

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

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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).

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³ E. Vassy, Ann. de physique 8, 679-778 (1937).

⁴ A. Vassy and E. Vassy, J. de phys. et rad. 10, 408 (1939).

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⁸ A. Vassy, Comptes Rendus 206, 1638 (1938).

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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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September 30, 1948

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 NH_4Cl , illustrates such a transition.

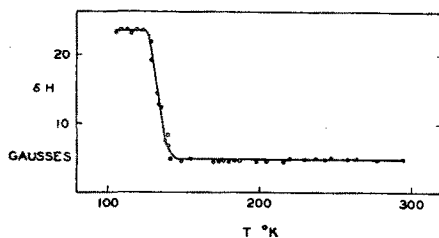


FIG. 1. Line width versus temperature for the proton resonance absorption line in NH_4Cl crystal powder.

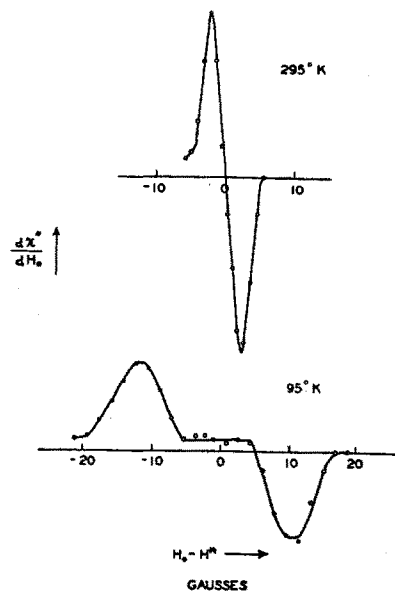


FIG. 2. Derivatives of the proton resonance absorption line in NH_4Cl crystal powder at 95°K and 295°K . H^* was approximately 6820 gauss.

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, $\Delta H_2 = \langle (\Delta H)^2 \rangle^{1/2}$. The proton line was observed at 29.0 megacycles/sec. for all salts investigated.

Of eleven ammonium salt powders investigated, NH_4Cl , NH_4Br , NH_4IO_3 , and NH_4CNS 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 NH_4Cl crystal powder at 95°K and 295°K . The root-second-moment³ 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 $1.01 \pm 0.01 \text{ \AA}$. Since this is close to the N-H distance in the ammonia (NH_3) molecule, it appears that the broad lines indeed correspond to a crystal lattice in

TABLE I.

Compound	Temperature T_w of line-width transition	Width ΔT of transition	Specific heat anomaly
NH ₄ Cl	133°K	16°	242.8°K
NH ₄ Br	108	16	235.2
NH ₄ I	< 95	—	230.7
NH ₄ IO ₃	120	7	—
NH ₄ CNS	100	20	—
NH ₄ NO ₃	< 95	—	212.8
(NH ₄) ₂ SO ₄	< 95	—	223.4

which the ammonium tetrahedra may be considered stationary. It has therefore been assumed in Table I that at sufficiently low temperatures the other ammonium salts will undergo similar line-width transitions.

It can be shown⁶ that the critical frequency above which relative nuclear motions should begin to narrow the absorption line is near the width, expressed as a frequency, of the broad line corresponding to the stationary nuclear configuration. We can account for the line width at temperatures just above the transition region by assuming hindered rotation or quantum-mechanical tunneling of the NH₄ tetrahedra at frequencies of the order of 100 kilocycles. Such a frequency will contribute negligibly to the specific heat.

The second-moment formula of Van Vleck has been used to investigate the nature of the rotation or tunneling of the ammonium tetrahedra above the line-width transition, and the results will be discussed in a more detailed account to be submitted to this journal.

In addition, the same theoretical considerations have been used in the interpretation of line-width transitions observed for the proton lines in a number of the simpler organic compounds. Also, the relation between the second-moment and interatomic distances in a stationary lattice has been used to determine molecular structure in several cases, including diborane, for which the experimental data support the ethylene-bridge structure. Reports of these experiments and findings are also in preparation.

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¹ G. E. Pake and H. S. Gutowsky, *Phys. Rev.* **74**, 979 (1948).

² F. Bitter and co-workers [*Phys. Rev.* **71**, 738 (1947)] have reported a qualitative observation that the proton line in NH₄Cl is slightly broader at low temperatures than at room temperature, but is consistently broad as is characteristic of normal solids.

³ G. E. Pake and E. M. Purcell, *Phys. Rev.* **74**, 1184 (1948).

⁴ J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

⁵ N. Bloembergen, E. M. Purcell, and R. V. Pound [*Phys. Rev.* **73**, 679 (1948)] give, on page 704, the general nature of the relation.

An Equation of State for Gases at High Pressures and Temperatures from the Hydrodynamic Theory of Detonation

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September 13, 1948

IN regard to the criticisms of my paper^{1,2} by Dr. Stewart Paterson^{3,4} I find, after looking more carefully into my method (a) solution of the equations of the hydrodynamic theory, that Dr. Paterson is correct in pointing out that

method (a) is an unsatisfactory solution. In carrying out the solutions by method (a), I was including, rather naively, a step which had been introduced as a convenient short cut in earlier studies by method (b) which, although I failed to realize it, actually did depend on the nature of the solutions of method (b). The data reported in my paper,¹ while calculated by the procedure in question (although not as described in reference 1) are actually identical with those which would be obtained by the direct application of method (b). The slight difference between the two curves of Fig. 1 of my paper was due to the use of slightly different detonation velocities. This was, in fact, mentioned in the paper of reference 1. As far as I am concerned, Dr. Paterson and I are now in agreement on all essential points of discussion. As a matter of fact, the recent work of Paterson⁵ together with the arguments in reference 1, I believe, present strong evidence for the validity of the equation of state

$$pv = nRT + \alpha(v)p$$

for gases under the conditions encountered in the detonation of solid and liquid explosives.

¹ Melvin A. Cook, *J. Chem. Phys.* **15**, 518 (1947).

² Melvin A. Cook, *J. Chem. Phys.* **16**, 554 (1948).

³ Stewart Paterson, *J. Chem. Phys.* **16**, 159 (1948).

⁴ Stewart Paterson, *J. Chem. Phys.* **16**, 847 (1948).

⁵ Stewart Paterson, *Research* **1**, 221 (1948).

The Vapor Pressure and Melting Point of Graphite

LEO BREWER

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September 24, 1948

IN a letter to this Journal, L. H. Long has listed four types of experimental data which he believes will not admit a value of 170 kilocalories for the heat of sublimation of graphite. Careful examination of these data indicate that they are not capable of contradicting a heat of sublimation of 170 kilocalories, an atmospheric sublimation point of around 4600°K, or a melting point of over 5000°K.

(i) At temperatures above 3400°K where the carbon partial pressure is above 1 mm, the smoke due to carbon gas condensing in the cooler portions of an apparatus invalidates direct observations of the temperature by an optical pyrometer. Thus the temperatures given by Ribaud and Begue,¹ Basset,² and others who have worked in this high temperature range are much too low. In addition, their degassing procedures were poor. Both these effects produce results which make carbon seem more volatile than it really is.

(ii) Long lists various values for the melting point of carbon. However, Steinle³ has clearly shown that these previous workers had not actually reached the melting point. The pressure work of Basset² and Steinle³ show that the triple point of carbon occurs above 100 atmospheres. From the vapor pressures given by Brewer, Gilles, and Jenkins,⁴ this must mean that carbon melts above 5000°K.

Carbon can be melted in contact with tantalum carbide at temperatures above 3300°C, but this is due to the eutec-