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THE IONIZATION BY SLOW ELECTRON IMPACT OF AMMONIA AND HYDROGEN SULPHIDE

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ABSTRACT

The molecules of ammonia and hydrogen sulphide have been studied by the usual method of positive-ray analysis, such as used by Dempster, Smyth, and others. In the case of ammonia, three principal types of ion at $m/e = 15$, 16 and 17, respectively, occurred. These are interpreted as having the compositions $(NH)^+$, $(NH_2)^+$, and $(NH_3)^+$, with *ionization potentials* of 11.2 ± 1.5 volts, 12.0 ± 1.5 volts, and 11.2 ± 1.5 volts, respectively. Since, with increasing pressure, the $(NH)^+$ ion increases, the $(NH_2)^+$ ion remains sensibly constant, and the $(NH_3)^+$ ion decreases, it is concluded that the $(NH_3)^+$ and $(NH_2)^+$ ions result directly from the electron impact with the neutral NH_3 molecule, while the $(NH)^+$ ion is probably produced by breakdown of the $(NH_3)^+$ ion by a reaction such as $(NH_3)^+ + NH_3 = (NH)^+ + H_2 + NH_3$. For both ammonia and hydrogen sulphide, very few, if any, hydrogen ions and no negative ions were observed, tending to show that thermal dissociation was of little importance in affecting the results. For ammonia, very small peaks at $m/e = 14$ and 18, respectively, were observed. Their compositions are probably $(N)^+$ and either $(NH_4)^+$ or $(H_2O)^+$, and their origin is either secondary (from collision of ions with neutral molecules) or they result from impurities. In the case of hydrogen sulphide, three principal types of ion were likewise observed. They occur at $m/e = 32$, 33, and 34 and are interpreted as having the compositions $(S)^+$, $(HS)^+$, and $(H_2S)^+$, respectively. Using Mackay's value of the lowest ionization potential as a standard for the calibration of the voltage scale, the *ionization potentials* are approximately 10.4 volts, 16.9 volts, and 15.8 volts, respectively. Variation of the pressure, at low pressures, indicates that no secondary processes occur, i.e. that the ions above named are all formed by the initial process of the electrons colliding with the gas molecules. No S_2^+ ions were observed, nor any which could be due to isotopes of sulphur.

IN AN attempt to evolve systematic rules concerning the structure of molecules, progress is hastened if a wealth of empirical data concerning their behavior is at hand. While many diatomic molecules have been investigated[1] by the method of positive-ray analysis, comparatively little has been done in the field of more complex molecules. Accordingly, after an investigation of the water vapor molecule[1] in conjunction with Dr. Barton, the above method was likewise applied to the study of the ammonia and hydrogen sulphide molecules.

AMMONIA[2]

Ammonia was evaporated from a chemically pure ammonium hydroxide solution, and dried thoroughly over potassium hydroxide sticks. That these were efficient was evidenced by the very small proportion of water vapor ions which was observed, if any.

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[1] For details and references to the literature, see H. A. Barton and J. H. Bartlett Jr., Phys. Rev. **31**, 822 (1928). A comprehensive view of the work done and an attempt at interpretation is given in an article by R. S. Mulliken, Phys. Rev. **32**, 186 (1928). See also T. R. Hogness and R. W. Harkness, Phys. Rev. **32**, 784 (1928).

[2] A preliminary report has been published, Phys. Rev. **31**, 1129 (1928).

At low pressures, of the order of less than 10^{-4} mm, a mass spectrum such as is shown in Fig. 1 was obtained. If water vapor be admitted to the apparatus with no ammonia present, then the usual peaks at m/e of 17 and 18 are found. This, together with an additional calibration of the mass scale by the admission of nitrogen, indicates that the peaks here shown correspond to ions of $m/e=15$, 16, 17, and 18. The occurrence of the peak at $m/e=17$ cannot be due to the formation of the ion $(OH)^+$, since this occurs in lesser amounts[1] than $(H_2O)^+$, and it is seen from the figure that the peak at $m/e=18$ is quite small in comparison with that at $m/e=17$. In addition, the presence of the peak at $m/e=16$ is not to be interpreted as due to $(O)^+$, since especial care was taken in introducing the ammonia so that no such impurity could be present in appreciable quantities. Further evidence is furnished by the value of the ionizing potential found for each type. It seems, therefore, justifiable to assign to the ion at $m/e=17$ the composition $(NH_3)^+$ and to that at $m/e=16$ the composition $(NH_2)^+$. A distinct peak appears at $m/e=15$, and the only logical interpretation evident is that which assigns to it the composition $(NH)^+$.

