PHYSICAL REVIEW VOLUME 101, NUMBER 2 JANUARY 15, 1956

Interpretation of Spectra of Atoms and Molecules in Solid Nitrogen Condensed at 4.2°K†

C. M. HERZFELD AND H. P. BROIDA
National Bureau of Standards, Washington, D. C.
(Received October 13, 1955)

The emission spectra observed from solids condensed at 4.2°K from an electric discharge through nitrogen are explained by assuming that large numbers of nitrogen atoms are deposited in the process. Approximate calculations of the interactions of the atoms with the surrounding solid show that the observed shifts, splittings, and changes of half-life of some atomic lines have the proper direction and magnitude. Analysis of a new band system provides evidence for the formation of nitrogen molecules from atoms in the solid and provides information about a new electronic state of N_2 which may be the $^5\Sigma_g{}^+$ state. On this basis a lower limit of 9.632 ev can be given to the heat of dissociation of nitrogen.

1. INTRODUCTION

RECENTLY, techniques have been developed to condense short-lived species at low temperatures into solids.[1–3] Underlying all such attempts is the hope that unstable species have a long enough life at low enough temperatures to make extensive studies possible. Condensation, if successful, also promises to make possible the accumulation of appreciable quantities of active species. The solids which have been produced in this manner have often exhibited unusual properties which generally have been ascribed to the presence of some active species.

Once it can be shown beyond reasonable doubt that such solids contain active species in appreciable concentrations, and if means are found to study their properties quantitatively, a number of developments may be expected in the study of discharge and afterglow phenomena, chemical kinetics, and in this new area of solid state physics and chemistry.

We have been able to interpret, in some detail, the experiments of Broida and Pellam[3] on the phosphorescence of nitrogen condensed from an electric discharge and report the result in this paper. We show how these results can be understood if it is assumed that large numbers of nitrogen atoms in various excited states are deposited along with nitrogen molecules from the electric discharge. In fact, many of the spectroscopic results[4] can be explained as the radiation emitted by nitrogen atoms after deposition, and by the subsequent formation of nitrogen molecules in the solid.

Our considerations are as yet semiquantitative or qualitative on some points because of the complexity of the phenomena. However, detailed calculations are possible on some of these effects and are in progress. Although we cannot yet give a complete discussion of the various phenomena encountered, we believe that our point of view opens the possibility of quantitative study both experimentally and theoretically.

Various indirect pieces of evidence make our fundamental hypothesis, i.e., the deposition of large number of atoms in the solid, quite plausible. The presence of large quantities of atoms in certain electric discharges is well established.[5] The formation of solid ozone by condensing the products of a discharge in oxygen has recently been reported.[6] Chemical effects take place when first nitrogen and then oxygen products are deposited and allowed to warm up. We believe, however, that the detailed discussion in Sec. 3 gives the strongest confirmation of the general hypothesis.

2. THE EXPERIMENTS

The experimental setup, the procedure, the qualitative results,[3] and the observed details of the spectra[4] have been reported. Only the essential features of these experiments are presented here. Nitrogen gas is passed through an electric discharge at low pressure. The products of the discharge are pumped through a tube whose wall is kept near room temperature to prevent premature condensation at intermediate temperatures, and are finally collected on a surface kept at the normal boiling temperature of helium, about 4.2°K. While the discharge is running the condensation products emit a blue-green and a yellow-green glow. Occasional brilliant blue flashes are observed on the condensed material. When the discharge is turned off the yellow-green glow disappears immediately, and the blue-green glow continues with gradually diminishing intensity for several minutes. If, after the blue-green glow has subsided, the solid is allowed to warm up to about 35°K a blue flash or glow is observed, depending on whether the warmup is fast or slow.

Spectra of the several optical events indicated above have been obtained and measured[4] between 2300 A and 7000 A. The most prominent features (see Fig. 1) are listed in Table I and are arranged according to their general appearance. Measured wavelengths λ, wave numbers ν, and visual estimates I of relative plate

---

† This research was supported by the U. S. Air Force, through the Office of Scientific Research of the Air Research and Development Command, and by the Office of Naval Research.

[1] F. O. Rice and M. Freamo, J. Am. Chem. Soc. 73, 5529 (1951); 75, 548 (1953).

[2] P. A. Giguere, J. Chem. Phys. 22, 2085 (1954).

[3] H. P. Broida and J. R. Pellam, Phys. Rev. 95, 845 (1954).

