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Letters to the Editor

*T*HIS section will accept reports of new work, provided these are terse and contain few figures, and espeically few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the first of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($4.00 per page) will not be made and no reprints will be furnished free.

Raman Spectra of Certain Phosphoric Acids and Their Salts

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*I*N investigating the Raman spectra of certain phosphoric acids and their salts several new lines were found. The wave number displacements were measured from the 4358-angstrom line and are tabulated as follows:

For tripotassium phosphate

Simon and Schultze:[1] 420, 562, 937, 1022.
Hoffman and Hanwick: 420, 573, 704, 936, 1014, 2385.

For dibasic sodium phosphate

Ventakeswaren:[2]   886, 971, 1085.
Hoffman and Hanwick: 381, 527, 860, 992.

Among compounds not previously investigated we have found the following:

For metaphosphoric acid

359, 494, 719, 887, 1081

For potassium pyrophosphate

328, 473, 698, 1014

This work is being extended, and depolarization measurements are in progress.

[1] Simon and Schultze, Zeits. f. anorg. allgem. Chemie **242**, 313–369 (1939).
[2] C. S. Ventakeswaran, Proc. Ind. Acad. Sci. **3A**, 25 (1936).

Effect of Temperature on the Absorption Spectrum of Ozone: Chappuis Bands

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*I*N 1882 Chappuis[1] observed, while examining through a spectroscope the ozone bands which he had discovered two years previously, that these bands became more visible when the gas was cooled to about −50°C. Mme. Lefebvre,[2] in 1935, found no appreciable effect of temperature on the same bands.

In 1937 one of the present authors (E.V.)[3] confirmed Chappuis' results and published a graph giving a quantitative estimate of the change in the absorption coefficients for different temperatures. Unfortunately, an error in the wave-lengths appeared in this graph, and the proper correction was made later in two different publications.[4,5]

Recently, G. L. Humphrey and R. M. Badger[6] reinvestigated the phenomenon of absorption in ozone and did not find, within the limit of photometric errors, any change when the temperature was decreased.

Because of the discrepancies in these results and the importance of ozone in the field of atmospheric optics, we have undertaken new computations on the plates obtained in 1937. At that time these spectrograms were only a secondary result in an extensive program, occasioned by the opportunity given by an experimental device which was convenient for checking this point of contention, but as the plates were photographed under strictly correct photometric conditions, they deserve a more detailed study. Moreover, we have now designed a more accurate microphotometer[7] which offers the advantage of constant precision for all densities.

The results definitely show the effect of temperature. The records of spectra of the same quantity of ozone at 20°C and at lower temperatures to −105°C show a perfect coincidence in the blue region where ozone is a weak absorber; they are markedly different in the region of the strong bands (6010 and 5734A).

Table I gives the absorption coefficient for different temperatures; those in column 2 were determined by one of the

TABLE I.

Wave-length A.U.	+18°C	−42°C	−80°C	−105°C
6010	0.068	0.072	0.078	0.083
5872	0.0575	0.595	0.067	0.0695
5730	0.062	0.067	0.075	0.0775
5600	0.052	0.056	0.0625	0.067
5400	0.038	0.042	0.0485	0.051
5056	0.021	0.0225	0.0265	0.0265
4800	0.0095	0.011	0.0115	0.0115
4500	0.0014	0.0015	0.0015	0.0015

authors (A.V.) in 1938.[8] It should be emphasized that the secondary maxima corresponding to Chappuis bands (Numbers 5, 6, and 8) are more prominent at low temperatures, as was reported by Chappuis. It has been suggested that the effect of temperature could be related to high concentrations of ozone. In fact G. L. Humphrey and R. M. Badger, and also Mme. Lefebvre, used low concentrations (6 percent), while we used a far higher one (between 60 and 75 percent). In Chappuis' experiments the concentration was low, about 5 percent. For this reason, the argument does not seem valid.

Concerning the atmosphere, Arnulf, Dejardin, and Falgon,[9] investigating the spectrum of atmospheric ozone, brought forward a very good verification of our numerical data. They first determined the ozone thickness and mean temperature in Huggins' bands using Ny and Choong's[10]

coefficients and the method proposed by one of the authors (E.V.). They found 0.290 cm and −35°C; next, with our temperature data and absorption coefficients (brought into agreement with Ny and Choong's) in Chappuis bands, they found 0.296 cm, pointing out that only this procedure gives a good agreement with the ultraviolet result.

We consider these comparative computations as a convincing proof of the influence of temperature on Chappuis bands in atmospheric ozone.

