that deserves attention in the previous assignment of the anhydrous alloxan in the IR [4] refers to the 600-700 cm^{-1} region, where a weak band at 623 cm^{-1} was assigned to the out of plane carbonyl deformation of B_2 species, and a medium to strong band at 699 cm^{-1} was assigned to the ring breathing of A_1 species. Taking into account that in the Raman spectrum the 623 cm^{-1} band is amongst the strongest bands and that the 693 cm^{-1} band is very weak, it seems that the previous assignment of these two modes should be reverted. In the case of barbituric acid, whose Raman spectrum was recently investigated [8], the most intense Raman band is by far the one at 679 cm^{-1}, assigned to ring breathing, while the very weak band at 642 cm^{-1} is assigned to the carbonyl out of plane deformation. In another structurally related molecule, violuric acid, the strongest Raman band at 644 cm^{-1} was assigned to the ring breathing mode, while the CO out of plane deformation was assigned to the very weak band at 505 cm^{-1} [9]. Such comparisons with the chemically related molecules, barbituric and violuric acids, strongly reinforce the proposed reversal of the previous assignment of the forementioned modes.

ACKNOWLEDGMENTS

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