[4] A. Bass and H. P. Broida (to be published).

[5] E.g. L. C. Copeland, Phys. Rev. 36, 1221 (1930).

[6] H. P. Broida and J. R. Pellam, J. Chem. Phys. 23, 409 (1955).

blackening are given. None of these lines and bands are observed in the discharge or in the gas afterglow.

3. THEORY OF THE PHENOMENA

The basis of our explanation of the phenomena described above is the assumption that appreciable numbers of nitrogen atoms in various excited states are produced in the electric discharge, that some of these atoms radiate on condensation, and that on subsequent heating of the condensed phase, atoms form nitrogen molecules in excited states which go to lower states by radiation.

We shall take up in succession the main types of radiation observed, and show how these can be interpreted.

A. The α Lines (Sharp, Blue-Green)

We propose that the α lines are due to radiative transitions from the excited metastable state $2p^3\,{}^2D$ of the N atom which is perturbed by the solid, to the ground state $2p^3\,{}^4S$ of the N atom.

In the free N atom two levels, $2p^3\,{}^2D_{5/2}$ and ${}^2D_{3/2}$, lie 19223 and 19231 cm^{-1} respectively[7] above the ground state $2p^3\,{}^4S_{3/2}$. Radiative transitions from these ${}^2D$ levels to the ground state are highly forbidden. They connect states whose spins differ and which have practically no spin-orbit coupling. They cannot be electric dipole transitions, hence they are at most electric quadrupole plus magnetic dipole transitions. These transitions are observed,[8] however, in the upper atmosphere with a half-life of about nine hours.

TABLE I. The intense lines emitted from the condensed solid nitrogen.

λ, *A* (air)	ν, cm^{-1} (vacuum)	*I*	v', v''
	1. The α lines, blue-green		
5214.2	19173.1	2	
5220.1	19151.4	8	
5228.5	19120.6	10	
5235.0	19096.9	6	
5240.4	19077.2	4	
	2. The β lines,[a] yellow-green		
5549	18016	8	
5616	17801	6	
5657	17672	2	
	3. The *A* bands, blue		
3572.4	27984.4	4	2,0
3769.5	26521.2	4	1,1
3986.4	25078.2	6	0,2
4224.1	23667.0	6	0,3
4487.8	22276.4	8	0,4
4782.0	20905.9	6	0,5
5111.7	19557.5	4	0,6
5483.3	18232.1	2	0,7
5906.1	16927.0	0	0,8
6390.5	15643.9	0	0,9

[a] The widths of these lines are about 100 cm^{-1}.

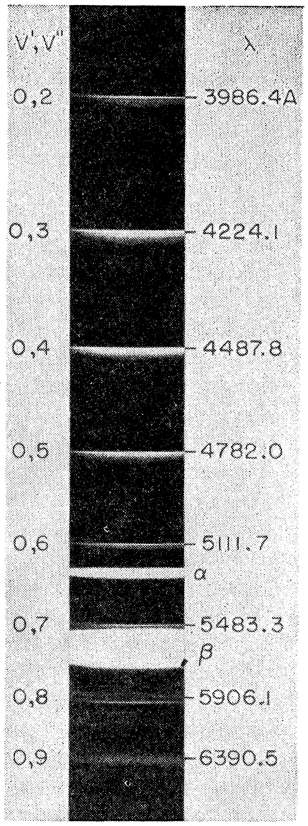

FIG. 1. Typical spectrum of condensation products. Four minute exposure on a red sensitive plate [103*a F* Eastman Kodak] with an *F*/4 glass spectrograph. The α and β lines are overexposed on this plate in order to emphasize the weaker *A* bands.

The small multiplet separation of the ${}^2D$ levels needs comment, because it complicates our interpretation. It is well known[9] that the levels ${}^4S$, ${}^2D$, and ${}^2P$ of the $2p^3$ configuration have zero spin-orbit coupling in the pure Russell-Saunders coupling case. The small split of -8 cm^{-1} of the ${}^2D$ multiplets cannot be ascribed to incipient breakdown of *LS* coupling, because in that case the ${}^2P$ level should show a corresponding multiplet separation, but this is not observed for nitrogen. Recently, Allen, Ufford, and Van Vleck[10] have studied the same effect in O$^+$ which is iso-electronic with N, and have found that spin-spin and spin-other-orbit interactions can account for the splitting of the ${}^2D$ levels.

