MODIFICATIONS IN THE IODINE OXIDATION OF HYDROXY FLAVANONES AND THEIR METHYL ETHERS

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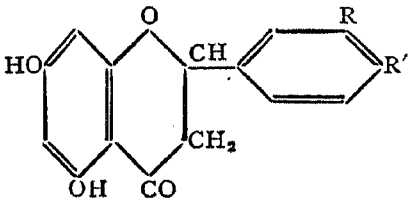
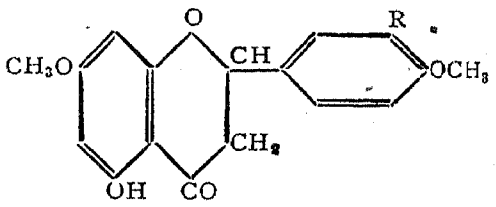
In a previous publication[1] the action of iodine and silver acetate on flavanones in absolute alcoholic solution was discussed. Naringenin (I *a*) and hesperetin (I *b*) were found to yield the corresponding 3-acetoxy-flavanones while naringenin dimethyl ether (II *a*) and 5 : 7-dimethoxy-flavanone (III *a*) yielded the corresponding 3-iodo-compounds (IV *a* and III *b*). Considerable difference was recorded regarding the behaviour of these 3-iodo-compounds towards alcoholic potash. The 3-iodo-5-hydroxy-7 : 4′-dimethoxy flavanone (IV *a*) on treatment with this reagent yielded the corresponding flavone, apigenin-7 : 4′-dimethyl ether (V *a*) while the 3-iodo-5 : 7-dimethoxy flavone was reported to yield the corresponding flavonol, galangin-5 : 7-dimethyl ether (VI *a*). A more detailed study of these reactions has now been made.



I

(*a*) R=H, R′=OH.

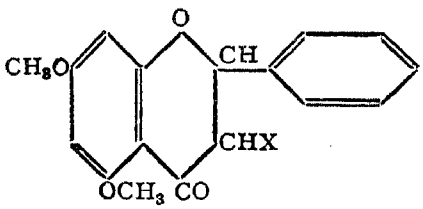
(*b*) R=OH, R′=OCH_3.



II

(*a*) R=H.

(*b*) R=OCH_3.



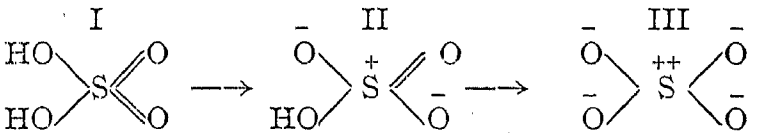
III

(*a*) X=H.

(*b*) X=I.

and the ratio of depolarisation of the components is distinctly lower than 6/7. The broad line 1140 is also polarised. These four, thus, represent the polarised vibrations of the distorted tetrahedron. Three out of the five depolarised vibrations are 564, 970 and 1364 and the remaining two are probably too feeble to be recorded on the plate.

The lines which are known to belong definitely to HSO_4' ions are 1045, 1223 and 1334. Of these the most intense line at 1045 possesses a depolarisation ratio of about 0·24 and evidently corresponds to the expansion and contraction of the tetrahedron. It is interesting to observe that the depolarisation ratio of the breathing frequency which is almost zero in the SO_4'' ions is about 0·17 in the undissociated molecule and attains a value of more than 0·24 in the HSO_4' ions. If we assume that the extent of polarisation is a measure of the symmetry of structure of the molecular species, we are led to infer that HSO_4' ion is the most asymmetrical of the three. A mechanism which could satisfactorily explain these experimental results may be outlined as follows :—



The undissociated molecule having a structure given by formula I changes to form II after the first stage of ionisation and on further dissociation yields the symmetrical SO_4'' ion. The tetrahedral structure is preserved throughout ; but as may be easily seen the middle form representing HSO_4' ion has the least symmetry.

Selenic Acid.—In a detailed investigation of the Raman spectrum of selenic acid,[20] it has been pointed out that it behaves in Raman effect in a manner analogous to sulphuric acid and it is gratifying to note that the polarisation characters of the lines also correspond closely to that of the latter. The molten acid yields eight lines of frequency shifts 294 (3), 361 (6), 388 (6), 756 (10), 914 (8), 996 (3), 1105 (0) and 1186 (0). Of these 756, 996 388, 361 and 294 as well as 1105 and 1186 have been assigned to H_2SeO_4 molecule and 914 to the $HSeO_4'$ ion. If we assume the tetrahedral structure to H_2SeO_4 molecule and its dissociation products, the high degree of polarisation of 756 and 914 shows that they represent the symmetrical vibrations of H_2SeO_4 molecule and $HSeO_4'$ ion respectively. The polarisation characters of the other lines follow, in general, closely those of the corresponding

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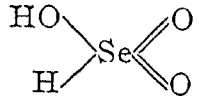
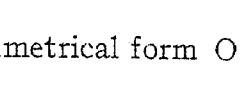
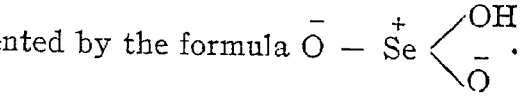
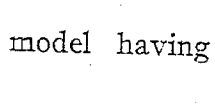
[20] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 307.

lines of sulphuric acid. But the greater asymmetry of the $HSeO_4'$ ion is not so clear as in the case of HSO_4' ion.

