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## Intensities of Electronic Transitions in Ammonia

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Absolute intensity measurements of the transitions in ammonia vapor with maxima at 52,500, 66,000, and 77,000  $\text{cm}^{-1}$  are reported. Calculations are made of the intensities of the first and third transitions, using non-bonding nitrogen orbitals, of the form suggested by Slater. The calculated values are considerably lower than the measured values, but may be improved by variation of the effective nuclear charge. Similar calculations for the second transition are less conclusive, but seem to indicate that it also may originate from a nearly non-bonding nitrogen orbital. Some other possible origins of this transition are considered and rejected on the basis of either their energy or their intensity.

### INTRODUCTION

PREVIOUS investigation of the absorption spectrum of ammonia vapor<sup>1,2</sup> has revealed the presence of four electronic levels in the frequency range 45,000–120,000  $\text{cm}^{-1}$ . We report here absolute intensity measurements of transitions from the normal level to the two lowest of these electronic levels, designated as transitions I and II, with intensity maxima at about 52,500 and 66,000  $\text{cm}^{-1}$ . In addition, the intensity of the transition III with maximum at about 77,000  $\text{cm}^{-1}$  may be estimated by comparison with I and II using previously obtained appearance-pressure data. There appears to be little hope of obtaining a direct measurement of the intensity of III or IV with present experimental techniques.

As is well known, an experimental value of the absolute intensity of absorption associated with an electronic transition in a pure vapor is

found by evaluation of  $\int \alpha_\nu d\nu$  over the entire absorption region. At a single frequency,  $\alpha_\nu = (1/I_0) \log_e (I_0/I)$ , where  $I_0$  is the intensity of the incident light and  $I$  is the intensity after passage through a column of the absorbing gas of length  $l_0$  measured at 0°C and 760-mm pressure. The light source used should emit sharp, well-resolved lines of known frequency, well distributed over the wave-length region in question.

Values of  $\alpha_\nu$  in  $\text{cm}^{-1}$  are plotted against wave number, and the value of  $\int \alpha_\nu d\nu$  determined with a precision planimeter. The value of the integral multiplied by  $mc^2/n\pi e^2 (= 4.2 \times 10^{-8} \text{ cm}^2)$  gives the  $f$  number or oscillator strength of the transition. In order to compare experimental intensities with calculated values, we may compute the square of the dipole moment integral (in square angstroms) from the approximate relation

$$Q^2(\text{exptl}) \cong (3hf/8\pi^2\nu mc) \times 10^{16} (\cong 9.12 \times 10^4 f/\nu_m),$$

where  $\nu_m$  is the wave number of the intensity maximum of the transition.

\* Part of a dissertation presented to the Faculty of the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>1</sup> A. B. F. Duncan, Phys. Rev. **47**, 822 (1935).

<sup>2</sup> A. B. F. Duncan, Phys. Rev. **50**, 700 (1936).

Two methods of photographic photometry may be used to evaluate  $I_0/I$  at a single known frequency from measurements of photographic density. In both methods the intensity of the source must be kept as constant as possible. In the first method (intensity scale method) the intensity through the absorption cell is varied by a system of calibrated diaphragms. On each plate a series of exposures for equal time intervals is made through each of the diaphragms with the cell evacuated, then one or more exposures are made through one of the diaphragms with the cell filled with vapor at a measured pressure.

For every line within the absorption band, a series of density values corresponding to the series of exposures is recorded with a Moll type microphotometer. From a plot of density against  $\log_{10} (I_0/I)$  for each line,  $I_0/I$  for the exposure through the vapor, and hence  $\alpha_\nu$ , may be obtained directly.

In the second method (time scale method) the intensity through the evacuated cell is kept constant and a similar series of exposures is made for different time intervals. In this case, density  $-\log$  time curves give  $\log_{10} (t_0/t)$ , which is equivalent to  $\log_{10} (I_0/I)$  by the usual photographic reciprocity law. The exposure through the vapor is then made for time  $t_0$ . In this work we have used both methods.

