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Infrared Absorption Spectra of Nitric Acid and Its Solutions*

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Infrared spectra of reactive liquids such as anhydrous nitric and sulfuric acids were determined using silver chloride windows and, in some cases, Teflon spacers. The absorption frequencies of nitric acid agree well with those found from Raman spectra.

A nitronium ion frequency was observed at 2360 cm^{-1}. The intensity of this band is enhanced by the addition of nitronium fluoborate, sulfuric acid, phosphorous pentoxide, or small amounts of acetic anhydride. It is reduced by addition of sodium nitrate, potassium dihydrogen phosphate, water, or larger amounts of acetic anhydride. Its behavior in these media provides information about pertinent equilibria. A nitronium ion combination band was observed near 3745 cm^{-1} when the concentration of this ion was particularly large. Bands arising from unionized nitric acid are completely absent when a small amount of nitric acid is added to 100% H_2SO_4.

Various bands found in aqueous nitric acid solutions are attributed to hydrogen-bonded structures, both because of their behavior in different media and by analogy with effects observed in Raman studies.

INTRODUCTION

THE properties of nitric acid and its solutions have been investigated in the liquid phase by means of the Raman effect[1] and in the vapor by infrared techniques.[2] The Raman studies have also served to identify a nitronium ion frequency at 1392 cm^{-1}. This direct evidence for the nitronium ion has in turn supported the results of many indirect physical studies.[3]

Little has been reported on the infrared spectrum of liquid anhydrous nitric acid. Dalmon and Freymann[4] examined the behavior of the anhydrous acid in the near infrared region of 10 000 cm^{-1}. Freymann and Freymann studied it in the rock salt region with sodium chloride windows[5] and, after subtracting for the sodium nitrate produced, reported several possible lines. Using silver chloride windows, Bethell and Sheppard[6] obtained the spectrum of fuming nitric acid (about 90% HNO_3, based on comparison of these data with ours).

The configuration of the nitronium ion, similar in many respects to carbon dixoide, allows one Raman active and two infrared active fundamental frequencies. The Raman active band occurs near the corresponding one for nitronium ion, and the other two occur at 2349 and 667 cm^{-1}. The present study was undertaken in part to see if corresponding absorption bands could be detected for the nitronium ion.

EXPERIMENTAL

Apparatus

All spectra were recorded with a Perkin-Elmer Model 21 double beam spectrophotometer equipped with a rock salt prism. Silver chloride windows and a Perkin-Elmer stainless steel demountable cell assembly were employed. These windows suffered no loss in weight upon standing overnight in anhydrous nitric acid.

The strongest absorption bands were identified by pressing the liquid between silver chloride windows. Some of the weaker bands were recorded using spacers cut from $\frac{1}{2}$, 1, 2, and 20-mil Teflon tape. Cell thicknesses

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[1] C. K. Ingold and D. Millen, J. Chem. Soc. (1950), 2612 and references cited therein.

[2] Cohn, Ingold, and Poole, J. Chem. Soc. (1952), 4272.

[3] For summary, see R. J. Gillespie and D. Millen, Quart. Revs. (London) 2, 277 (1948).

[4] R. Dalmon and R. Freymann, Compt. rend. 211, 472 (1940).

[5] M. Freymann and R. Freymann, Compt. rend. 222, 1339 (1946).

[6] D. E. Bethell and N. Sheppard, J. chim. phys. 50, C72 (1953).