The solid affects the levels of N atoms in a way which is formally equivalent to the Stark effect produced by crystal fields encountered in the study of the optical and magnetic properties of compounds of the transition elements.[11,12] The major difference in the N$_2$—N system is the fact that the forces acting on the N atoms probably arise from the electric quadrupole moments of the N$_2$ molecules, and are therefore much weaker and have

---

[7] *Atomic Energy Levels*, U. S. National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington 25, D. C., 1948), Vol. 1.

[8] G. Cario and L. H. Reinecke, Abhandlungen d. Braunschweiger Wissenschaftl. Gesellsch. **I**, 11 (1949).

[9] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), Chap. 7.

[10] Allen, Ufford, and Van Vleck, Astrophys. J. **109**, 42 (1949).

[11] B. Bleaney and K. W. H. Stevens, Repts. Progr. Phys. **16**, 108 (1953).

[12] J. Owen, Proc. Roy. Soc. (London) **A277**, 183 (1955)

much shorter range than do the forces occurring in crystals containing ions and electric dipoles. We expect therefore any splittings of levels of N atoms by the solid nitrogen to be much smaller than the splittings found in ionic systems, and the levels and hence the spectral lines of N atoms to be much sharper in the N_2 than in ionic systems. These splittings are, however, large compared to Stark splittings produced by laboratory fields.

The center of gravity of the transitions $^2D \rightarrow {}^4S$ in the free atom occurs at 19225 cm^{-1}, while the center of the α lines lies at about 19121 cm^{-1}, a shift of 104 cm^{-1} to the red. The over-all separation of the α lines is 96 cm^{-1}, which is comparable to the shift. The ground state, ^4S, will be split by the crystal field much less than one cm^{-1}. The effect arises only in very high approximation and it is too small to matter here. Hence all the separation of the α lines is due to the splitting of the ^2D levels. The magnitude of this splitting, the number of resulting levels, and the ratios of their separations depend on the details of the crystal field and of the multiplet separation of the free atom. Because of the short range of the forces, the field acting on the atoms depends mainly on the arrangement of the molecules nearest to the atoms. This arrangement is not yet known. In fact it is not certain whether the deposited material has the crystal structure of N_2 corresponding to the depositing temperature and contains the atoms as lattice defects, or whether the material is deposited in an amorphous layer whose structure is similar to that of a super-cooled liquid. Nor is it known whether the N atoms can occupy several distinct types of sites, or whether all sites are equivalent. A detailed crystal field calculation which takes into account the multiplet splitting of the free atom may enable one to limit the range of possibilities just described. At present we can give only a semi-quantitative discussion.

The field splitting is evidently larger than the multiplet separation, hence the action of the field on a D state gives the main effects. In a field of cubic symmetry a D state splits into two levels (in Bethe's notation[13]) $\Gamma_3^c(2)$ and $\Gamma_5^c(3)$, in a field of tetragonal symmetry into four levels $\Gamma_1^t(1)$, $\Gamma_3^t(1)$, $\Gamma_4^t(1)$, and $\Gamma_5^t(2)$, and in a field of rhombic symmetry into five levels which are orbital singlets. The numbers in parentheses after the term symbols give the orbital degeneracy of each level. The N atom has an odd number of electrons and therefore, by Kramers' theorem, each level retains at least the twofold spin degeneracy.

Five lines are observed. If the multiplet splittings of the free atom were zero then five lines would imply either one type of site and rhombic symmetry or several types of sites and symmetry higher than rhombic. We assume for the present one type of site and rhombic symmetry as the simpler hypothesis. The multiplet splitting is less than the field splitting, and so we ignore the multiplet splitting at present.

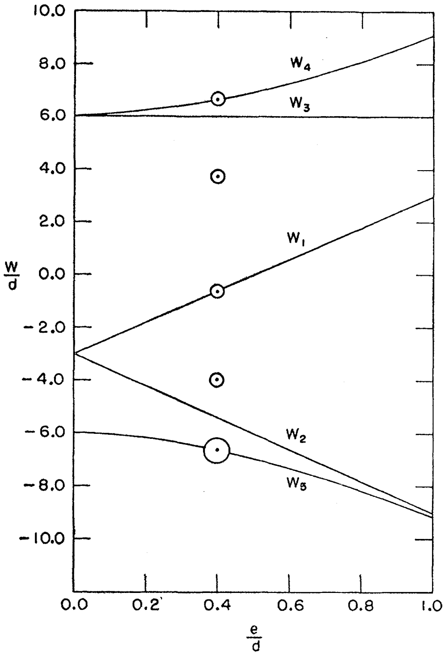

FIG. 2. Calculated energy levels of D state in a rhombic field and levels inferred from observed α lines.