The general method outlined in the preceding five paragraphs should give correct intensity values in the case of strictly continuous spectra. While the absorption spectrum of ammonia is not truly continuous, it approximates continuity sufficiently under the experimental conditions used here, since  $\alpha_\nu$  does not change anywhere very abruptly with frequency. At considerably lower pressures than were used in the present work and with slit widths 0.008–0.015 mm, vibrational structure is easily resolved, and in transition II, rotational structure is partly resolved.<sup>1</sup> In the present work, with slit 0.2 mm wide, and with pressures 5–10 times that used to resolve fine structure, vibrational structure can be recognized as broad low maxima in the absorption curves for transition II. The frequencies, at which  $\alpha_\nu$  were measured, are sufficiently close together to show the detailed shapes of these curves. Not even vibrational maxima

are clearly recognized in the curves for transition I, and no rotational structure is apparent in any case.

The integrated absorption coefficients for transitions I and II are independent of the pressure in the range used, or rather, any pressure dependence is concealed and included in the total experimental error in the  $f$  numbers (5–10 percent).

## EXPERIMENTAL

The ammonia gas used in this study was purified by a large number of distillations in vacuum through KOH pellets, and subsequent fractionation. It was dissolved in dried  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{SCN}$  in the molar proportions 1:3 for storage, the resulting solution giving a convenient  $\text{NH}_3$  pressure of about 180 mm. The desired pressures were obtained by expansion through calibrated volumes, and the pressure in the cell was read with a McLeod gauge.

The apparatus used to study transitions I and II was in all essentials the same as that of Ladenburg and Van Voorhis<sup>3</sup> and need not be described in detail. The background for observation of absorption was a discharge in pure  $\text{CO}_2$  for the region 45,000 to 61,000  $\text{cm}^{-1}$  (transition I) and in pure  $\text{H}_2$  for the region 60,000 to 71,000 (transition II). In the former case the well-known  $A^1\Pi - X^1\Sigma$  bands of CO appeared with great intensity and the heads were sufficiently sharp to serve as lines for photometric measurement. The wave-lengths given by D. N. Read<sup>4</sup> were used. In the second case the rotational lines in the  $\text{H}_2$  bands of the Lyman ( $^1\Sigma_u^+ - ^1\Sigma_g^+$ ) system<sup>5</sup> were used.

The discharge tube was operated at a constant direct current of 0.065 ampere through a voltage regulator and a transformer-rectifier unit. Less than 0.001-ampere variation in current was observed with the longest exposures. The light from this discharge was made parallel by a LiF lens, passed through an absorption cell 17.7 cm long, and was focused on the slit of the vacuum spectrograph by a second LiF lens. The spectra were photographed from a 2-meter radius,

<sup>3</sup> R. Ladenburg and C. C. Van Voorhis, *Phys. Rev.* **43**, 315 (1933).

<sup>4</sup> D. N. Read, *Phys. Rev.* **46**, 571 (1934).

<sup>5</sup> T. Lyman, *Astrophys. J.* **23**, 181 (1906).

TABLE I.

Transition	Frequency maximum (cm <sup>-1</sup> )	Assumed type	Q/a <sub>0</sub>		f	
			obs.	calc.	obs.	calc.
I	52500	2p <sub>z</sub> -3s	0.90	0.29	0.13	0.0134
II	66000	2p <sub>z</sub> -3d <sub>z</sub>	0.22	0.092	0.0095	0.0017
III	77000	2p <sub>z</sub> -4s	0.52	0.02	0.064	0.0001
IV	85000	2p <sub>z</sub> -5s	—	0.01	—	0.00003

120,000-line grating, used in the first order.<sup>6</sup> The dispersion was about 4.15Å per mm. The exposure times were 40 to 60 minutes. Eastman III-O and I-O ultraviolet sensitized plates were used, and were processed with the special precautions required in photographic photometry.