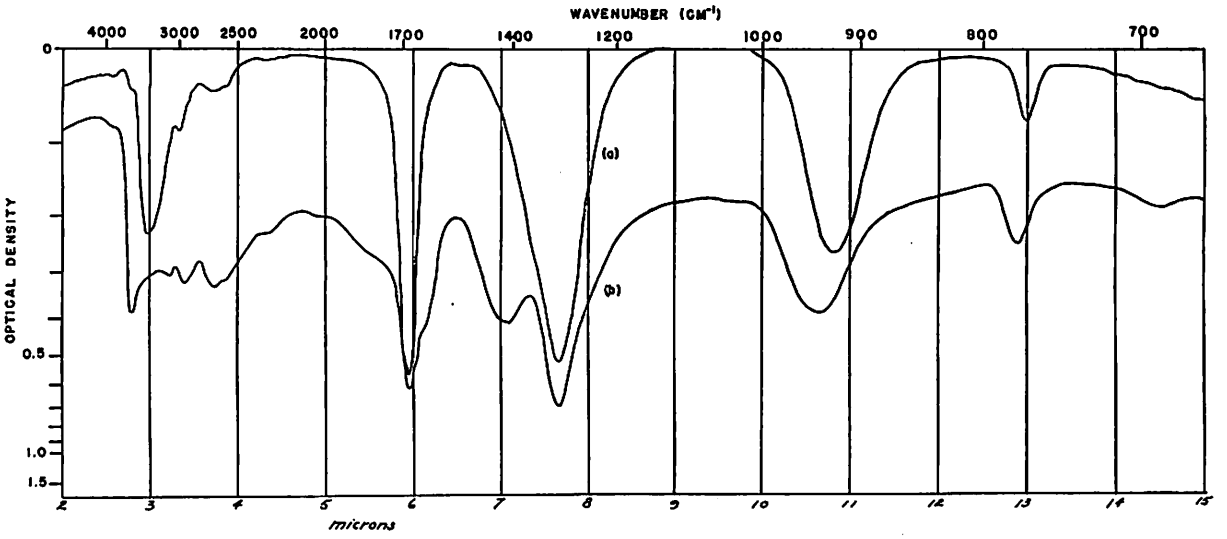

FIG. 1. Infrared spectrum of nitric acid: (a) 99.2% by weight (cell thickness ~2 μ), (b) 80% by weight (cell thickness ~5 μ).

were measured interferometrically, except for those in which the windows were merely pressed together. In this case it was estimated approximately by comparison of the liquid absorption with that in a cell of known thickness. It was usually about 5 μ, although 2 μ could be obtained with relatively new windows.

For relative absorbance measurements, a fixed thickness absorption cell containing a Teflon spacer was prepared by drilling a pair of $\frac{1}{32}$-in. diameter holes through one window. The borings were made on the flat surface of the window, on either side of the spectrometer beam path. Successive solutions could be transferred by a finely drawn out glass tube. They were removed by flushing and drying by a stream of warm nitrogen. During exposures sample evaporation was minimized by plugging each window hole.

Reagents

Colorless, anhydrous nitric acid was prepared by vacuum distillation from sulfuric acid and sodium or ammonium nitrate at room temperature. The acid was assayed, usually at 99.4%, by weighing out a known amount in a stoppered bottle and opening the latter under a water surface. The resulting solution was titrated with standard base.

Concentrated reagent grade sulfuric acid used for spectral purposes was strengthened to "100%" by addition of oleum. The acidity of the resulting solution was determined as above.

All other chemicals were reagent grade. Acetic anhydride-nitric acid solutions were prepared by precooling both agents to −78°C and slowly mixing them at low temperature to minimize decomposition.

RESULTS AND DISCUSSION

Infrared spectra were obtained for anhydrous nitric acid, alone and in solutions containing nitronium fluoborate, sulfuric acid, phosphorous pentoxide, sodium nitrate, potassium dihydrogen phosphate, acetic anhydride, and water. The spectra of several other compounds including anhydrous sulfuric acid were recorded as by-products of this study.

1. Nitric Acid

The infrared spectrum of 99.2% nitric acid is given in Fig. 1(a) and Table I (cell thickness about 2 μ). The infrared bands of the vapor and the Raman bands of the liquid are included in this table for comparison, the assignment of the vibration frequencies being that of Cohn, Ingold, and Poole.[2] The agreement between the Raman and infrared frequencies for the liquid is excellent. Differences between liquid and vapor have been interpreted in terms of hydrogen bonding.[2]

TABLE I. Vibrations and frequencies of nitric acid (cm^{-1}).

Assignment[a]	Infrared vapor[a]	Raman liquid[1]	Infrared liquid
(7)	3560 m	3400 band	3380 m
2×(4)	3390		
(1)+(4)	3000		3010 w
2×(1)	2627		2690 w
(2)+(4)	2585		2600 w
(4)	1710 s	1675 m	1680 s
2×(6)		1535	1538 w
(8)	1335 s	...	
(1)	1320 s	1300 s	1308 s
(6)+(9)	1206		
(2)	886 s	925 s	924
(6)	765 m	(767)[b]	769
(3)	...	680 m	...
(5)	583 m	610 m	beyond NaCl region
(9)	465 s	480 w	

[a] For a description of these vibrations see reference 1. Compare O. Redlich and L. E. Nielsen, J. Am. Chem. Soc. 65, 654 (1943).
[b] Observed only as overtone.