Let the field have the form

$$V = \sum_i^N \left[a x_i^2 + b y_i^2 - (a+b) z_i^2 \right], \tag{1}$$

where x, y, and z are the coordinates of the electrons on the N atom, a and b are constants giving the field strength, and the summation extends over all electrons of the atom not in closed shells. With the matrix elements for V given by Schlapp and Penney,[14] the perturbed energy levels of the D state are

$$\begin{aligned} W_1 &= 6d, \\ W_{2,3} &= \pm(36d^2+48e^2)^{1/2}, \\ W_{4,5} &= -3d \pm 6e, \end{aligned} \tag{2}$$

where d and e are proportional to $(a+b)$ and $(a-b)$ respectively, and to $\langle r^2 \rangle$ of the p electrons on the N. It was pointed out above that it is possible to infer the separation of the upper levels from the observed α lines. These observed levels can be fit approximately to the predicted levels of Eq. (2). Figure 2 shows the theoretical levels as a function of e/d, and the observed levels with the values of d and e giving the best visual fit. When $d = 7.3$ cm^{-1} and $|e| = 2.9$ cm^{-1}, three of the observed levels fit within experimental error with those of Eq. (2), while the remaining two levels agree with the corresponding predicted levels to within the order of magnitude of the multiplet separation of the ^2D

---

[13] H. Bethe, Ann. Physik 3, 133 (1929).

[14] R. Schlapp and W. G. Penney, Phys. Rev. 42, 666 (1932).

state of the free atom, which has been ignored in this calculation. Hence the relative positions of the observed levels can be predicted as well as can be expected from this incomplete theory. The values of the parameters d and e will no doubt be refined when a more complete theory is worked out.

The shift of the center of gravity of the atomic lines cannot be explained by the simple arguments above. The simple crystal field theory predicts that the centers of gravity of levels belonging to the same configuration are not moved relative to each other. A shift of levels such as we note has, however, also been found by Owen,[12] in the transition element compounds. The shift of the α lines is toward the red, in the same direction as that found by Owen, and is much smaller than his, corresponding to the smaller splitting. The qualitative reason is probably the deformation of the radial wave function of the electrons on the N atom by the crystal field, via configuration interaction. This would change the Coulomb repulsion of the electrons and thus shift the center of the lines.

The average half-life of the α lines is about 15 seconds. According to our hypothesis this is the half-life of the ^2D components in the crystal field, and it is less than the free atom value by a factor of 10^3. This reduction is probably caused by the fluctuating asymmetric fields produced by the zero-point vibrations of the neighbors in the lattice, similar to the mechanism which makes the otherwise forbidden transitions in the transition element compounds weakly allowed.[15]

Among the very weak sharp lines coming from the solid, one is observed at 3469.6A. This can be identified similarly, with the forbidden transition $2p^3\,{}^2P\rightarrow 2p^3\,{}^4S$ which occurs at 3466.5A in the gas with a half-life of about one second.[8] The line from the solid is shifted to the red by 25.8 cm^{-1}. This shift has the same direction and similar magnitude to the shift of the $^2D\rightarrow{}^4S$ transition discussed above. The ^2P level is split by fields of rhombic symmetry, but because of the low intensity of the line it may appear as a single line.

To summarize, the α lines, together with the weak ultraviolet line mentioned correspond to all transitions among the levels of the $2p^3$ configuration which fall into the spectral region investigated. The effects of the crystal on the transitions can be understood qualitatively, though some questions of detail remain unanswered. A weak line at 5940 A with a half-life comparable to that of the α lines has not been identified.

B. The β Lines (Diffuse, Yellow-Green)

These lines are not observed in the discharge or in the stream of gas after the discharge, hence the half-lives of the upper states involved are probably long compared to the transit time from the discharge to the solid which is about 10^{-3} to 10^{-4} second. Moreover, since these intense lines disappear without visible time lag when the discharge is turned off, the half-lives are certainly less than 10^{-1} second. The gas flow rate and the geometry are such that in 10^{-2} second a layer is deposited which would be about two molecules thick if it were uniform. This means that the β lines come from species in the surface layer of the solid. We propose that these lines come from N atoms on various sites in the surface, and that the irregularities of the surface produce strong local variations in the crystal field and hence make the lines diffuse.