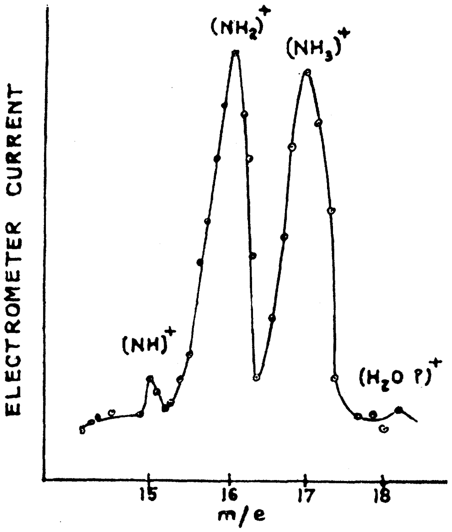

Fig. 1. Mass spectrum of ions produced by electron impact in ammonia, low pressure.

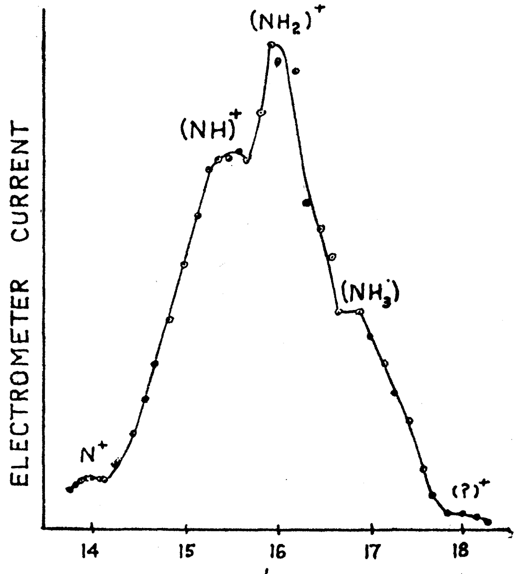

Fig. 2. Mass spectrum of ions produced by electron impact in ammonia at higher pressure.

The character of the mass spectrum at higher pressures, of the order of 20×10^{-4} mm, is indicated by Fig. 2. The $(NH)^+$ peak has become more intense and the $(NH_3)^+$ peak less so. There is distinct evidence of peaks at $m/e=14$ and 18. The composition of the former peak is doubtless $(N)^+$, while that of the latter peak may be due to $(NH_4)^+$, or possibly $(H_2O)^+$. The latter alternative is possible, since there was no convenient method of ascertaining whether or not the gas was absolutely dry.

No negative ions, and few, if any, hydrogen ions were observed. This latter fact tends to indicate that thermal dissociation processes do not play an important rôle. This is probably due to the rapid motion of the gas through the tube together with the fact that collisions take place at some distance from the filament, an arrangement recommended by Waldie,[3] who found that ammonia is almost entirely dissociated in the immediate neighborhood of the filament.

A comparison of the ionizing potentials for $(NH_3)^+$, $(NH_2)^+$, and $(NH)^+$ is shown in Fig. 3. The three curves were plotted from three consecutive runs made under quite favorable conditions, although the curve for $(NH)^+$ probably shows in its curvature the effect of a somewhat unsteady filament emission current. Its ionization potential, however, is fairly definite, and is about 11.2 ± 1.5 volts. There is an apparent difference between the ionization potentials for $(NH_3)^+$ and for $(NH_2)^+$, that for the former being 11.2 ± 1.5 volts, a mean of twelve observations, and that for the latter being 12.0 ± 1.5 volts, a mean of ten observations. These observations were weighted in accordance with the sensitivity of the apparatus, as determined by the peak height at a definite V_1, in this case 18 volts. The ionization potential of $(NH_3)^+$ is in good agreement with that of 11.1 volts observed by Mackay,[4] and with that of 11 volts observed by Waldie.[3]

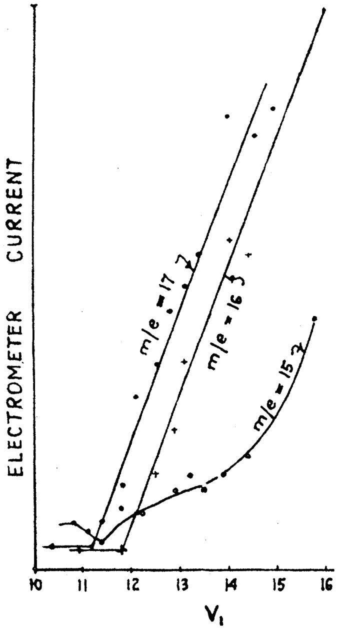

Fig. 3. Comparison of the ionizing potentials for $(NH_3)^+$, $(NH_2)^+$ and $(NH)^+$.