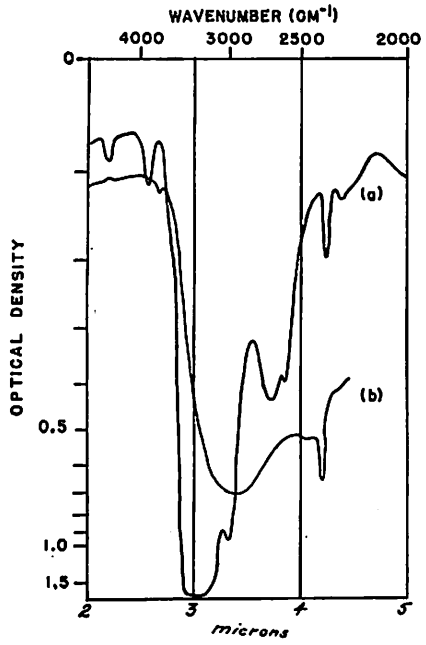

FIG. 2. Infrared spectrum of (a) 99.6% nitric acid (cell thickness=18.4 μ) and of (b) a solution containing 11.8% (wt) of anhydrous nitric acid and 88.2% (wt) of 99.8% sulfuric acid (cell thickness ~5 μ).

Using a much thicker cell (18.4 μ) new bands were observed at 2290 and 2360 cm^{-1}, the 2 to 5 μ wavelength region portion of the spectrum being given in Fig. 2(a). On the basis of the experiments outlined below, the former band is assigned to a combination or overtone of nitric acid and the latter to the antisymmetrical stretching vibration of the nitronium ion.

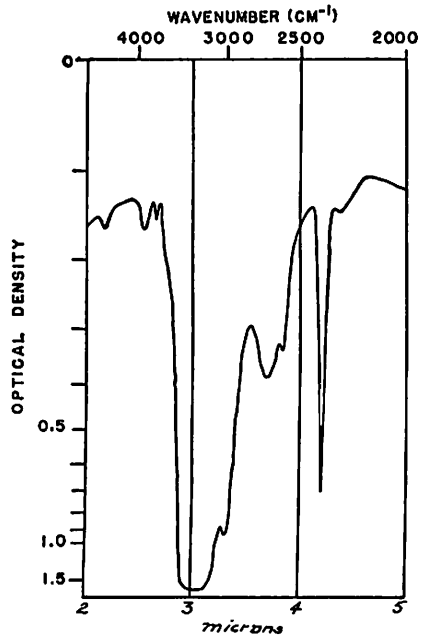

FIG. 3. Infrared spectrum of nitronium fluoborate in 99.2% nitric acid (cell thickness ~15 μ).

2. Nitronium Fluoborate-Nitric Acid

The infrared spectrum of a solution of nitronium fluoborate‡ in 99.2% nitric acid was recorded in an absorption cell about 15 μ thick. The spectrum obtained in the 2 to 5 μ wavelength region is given in Fig. 3. Comparison with Fig. 2(a) shows that the 2360 cm^{-1} band is very sharp, that it has become exceedingly intense and that a new, weaker band has appeared at 3745 cm^{-1}. On the basis of these results and those obtained in subsequent sections, the new band is assigned to a nitronium ion combination band (1392+2360), which is allowed by infrared selection rules.

No nitronium ion frequency near 667 cm^{-1} was observed. However, this is not only near the edge of the rock salt prism region but observation is further complicated by a pronounced background absorption of nitric acid. In carbon dioxide the 667 cm^{-1} band is only about one fifth as intense as the one at 2349 cm^{-1}.

3. Sulfuric Acid—Nitric Acid

The spectrum of 99.8% sulfuric acid, given in Fig. 4, was determined with a cell about 5 μ thick or less. The observed bands of this acid are listed in Table II together with those found in its solutions with nitric acid. The 2 to 5 μ portion of the spectrum of the solution containing 11.8 weight % HNO_3 is recorded in Fig. 2(b).