These lines can be explained in two different ways. Either the three β lines connect the levels derived from three pairs of free atom levels, then each β line corresponds to the whole set of α lines; or the three β lines connect three levels which all come from one pair of free atom levels, then the whole set of β lines corresponds to the set of α lines. The spectrum of N is very rich in highly excited levels having suitable energy differences, so it is possible to find plausible pairs of atom levels for either alternative, and no decision can be made on this basis. We believe, however, for the following reason that the second alternative is correct, i.e., that the whole set of β lines belongs to one free atom transition. In either of the two alternatives the levels needed to explain the transitions involve electrons with large principal quantum numbers, $n=4$ and larger, hence, their wave functions are widely spread out and the field splittings for these levels larger than for the α lines. But only the second alternative agrees with splittings much larger than that of the α lines. It is in fact possible to make some very rough numerical estimates. The field splitting is approximately proportional to the sum of $\langle r^2\rangle$ for the electrons, and $\langle r^2\rangle$ for H-like atoms is proportional to n^4. If we assume that the free atom transition $2p^2 5d\,{}^2D\rightarrow 2p^2 3p\,{}^4D$ gives rise to the β lines (it has a reasonable energy difference and is somewhat forbidden, hence may have a suitable half-life), then the field splitting of the β lines should be roughly ten times that of the α lines. The data in Table I show that the observed splitting is about five times that of the α lines.

Other transitions of N atoms could account for lines in this spectral region, so that it is not yet possible to identify the transitions unambiguously. Nor is it clear why, if the above explanation is correct other, analogous, systems of lines are not observed.

C. The A Bands (Blue)

Several systems of bands are observed in the radiation emitted from the solid, but they are not found in the discharge or in the gas afterglow. The most intense band system consists of sharp lines and we call it the A bands. The other systems are less intense and some of them consist of broad, diffuse regions of emission. It is possible to give a fairly complete discussion of the A bands which is quite consistent with the other features of the observations.

---

[15] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753, 766 (1954).

The A bands have been observed under high resolution only with the discharge on. Presumably they come from the blue flashes which occur when the discharge is on. However, they have been observed under low resolution, long after the discharge was turned off, in the blue glow which appears on heating the condensed products. No atoms or molecules are likely to remain in excited states for such long times. We propose, therefore, that the A bands arise from transitions connecting some molecular state newly formed from ground state N atoms, with some lower molecular state. On this basis it is possible to make a complete analysis of the A bands.

Four electronic molecular states can arise from two identical atoms in ^4S states. They are $X^1\Sigma_g{}^+$ which is the ground state of N_2, $A^3\Sigma_u{}^+$ the upper state of the Vegard-Kaplan bands, $^5\Sigma_g{}^+$, and $^7\Sigma_u{}^+$. The $^5\Sigma_g{}^+$ has been postulated by Cario[8] and others[16] to be a weakly bound state with large internuclear separation, in order to account by a predissociation mechanism for the unusually large populations of some vibrational levels of $B^3\Pi_g$ which have been observed. Our analysis indicates that the upper state for the A bands is indeed weakly bound and has a large internuclear separation and it is plausible to identify this upper state with Cario's $^5\Sigma_g{}^+$. According to our analysis the lower electronic state is $A^3\Sigma_u{}^+$.

Below about 35°K, N_2 molecules in the solid cannot rotate, while rotation begins near 35°K.[17] Therefore one or a very few lines correspond in the solid to each band in the gas spectrum. Each strong line of the A bands has one or two weak companions on the long-wavelength side.

The equation which fits the ten strong lines of the system is

$$\nu = 27961.1 + 12.1v' - (1462.2v'' - 10.20v''^2 + 1.6 \times 10^{-2}v''^3 + 1.0 \times 10^{-5}v''^6). \quad (3)$$

The assigned quantum numbers of each observed line are given in Table I. The equation fits the data extremely well, the mean absolute deviation between observed and calculated values for the ten lines is 0.5 cm^{-1}, no larger than the experimental uncertainty in the data.