The conclusions resulting from the work of G. L. Humphrey and R. M. Badger raise another question. The measurements made at Mont Blanc by Arnulf, Dejardin, and Falgon are correct, because there is little or no more water vapor above this height. The situation is quite different at low altitudes, where the ozone bands are superimposed on the δ-band and rain bands of water vapor, and also on the α-oxygen band. The water-vapor bands are the more troublesome, and we gave numerical data concerning their contribution in our investigation of atmospheric absorption made in Morocco in 1938.[11]

[1] Chappuis, Ann. Ecole Norm. Sup. 11, 137 (1882).
[2] L. Lefebvre, Comptes Rendus 200, 653 (1935).
[3] E. Vassy, Ann. de physique 8, 679–778 (1937).
[4] A. Vassy and E. Vassy, J. de phys. et rad. 10, 408 (1939).
[5] E. Vassy, Ann. Astrophys., 5eme annee, No. 2, 82 (April, 1942).
[6] L. Humphrey and R. M. Badger, J. Chem. Phys. 15, 794 (1947).
[7] A. Vassy and E. Vassy, Sci. et Ind. Photo. 19, 56 (1948); 16, 1, 65 (1945).
[8] A. Vassy, Comptes Rendus 206, 1638 (1938).
[9] A. Arnulf, G. Dejardiñ, and Falgon, Comptes Rendus 205, 1086 (1937).
[10] Tsi-Ze Ny and Shin-Piaw Choong, Comptes Rendus 195, 309 (1932); 196, 916 (1933).
[11] A. Vassy and E. Vassy, J. de phys. et rad. 10, 75, 403, 459 (1939).

Nuclear Magnetism in Studies of Molecular Structure and Rotation in Solids: Ammonium Salts

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USING apparatus previously described,[1] we have carried out a series of measurements on the width and structure of nuclear resonance absorption lines in various types of solids at temperatures ranging from 90°K to room temperature. In crystal powders of certain ammonium salts,[2] the line width is found to undergo a relatively sharp transition at temperatures 100° or more below the well-known specific heat anomalies for these substances. Figure 1, which plots against temperature the width of the proton line in NH₄Cl, illustrates such a transition.
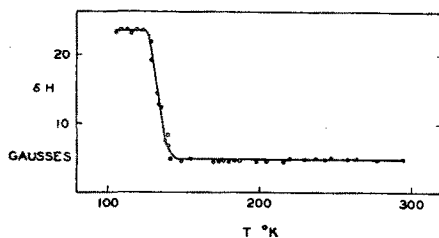

FIG. 1. Line width *versus* temperature for the proton resonance absorption line in NH₄Cl crystal powder.
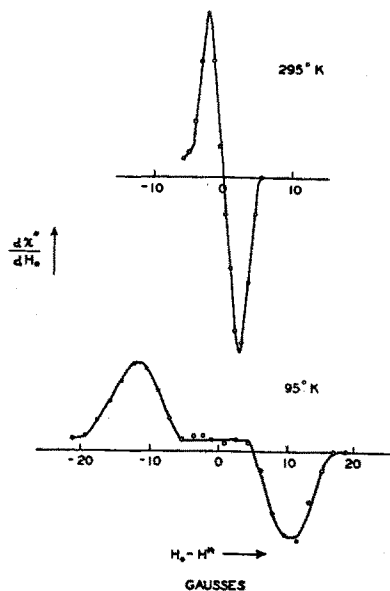

FIG. 2. Derivatives of the proton resonance absorption line in NH₄Cl crystal powder at 95°K and 295°K. H^* was approximately 6820 gauss.

In these experiments, "line width," denoted δH, is taken to be the width in gauss between points of maximum and minimum slope on the absorption curve, and is to be distinguished from the root-second-moment of the line, $\Delta H_2 = \langle (\Delta H)^2 \rangle_{Av}^{\frac{1}{2}}$. The proton line was observed at 29.0 megacycles/sec. for all salts investigated.

Of eleven ammonium salt powders investigated, NH₄Cl, NH₄Br, NH₄IO₃, and NH₄CNS were found to have proton line widths of approximately 20 gauss at our lowest attainable temperature of 90°K to 95°K. At higher temperatures, the line in each of these four salts undergoes transition, within a temperature interval usually smaller than 20°, to a narrower line of width from 3.5 to 5.3 gauss which remains essentially unchanged through the specific heat anomaly and up to room temperature. Line widths of the other ammonium salts fell between 2.6 and 6.6 gauss, staying nearly constant for a given salt over the entire accessible temperature range. Table I tabulates the values of the temperature T_w at the center of the line-width transition and the length of the temperature interval ΔT in which the transition takes place. For comparison, temperatures of the known specific heat anomalies are also given.

Figure 2 presents experimental absorption curves for the proton line in NH₄Cl crystal powder at 95°K and 295°K. The root-second-moment[3] computed from the curve for 95°K is $\Delta H_2 = 7.55$ gauss. Using the theory developed by Van Vleck,[4] and assuming that at temperatures below the line-width transition the ammonium tetrahedra are stationary with respect to the crystal lattice, one finds that a theoretical root-second-moment in agreement with experiment corresponds to an N−H interatomic distance in the tetrahedron of 1.01±0.01A. Since this is close to the N−H distance in the ammonia (NH₃) molecule, it appears that the broad lines indeed correspond to a crystal lattice in