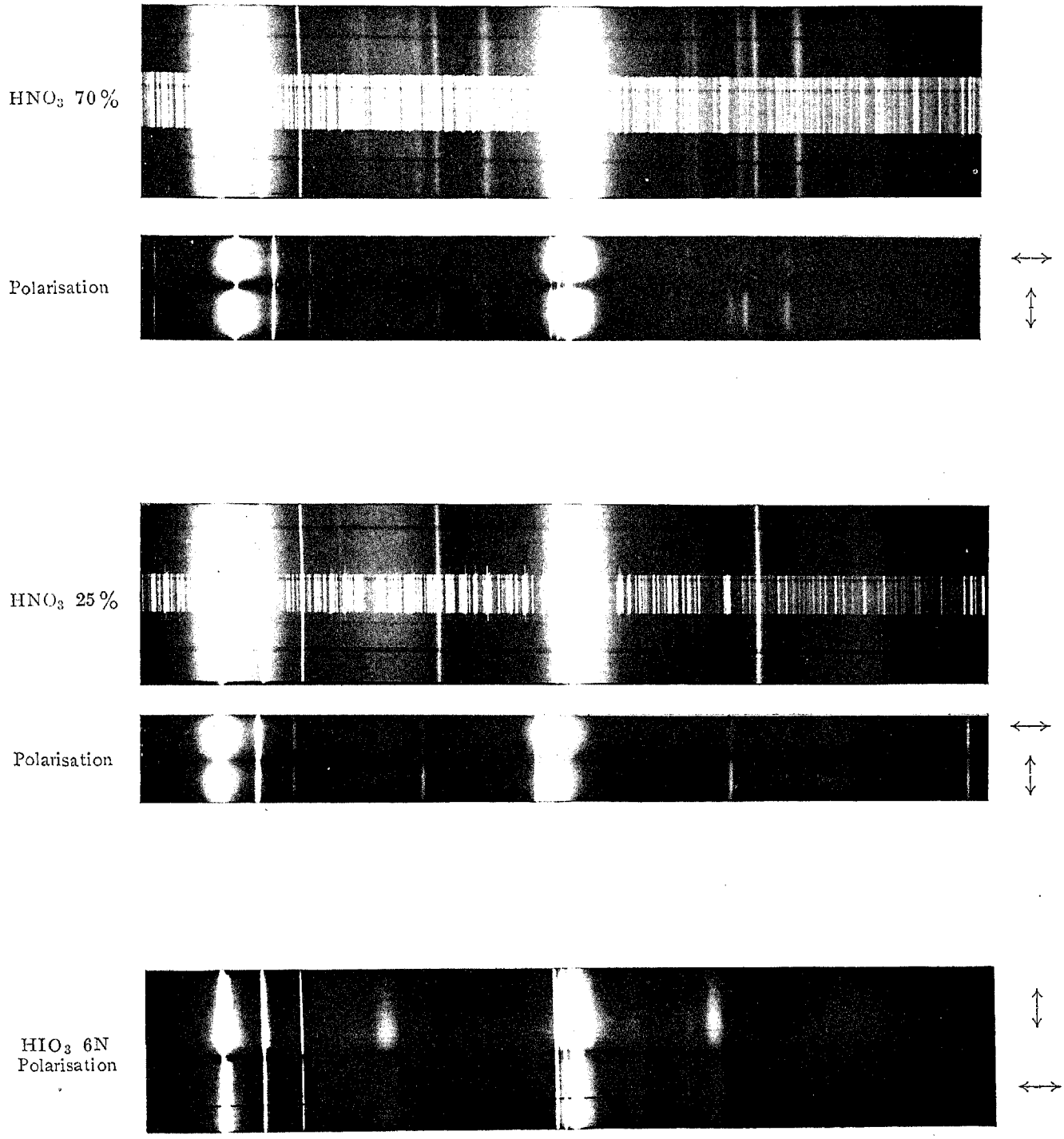
Selenious Acid.—The six frequencies reported previously[21] for the molten liquid are 238 (1), 343 (4), 380 (3), 545 (1), 690 (10) and 892 (10). The polarisation picture shows that the band 892 consists of two components with frequency shifts of 862 and 910 and are, therefore, listed separately in Table V. The broad lines 343 and 380 show a depolarisation of 6/7 and hence confirm their assignment to the lower degenerate vibrations of the molecular species which are assumed to possess a pyramidal structure. The line 545 is attributed to the unsymmetrical form  and the line 690 to the symmetrical form  . Both these lines are polarised indicating that they correspond to the vibrations having maximum symmetry in the respective molecules ; but their relative degree of depolarisation could not be determined due to the extreme feebleness of the line 545 in the molten liquid. The high degree of polarisation of 862 shows that $HSeO_3'$ ion is more symmetrical than the undissociated molecule and is, therefore, probably more accurately represented by the formula  .