The nitric acid bands are completely absent in the solutions of Table II, except for the sharp 2360 and 3745 cm^{-1} nitronium bands. This suggests that the acid is largely dissociated to NO_2^+ under these conditions, in agreement with cryoscopic data.[7]

$$HNO_3+2H_2SO_4=NO_2^++2HSO_4^-+H_3O^+.$$

Two other bands appear, one at 1050 and the other at 1680 cm^{-1}, and increase in intensity with increasing amounts of added nitric acid. In Table II these are assigned[8] to HSO_4^- and H_3O^+ ions, respectively.

TABLE II. Absorption frequencies of HNO_3—H_2SO_4 solutions (cm^{-1}).

HNO_3 (Mole %)				Assignment to ions
0	2.8	5.5	11.8	
		3750 vw	3740 w	NO_2^+
3000 s	3000 s	3000 s	2950 s	
2430 w	2430 w	2430 w	2430 vw	
	2360 vw	2360 w	2360 m	NO_2^+
	1681 vw	1661 w	1681 m	H_3O^+
1364 s	1366 s	1376 s	1376 m	
1171 s	1170 s	1174 s	1174 m	
	1049 w	1052 m	1052 m	HSO_4^-
967 s	969 s	962 s	not run	
903 m	902 m	904 m	not run	

‡ This material was prepared by Mr. Leonard Ciaccio of this Laboratory and of Charles Pfizer and Company.

[7] Gillespie, Graham, Hughes, Ingold, and Peeling, Nature 158, 480 (1956).

[8] The HSO_4^- ion absorbs near 1050 cm^{-1} [F. A. Miller and C. H. Wilkins, Anal. Chem. 24, 1253 (1952)] and the H_3O^+ ion absorbs near 1670 cm^{-1} [D. E. Bethell and N. Sheppard, J. Chem. Phys. 21, 1421 (1953) and reference 6].

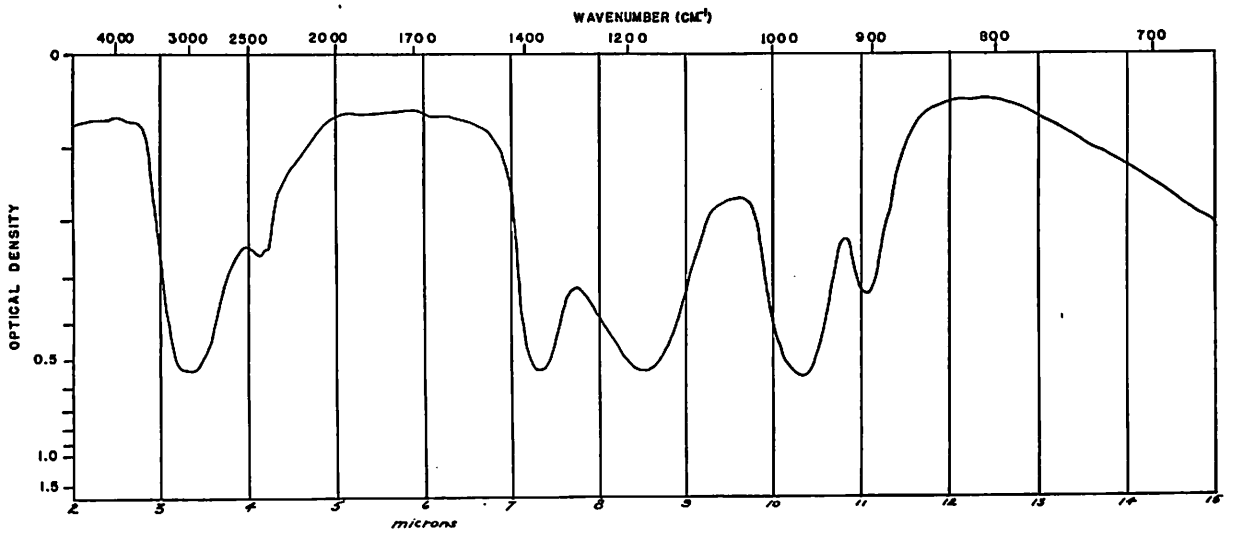

FIG. 4. Infrared spectrum of 99.8% sulfuric acid (cell thickness ~5 μ).