The decrease in effective transmission of the LiF lenses became quite appreciable below 1400Å (70,000 cm<sup>-1</sup>) when used in the optical system described. To observe transition III (and IV, with maximum at 85,000 cm<sup>-1</sup>) would have required prohibitively long exposures. We considered the possibility of using the spectrograph as an absorbing column and moving the discharge close to the slit, with a very thin LiF plate separating the two. However, we did not believe that the pressure of ammonia could be maintained sufficiently constant in the spectrograph, especially at the low pressures required.

### RESULTS

Seven plates, four on the intensity and three on the time scale, were used to obtain  $\int \alpha_\nu d\nu$  for transition I. The pressure of ammonia ranged from 0.150 to 0.875 mm, the most useful range being 0.2 to 0.5 mm. For transition II eight plates on the intensity scale and one on the time scale were used. The pressure range was 0.3 to 3.0 mm, the most useful range being between 1.0 and 2.0 mm. The results from the intensity and time scales checked within the experimental accuracy. Reciprocity law failure was negligible in these experiments.

Average experimental values of the dipole strength  $Q$  and the  $f$  number of transitions I, II, and III are given in Table I, together with two sets of calculated values for transitions I, II, III, and IV. These calculations will be discussed in the next section.  $a_0$  is 0.528Å, the Bohr radius of the normal hydrogen atom.

<sup>6</sup> A. B. F. Duncan, J. Chem. Phys. **8**, 444 (1940).

The experimental results for transitions I and II are estimated to be accurate to within 5 to 10 percent. The indirect values for transition III are subject to somewhat larger error, although this is not necessarily much larger. The probable accuracy of these values is difficult to estimate.

### DISCUSSION OF RESULTS

The electronic configuration of the ground state of ammonia, omitting the 1s electrons of N, is given by Mulliken<sup>7,8</sup> as  $(sa_1)^2(\pi e)^4(za_1)^2$ . The orbital  $sa_1$  is primarily a N atom 2s orbital which, however, contributes a little to the three N-H bonds. The two  $\pi e$  orbitals are strongly bonding. The orbital  $za_1$  is non-bonding and is approximately just a 2p<sub>z</sub> orbital of the N atom. Mulliken suggests that the lower excited states correspond to the excitation of one  $za_1$  electron from this configuration, and that the lowest electronic transition should be  $2za_1-3sa_1$ .

### Dipole Moment Integrals for Transitions I, III, and IV<sup>9</sup>

We have assumed that the transitions  $(za_1) - (nsa_1)$  in ammonia may be approximated, for the purpose of intensity calculations, by the transitions  $2p_z - ns$  in the N atom. The dipole moment integrals will be of the form

$$Q = Q_z = (2)^{\frac{1}{2}} \int \psi_{2p_z} z \psi_{ns} d\tau$$

and may be evaluated in spherical polar coordinates, with  $z = r \cos \theta$ . The factor  $(2)^{\frac{1}{2}}$  allows for the fact that there are two equivalent 2p<sub>z</sub> electrons, either of which may make the transition. The functions  $\psi_{2p_z}$  and  $\psi_{ns}$  may be approximated

<sup>7</sup> R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933).

<sup>8</sup> R. S. Mulliken, J. Chem. Phys. **3**, 506 (1935).

<sup>9</sup> The general method used here is discussed by R. S. Mulliken, J. Chem. Phys. **7**, 14 (1939); *Reports on Progress in Physics* (1941), Vol. VIII.

by the radial functions given by Slater,<sup>10</sup> multiplied by the appropriate angular factors. The normalized radial parts of the functions are:

$$R_{nl}(r) = \frac{(2Z^*/n^*)^{n^*+\frac{1}{2}}}{a_0^{\frac{1}{2}}(\Gamma(2n^*+1))^{\frac{1}{2}}} (r/a_0)^{n^*-1} \times \exp[-(z^*r/n^*a_0)].$$