The energy of dissociation of the upper state $^5\Sigma$ can be found from the energy of dissociation of the ground state and the energy difference of $A^3\Sigma$ and $X^1\Sigma$, if effects of the solid on these quantities are neglected. It is 1060 cm^{-1} if the energy of dissociation of N_2 in the ground state is 78776 cm^{-1} (9.764 ev). The vibrational frequency constant of the upper state is about 12.1 cm^{-1}, the anharmonicity is of the order of the experimental uncertainty. The observed lines are $v'=0 \rightarrow v''>1$, $v'=1 \rightarrow v''=1$, and $v'=2 \rightarrow v''=0$, and the Condon parabola is very flat with an intensity maximum for $v''=4$. This is consistent with a weakly bound upper state, with an internuclear separation much greater than that of the lower state. These properties of the state are quite similar to those postulated by Cario[8] for the $^5\Sigma_g{}^+$ and therefore we identify tentatively our upper state with the $^5\Sigma_g{}^+$ (Fig. 3).

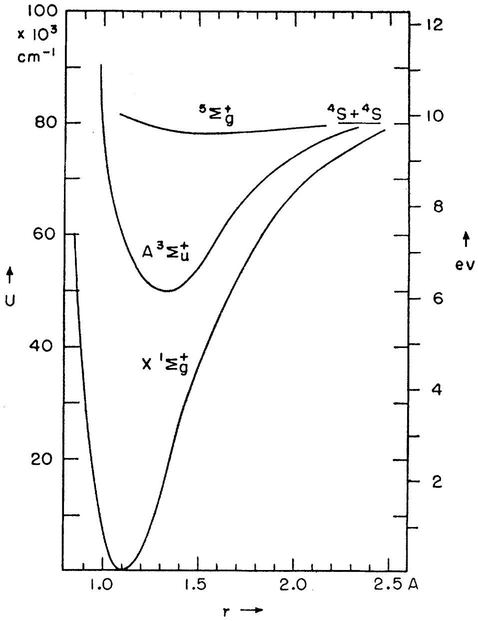

FIG. 3. Molecular states of N_2 coming from atoms in ground state.

The lower state is apparently the $A^3\Sigma_u{}^+$. The values of the constants in Eq. (3) differ somewhat from those given by Herzberg[18] or Bernard,[19] but agree much better with those for $A^3\Sigma_u{}^+$ than with those for other states. The force constant is increased by about 1% over the gas value and the anharmonicity decreased by about 20%. We ascribe these changes to the effects of the solid. It is known[20] from Raman spectroscopy that the separation between states $v''=1$, and $v''=0$ of the electronic ground state of N_2 in the liquid is not changed from the gas value. However, little is known about the potential curves of excited states of molecules in solids. Repulsion between neighboring molecules increases very rapidly with decreasing distance between them. Therefore, it is likely that a molecule in an excited electronic state (with r_0 greater than r_0 of the ground state) will be repelled more strongly by its neighbors than in the ground state. This will make it more difficult for the molecule to vibrate because it is "hemmed in" more, and hence the force constant would be expected to be

---

[16] J. Berkowitz, thesis, Chemistry Department, Harvard University, 1955 (unpublished).

[17] L. Vegard, Z. Physik **58**, 497 (1929); **88**, 235 (1934); M. Ruhemann, Z. Physik **76**, 368 (1932); W. F. Giauque and J. O. Clayton, J. Am. Chem. Soc. **55**, 4875 (1933); L. Pauling, Phys. Rev. **36**, 430 (1930).

[18] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. van Nostrand Company, New York, 1953), Vol. 1.

[19] R. G. Bernard, Proceedings of Conferences on Auroral Physics, Geophysical Research Papers No. 30, 243 (1954).

[20] K. W. F. Kohlrausch, *Eucken-Wolf Hand und Jahrbuch d. Chemischen Physik* (Akademische Verlagegesellschaft, Leipzig, 1943), Vol. 9, p. 68.

larger than in the gas and the anharmonicity smaller. Both observed changes are in these directions; hence we believe they are qualitatively explained.

The "high" value of 9.764 ev of the heat of dissociation[18,21] of N_2 is used in our analysis, while the "low" value of 7.373 ev is not consistent with the results and our explanation. The A bands have been observed when the combining atoms were in the ground state, hence the upper state of the A bands is formed from ground-state atoms. The upper state of the bands is about 28 000 cm^{-1} above the $A^3\Sigma_u^+$. The "low" value rules out an upper state more than about 10 000 cm^{-1} above $A^3\Sigma_u^+$. In fact, our interpretation using the $A^3\Sigma_u^+$ level as the lower state of the A bands puts a lower limit of 9.632 ev on the heat of dissociation, very close to the "high" value.