In conclusion the author wishes to express his heartfelt thanks to his professor Sir C. V. Raman for his constant interest in the work.

Summary.

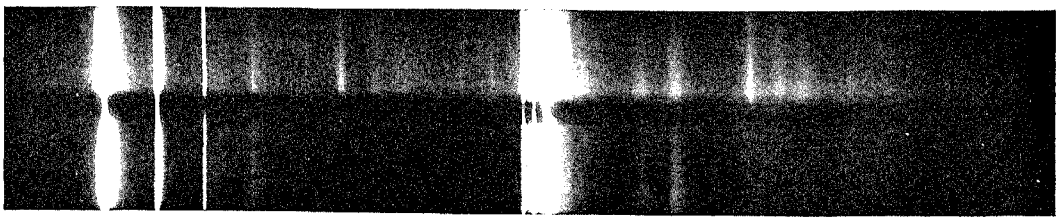
The polarisation of Raman lines of nitric, iodic, sulphuric, selenic and selenious acids is investigated making use of the usual double-image prism method. All the lines of the concentrated nitric acid except one at 1538 which is attributed to the deformation oscillation of the hydroxyl group, show varying degrees of depolarisation which are less than the limiting value 6/7. The lines due to the nitrate ion possess a state of polarisation which is in agreement with the plane equilateral structure attributed to it. From the results of polarisation six lines belonging to the undissociated nitric acid molecule are identified with the known modes of oscillation of an unsymmetrical pyramidal model having a structure  . The

[21] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, 3, 533.



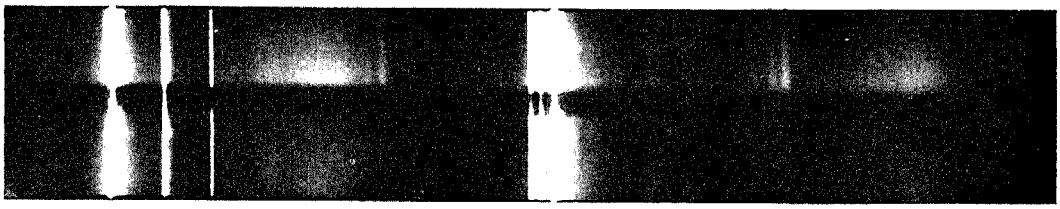
Raman Spectra—Polarisation

H_2SO_4 99 % Polarisation



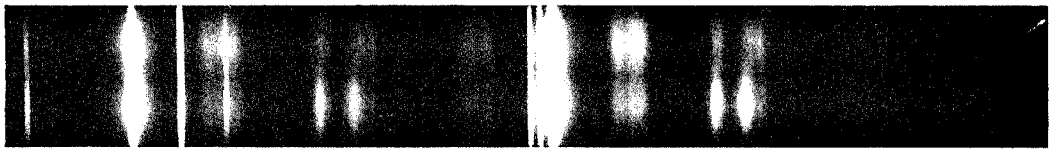
(1) ↕ ↔

H_2SO_4 25 % Polarisation



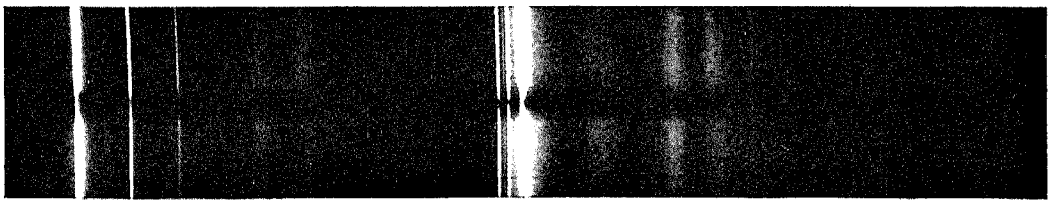
(2) ↕ ↔

H_2SeO_4 molten Polarisation



(3) ↔ ↕

H_2SeO_3 molten Polarisation



(4) ↕ ↔

Raman Spectra—Polarisation