At the other end of the concentration range the effect of adding small amounts of "100%" sulfuric acid on the 2360 cm^{-1} nitronium band was investigated. The absorbance of the peak relative to that of the background, estimated in a fixed cell, is given in Table III. The background absorbance was found approximately[9] by drawing a straight line between two points (4.300 and 4.175 μ) of the spectral curve on either side of the nitronium peak and reading the absorbance of this line at 2360 cm^{-1}. The concentration of nitronium ion, inferred in this manner, increased in an approximately linear way with added sulfuric acid. Strong absorption by sulfuric acid in this cell prevented observations beyond 13 mole % H_2SO_4.

4. Phosphorous Pentoxide-Nitric Acid

The spectrum of a concentrated solution of phosphorous pentoxide in nitric acid, obtained without spacer, showed a relatively intense nitronium band at about 3735 cm^{-1}, indicating the production of large amounts of this ion

$$P_2O_5+6HNO_3=6NO_2^+ + 6NO_3^- + 2H_3PO_4.$$

The intensity of the 2360 cm^{-1} band relative to background was also marked, but was partly obscured by strong background absorbance.

5. Sodium Nitrate-Nitric Acid

Sodium nitrate decreased the intensity of the 2360 cm^{-1} band and caused new bands to appear at 821(w) and 1047(m) cm^{-1}. The absorbances of the 2360 and 1047 cm^{-1} bands are given in Table III as a function of added nitrate. The spectrum of an aqueous solution of 8M $NaNO_3$ was recorded for comparison. It showed absorption bands at 829(w), 1048(s), and 1379(s) cm^{-1}, in addition to water bands at 1646(m) and 3425(s) cm^{-1}.

The 821 and 1047 cm^{-1} bands in anhydrous sodium nitrate-nitric acid solutions can be assigned to the nitrate ion. In crystals this ion has vibration frequencies

TABLE III. Effect of added reagents on the absorbance of the 2360 cm^{-1} NO_2^+band, A.[a]

Reagent	H_2SO_4[b]		$NaNO_3$			KH_2PO_4		Ac_2O		H_2O	
cell length	20.2 μ		18.4 μ			21.0 μ		31.1 μ		20.1 μ	
HNO_3 assay	99.8%		99.6%			99.3%		99.1%		100.0%	
H_2SO_4 (mole %)	A		$NaNO_3$ (mole %)	A	A at 1047 cm^{-1}	KH_2PO_4 (mole %)	A	Ac_2O (mole %)	A	H_2O (wt %)	A
0	0.083		0	0.076	0.000	0	0.073	0	0.056	0	0.080
0.6	0.093		1.05	0.052	not run	0.93	0.046	8[c]	0.252	0.9	0.048
3.6	0.154		2.1	0.041	0.015	1.74	0.021	18	0.152	1.7	0.035
7.1	0.264		4.9	0.028	0.050	4.70	0.014	31	0.00	2.7	0.014
13.0	0.357		*ca* 7.5	0.022	0.064	10.37	0.01	47	0.01[5]	3.2	0.00[4]
								81	0.00	4.4	0.00[4]
										10.0	0.00

[a] A is the absorbance relative to background (compare text). When the added reagent was a liquid, A was corrected for the decreased nitric acid concentration by assuming volume additivity.
[b] H_2SO_4 assay =96.5%.
[c] Some decomposition evident.

[9] Heigl, Bell, and White, Anal. Chem. 19, 293 (1947).

TABLE IV. Absorption frequencies of aqueous nitric acid (cm^{-1}).

Assignment	Nitric acid (wt %) 90	80	70	25	12
$HNO_3 \cdot H_2O$	3560 w	3570 m			
H_2O				3400 s	3390 s
(7)	3280 m	broad	broad		
$HNO_3 \cdot H_2O$		3100 w			
$HNO_3 \cdot H_2O$	2960 w	2960 w	2960 w		
$2\times(1)$	2670 w	2680 w	2680 w		
(2)+(4)		2590 vw	2570		
HNO_3	2270 vw	2290 vw	2280 w		
(4)	1675 vs	1680 s	1675 s	1675 sh	
H_2O		1639 sh	1639 sh	1639 m	1639 s
NO_3^-	1390 sh	1414 m	1425 m	1410 s	1380 s
				1335 s	1340 s
(1)	1303 vs	1304 s	1304 s		
(2)	923 s	939 s	948 m	952 w	
NO_3^-				828 w	830 vw
(6)	769 m	775 m	777 m		
(3)	692 vw	690 w	692 w		

at 720, 831, 1390, and 1050 cm^{-1}, the first one being infrared weak and the last one being infrared inactive. The latter's strong occurrence in $NaNO_3-H_2O$ and $NaNO_3-HNO_3$ solutions can be attributed to a breakdown of symmetry owing to hydrogen bonding of this ion.