The complete  $\psi_{2p_z}$  function is obtained by multiplying  $R_{2p}(r)$  by  $(6)^{\frac{1}{2}} \cos \theta / (2\pi)^{\frac{1}{2}}$ ; the complete  $\psi_{ns}$  function is obtained by multiplying  $R_{ns}$  by  $(2)^{\frac{1}{2}} / (2\pi)^{\frac{1}{2}}$ .  $a_0$  is the radius of the Bohr orbit on normal hydrogen. Substitution of these functions and integration yields

$$\frac{Q}{a_0} = (2)^{\frac{1}{2}} (3)^{\frac{1}{2}} / 3 \left\{ \frac{(2Z_1^*/n_1^*)^{n_1^*+\frac{1}{2}} (2Z_2^*/n_2^*)^{n_2^*+\frac{1}{2}}}{[\Gamma(2n_1^*+1)\Gamma(2n_2^*+2)]^{\frac{1}{2}}} \right. \\ \left. \times \left\{ \frac{\Gamma(n_1^*+n_2^*+2)}{[(Z_1^*/n_1^*)+(Z_2^*/n_2^*)]^{(n_1^*+n_2^*+2)}} \right\} \right\}. \quad (1)$$

The factor  $(3)^{\frac{1}{2}}/3$  is the result of integration over the angles  $\theta$  and  $\phi$ . Subscripts 1 and 2 refer to the lower ( $2p_z$ ) and upper ( $ns$ ) states.

The values of the parameters  $Z^*$  and  $n^*$  in the states considered are given by Slater as:

State	$2p$	$3s$	$4s$	$5s$
$Z^*$	3.9	1.6	1.0	1.0
$n^*$	2.0	3.0	3.7	4.0

The values of  $Q/a_0$  calculated with these values of the parameters are listed in Table I. The values of  $f$  were calculated for the transitions  $2p_z - ns$  on the assumption that these correspond to the observed transitions I, III, and IV, which were found earlier<sup>2</sup> to fit into a Rydberg series.

Table I shows that the experimental values of the dipole moment integrals associated with transitions I and III and the values calculated by means of Slater functions differ by factors of 3 and 26, respectively. The experimental value of the mean oscillator strength  $f$  (which is proportional to the intensity of the transition) is 10 times the calculated value for transition I and 550 times the calculated value for transition III.

This disagreement between theory and experiment may be considered from two viewpoints. First, the electron involved in the transitions I and III may not be completely non-bonding.

Second, the functions used in the numerical evaluation of the dipole moment integrals are probably crude approximations to the true functions. Even if the form of the wave functions is approximately correct, the appropriate values of the parameters  $Z^*$  and  $n^*$  for our use may not be those given by Slater.

The first viewpoint suggests that improvement in the calculated values may result from admixture of the orbitals  $2s(N)$ ,  $2p_z(N)$ , and  $1s(H)$  for the normal state wave function (as suggested by Mulliken<sup>7</sup>). Perhaps the upper states in the transitions should not be regarded as pure N atom states and a linear combination of orbitals should be used there also. Calculations employing such mixed functions appear to offer considerable difficulty and may be inconclusive in view of the undetermined coefficients appearing in these linear combinations. We have not made such calculations.

The second viewpoint suggests that we might vary  $Z^*$  in the Slater function to obtain better agreement between calculation and experiment. The variation of Slater's  $Z^*$  has been discussed by Mulliken.<sup>11</sup> We have varied the  $Z^*$  in Eq. (1) and find that if  $Z_{2p}^*$  is to be near the Slater value 3.9, then  $Z_{3s}^*$  must be increased to about 3.5 to get agreement with experiment in transition I. This is indeed a large increase, in comparison with the increases suggested by Mulliken in other cases.

This large increase in  $Z_{3s}^*$  appears improbable on the basis of simple energy considerations, such as have been used by Slater. Using the method of reference 10, the lowest ionization potential of ammonia, taken as the energy difference of the configurations  $1s^2 2s^2 2p^2 - 1s^2 2s^2 2p^3$  is close to the experimental value (11.56 ev obs., 12.88 calc.). Similarly, with  $Z_{3s}^* = 1.6$ , the Slater value, the difference between  $1s^2 2s^2 2p^2$  and  $1s^2 2s^2 2p^2 3s$  is 3.85 ev (obs. in ammonia, 5.05). An increase of  $Z_{3s}^*$  to 1.8 gives exact agreement with the observed term value, while an increase to 3.5 gives a term value greater than the normal state. It is uncertain how seriously these energy calculations should be considered.