The weak lines which are observed toward the red of each strong line have a diffuse appearance. They may arise from the levels of hindered rotation of the N_2 molecules in the $A^3\Sigma_u^+$ state in the solid. Thus the sharp intense lines may arise from transitions to the lowest level of hindered rotation, a sharp level associated with a rocking motion of the molecule. The weak diffuse lines may arise from transitions to the upper levels of hindered rotation, which may (because of cooperative effects) be diffuse. This is offered as a possible interpretation only, since the data are not complete enough to allow a definite explanation of these weak companion lines.

To summarize, the analysis of the A bands identifies the lower electronic state as $A^3\Sigma_u^+$, and gives some new quantitative information about the upper state $^5\Sigma_g^+$. Only the "high" value for the heat of dissociation of N_2 is consistent with the analysis presented here.

4. DISCUSSION

We have shown how the blue-green spectral emission of long persistence, the α lines, can be interpreted by assuming that the lines arise from transitions from the metastable state ^2D to the ground state ^4S, of nitrogen atoms. The semiquantitative treatment of the effects of the neighbors in the solid on the transition gives results in reasonable agreement with the observations. Further detailed calculations are needed to provide a complete explanation of the experimental results.

The analysis of the blue glow, the A bands, as electronic-vibrational transitions between states of nitrogen molecules gives excellent agreement with experiment. The transitions come apparently from a weakly bound excited state and go to the well-known $A^3\Sigma_u^+$. The upper state may be the state $^5\Sigma_g^+$, postulated before but previously not observed directly. Our analysis provides the heat of dissociation (1060 cm^{-1}), the vibrational frequency constant (12.1 cm^{-1}), and an approximate value of r_0 ($r_0 \approx 1.5$A) for this state. The analysis further leads to a lower limit for the heat of dissociation of nitrogen of 9.632 ev, which is only slightly less than the "high" value of 9.764 ev.

The tentative explanation of the yellow-green diffuse lines, the β lines, is quite uncertain. This is partly because the lines are so diffuse, hence difficult to assign and partly because of the many atomic transitions which might contribute to these lines.

Among the many important problems which remain unsolved are the structure of the deposited solid which determines the crystal field acting on the atoms, the nature of the weak companion lines of the A bands and their possible relation to the levels of hindered rotation, the mechanism of formation of the upper state of the A bands including the question whether atoms diffuse through the solid, and finally the rather striking absence of any well-developed sequences of the Vegard-Kaplan bands. Our analysis indicates that the lower state of the A bands is the upper state of the Vegard-Kaplan bands and it is not clear why the latter should not be observed.

It is interesting to note that Vegard[22] and McClennan and Shrum[23] were the first to observe the α and β lines some 30 years ago, when they bombarded solid nitrogen with electrons and positive ions. It was in these experiments that Vegard first observed the Vegard-Kaplan bands. These authors recognized the general significance of their results and Vegard stressed the importance of interactions in the solid, but at that time theory was not sufficiently developed to allow a detailed interpretation. McClennan, Ireton, and Thompson[24] observed as many as eight lines in the α group. In the light of modern theory and our hypotheses, this implies directly that they had atoms in excited states roughly equally distributed over at least two significantly different types of sites. Because their systems were prepared by particle bombardment this is not unlikely.

A final confirmation of the validity of our hypotheses depends on the outcome of more detailed calculations on the effects of neighbors on nitrogen atoms and molecules. However, the over-all agreement of the observed effects with those predicted on the basis of our hypotheses gives good indication that the basic argument about the existence of appreciable numbers of atoms in the solids is sound.

---

[21] A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, Ltd., London, 1953).

[22] L. Vegard, Nature **113**, 716 (1924); Ann. Physik **79**, 377 (1926).

[23] J. C. McClennan and C. M. Shrum, Proc. Roy. Soc. (London) **A106**, 138 (1924).

[24] McClennan, Ireton, and Thompson, Nature **118**, 408 (1926).

FIG. 1. Typical spectrum of condensation products. Four minute exposure on a red sensitive plate [103*a* *F* Eastman Kodak] with an *F*/4 glass spectrograph. The α and β lines are overexposed on this plate in order to emphasize the weaker *A* bands.