In $NaNO_3-HNO_3$ solutions a strong NO_3^- fundamental at 1380 cm^{-1} would be indistinguishable from the broad absorption of nitric acid in this region.

6. Potassium Dihydrogen Phosphate-Nitric Acid

Only the 2360 cm^{-1} band was examined closely. Its intensity decreased with added salt in a manner (Table III) analogous to that found with added nitrate. This suggests that in these media the following equilibrium is shifted to the right

$$KH_2PO_4+HNO_3=H_3PO_4+KNO_3.$$

7. Acetic Anhydride—Nitric Acid

The intensity of the 2360 cm^{-1} nitronium band, determined in various nitric acid-acetic anhydride solutions, is given in Table III. It is seen to increase at first with increasing acetic anhydride concentration and then to decrease. Assuming that nitrogen pentoxide forms some nitronium ion in these media, these observations are consistent with the following successive equilibria.

$$(CH_3CO)_2O+2HNO_3=N_2O_5+2CH_3COOH,$$
$$(CH_3CO)_2O+N_2O_5=2CH_3CO_2NO_2.$$

This supports a previous interpretation of vapor pressure measurements[10] of these solutions.

[10] R. Vandoni and R. Viala, Mém. serv. chim. état. (Paris) 32, 80 (1945).

8. Water—Nitric Acid

The absorption bands of various aqueous nitric acid solutions, obtained with a cell about 5 μ thick, are listed in Table IV. A spectrum of the 80% acid is given in Fig. 1(b). The effect of water on the nitronium ion band was studied quantitatively and is reported in Table III. In agreement with Raman studies, absorption by the ion disappears when the acid concentration falls to 95%.

Comparison of Tables I and IV reveals the following trends:

(1) In the region 100 to 70% HNO_3 the nitric acid bands arising from the unionized molecule do not change markedly in intensity. The 2290 cm^{-1} band behaves similarly, and partly for this reason was assigned in Sec. 1 to a combination or overtone of this molecule.

(2) The nitric acid bands disappear when the content of added water becomes large, and two new bands appear at 828 and 1380–1410 cm^{-1}. As discussed in Sec. 5 these can probably be assigned to the nitrate ion.

(3) Addition of water causes bands to appear at 3560, 3100, 2960,[11] and 690 cm^{-1} and then to disappear in solutions of higher water content. The first three bands and one at 2700 cm^{-1} have been observed in the Raman spectrum of aqueous nitric acid[12] and potassium nitrate-nitric acid solutions.[13] They were attributed to hydrogen-bonded structures, $H_2O \cdot HNO_3$ and $NO_3^- \cdot HNO_3$. In the present study the 2700 cm^{-1} band would be obscured by a broad nitric acid absorption near 2680 cm^{-1}.

The 690 cm^{-1} band occurs at the same frequency as vibration No. 3 of nitric acid (Table I). While this band is infrared weak or absent in the vapor state, distortion due to this hydrogen bonding with water could cause it to appear in the liquid.

CONCLUSIONS

The infrared spectra of highly reactive materials such as nitric and sulfuric acids can be conveniently studied in absorption cells having silver chloride windows and Teflon accessories. Information can be obtained in a variety of media about the behavior of the nitronium ion, about hydrogen-bonded structures, and about various equilibria which occur in these systems.

[11] In anhydrous nitric acid this band is indistinguishable from a nitric acid band at 3010 cm^{-1} but its intensity increases with addition of small amounts of water while that of the other nitric acid bands decreases.

[12] J. Chédin and S. Fénéant, Compt. rend. 224, 930 (1947).

[13] J. Chédin and S. Fénéant, Compt. rend. 228, 242 (1949).