It is well known that the upper level of

<sup>10</sup> J. C. Slater, Phys. Rev. **36**, 57 (1930).

<sup>11</sup> R. S. Mulliken, J. Chem. Phys. **8**, 234 (1940); *Reports on Progress in Physics* (1941), Vol. VIII, pages 244, 250, 269.

transitions I in ammonia is predissociated. The origin of this predissociation has not been examined theoretically in detail. If the perturbation causing the predissociation is merely of a vibrational nature, it should have no effect in a comparison of experimental and theoretical intensities. If the perturbation is caused by another electronic level, the experimental intensity may well be higher than the intensity calculated for a single, atom-like transition. It appears at least that no simple explanation can be offered at the present time for the intensity of transition I.

### Discussion of Transition II

It was suggested previously<sup>2</sup> that this transition might be to a triplet level associated with the upper level of transition III. From the present quantitative measurements, the experimental ratio of intensities of III to II is about 7:1, which appears to be too low for a singlet-triplet ratio. In some previous unreported work, we looked for transitions at frequencies lower than transition I, in an absorption tube 10 meters long with ammonia at one atmosphere pressure. None was found, indicating a very low intensity for any possible triplet transition associated with I. We would expect the triplet associated with III to have an even lower intensity. Accordingly, we withdraw this previous suggestion.

We will discuss briefly other possible explanations for this transition. Discussion will be limited to parallel transitions, since analysis of the rotational structure of the bands of transition II showed it to be of this type.<sup>12</sup>

Of the other atom-like transitions of a  $za_1$  electron we considered  $2za_1-3da_1$ , which we have assumed may be approximated by the N atom  $2p_z-3d_z$  transition. The dipole moment integral

<sup>12</sup> A. B. F. Duncan and G. R. Harrison, Phys. Rev. **49**, 211 (1936).

was calculated in the same way as before. The value of the integral is given by Eq. (1), except that integration over the angles now gives  $2(15)^{1/2}/15$ . The calculation was made using Slater's value of  $Z_{2p}^*=3.9$ ,  $Z_{3d}^*=1.0$ ,  $n_{2p}^*=2.0$ , and  $n_{3d}^*=3.0$ . The experimental and calculated results are compared in Table I. If  $Z_{3d}^*$  is increased from 1.0 to 1.5, complete agreement with experiment is obtained, without adjustment of any other parameters. By analogy with the energy levels of the nitrogen atom, this transition should occur at a higher frequency (about 80,000  $\text{cm}^{-1}$ ) in ammonia. However, as Mulliken points out,<sup>8</sup> the lower members of the Rydberg series in a polyatomic molecule may show abnormalities because of their relationship to orbitals in the core. For example, the frequency of transition I in ammonia is about 13,000  $\text{cm}^{-1}$  lower than would be expected by analogy with the corresponding transition in nitrogen. The transition  $2p_z-3d_z$  should therefore be considered as a possible explanation for transition II.

Transition II may, however, be caused by excitation of another electron in ammonia. The estimated ionization potential of an  $sa_1$  electron is given as 27 volts,<sup>8</sup> which indicates that even the first member of the  $(sa_1-nza_1)$  series should lie above the ionization potential of the  $za_1$  electron, and should not appear in the spectral region investigated. The ionization potential of a  $\pi e$  bonding electron is estimated to be about 16 volts, so it is quite possible that the first transition due to this electron may be in the region of transition II. The possible transitions consistent with parallel rotational structure are the  $N-V_\pi$  bonding to anti-bonding transition and the  $(\pi e)-(\pi e)'$  bonding to bonding transitions in which the upper state orbitals may possess atom-like characteristics. It should be interesting to attempt calculations of the intensities of such transitions in ammonia.