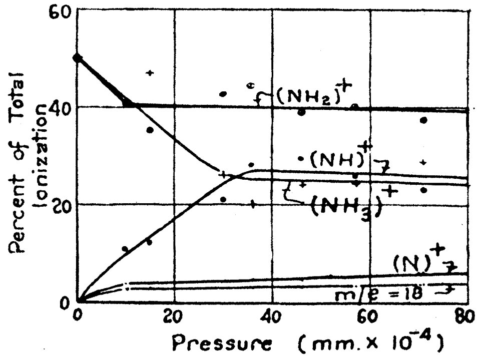

Fig. 4. Relative proportions of different types of ions as a function of pressure.

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[3] A. T. Waldie, Frank. Inst. J. **200**, 507 (1925).

[4] C. A. Mackay, Phys. Rev. **24**, 319 (1924).

Fig. 4 shows how the relative proportions of the different types of ion vary with the pressure. The $(NH_3)^+$ and $(NH_2)^+$ ions are present even at the lowest pressures and are probably the direct result of the electron impacts on the ammonia molecules, which is attested to by the observations that the ionization potentials for the two types were different. Since the relative amount of the $(NH)^+$ ion increases with increasing pressure from a small amount at low pressures, it must be largely, if not wholly, a secondary ion. Further, since its increase is similar to the decrease of the $(NH_3)^+$ type, it seems probable that there occurs a reaction of some such type as: $(NH_3)^+ + NH_3 = (NH)^+ + H_2 + NH_3$. The $(NH_2)^+$ ion seems to be more stable than the $(NH_3)^+$ ion, since its relative amount does not vary greatly within the range of pressures used. The $(N)^+$ type increases slightly with increasing pressure, and is probably a secondary type, although possibly an impurity. The ion at $m/e = 18$ also increases slightly with pressure. Nothing absolutely definite can be said as to its nature, in view of the alternatives $(NH_4)^+$ and $(H_2O)^+$, and since it occurred in such small quantities that its ionization potential could not be measured with certainty.

The main points of the above interpretation are not out of harmony with results obtained by other investigators, in that excited (and therefore probably ionized) molecules with compositions NH_3, NH_2, and NH are supposed to exist. In the visible spectrum of ammonia there are dominant the Schuster bands, supposedly due to NH_3, and the α-bands, which probably originate[5] from both NH_3 and NH_2. In the ultra-violet region there occur the β-bands, which resemble the known hydride bands in some respects and so are thought [6,7,8] to be emitted by the NH molecule. Thus, it is to be expected from spectral observations that one would find exactly those principal types of ion which have been observed in this research.

HYDROGEN SULPHIDE

Hydrogen sulphide, presumably 99.7 percent pure, was obtained from the Mathesen Co. in an ordinary lecture bottle. Special precautions were taken so that no air could be mixed with the gas as it was introduced to the system. After the usual process of solidification and evaporation to eliminate water vapor and other possible impurities, the gas was stored over phosphorus pentoxide before its final admission to the system. In order to protect the metal parts of the apparatus from the chemical action of the gas, an additional pump was connected to the storage chamber, so that large quantities of excess gas could be pumped off without passing through the main system. The gas was purified from time to time by solidification and evaporation in a liquid air trap. In the study of both hydrogen sulphide and ammonia, tungsten filaments were used for the most part, and proved quite satisfactory.

A typical mass spectrum is shown in Fig. 5. The resolving power of the apparatus was sufficient to distinguish between three types of ion, spaced one unit apart on the m/e scale, which was calibrated with the aid of water vapor and air. The peaks here shown are thereby identified as having

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[5] W. B. Rimmer, Proc. Roy. Soc. **A103,** 696 (1928).

[6] E. Hulthén and S. Nakamura, Nature **119,** 235 (1927).

[7] S. Barrat, Proc. Roy. Soc. **A98,** 40 (1920).

[8] E. Gaviola, Nature **122,** 313 (1928).

m/e's of 32, 33, and 34, respectively. Without doubt, the two latter peaks correspond to ions of composition $(HS)^+$, and $(H_2S)^+$, respectively. In the case of the former peak, however, it is imperative to make certain that one is not dealing with $(O_2)^+$ in addition to $(S)^+$. The presence of air mixed with the hydrogen sulphide may be detected by the quite low intensity of ionization observed, by the presence of a large peak at $m/e=28$ corresponding to $(N_2)^+$, by the rapid burning out of filaments (in the case of tungsten filaments), and by the existence of an ionizing potential for the $m/e=32$ peak of approximately 13 volts. The second test is the most certain criterion, although at high filament temperatures there is a small peak at $m/e=28$ due probably to $(CO)^+$ from the waxes in the tube. It was found possible to eliminate any impurity such as air, so that all these four tests showed its absence. The peak with $m/e=32$ still persisted and must be interpreted as having the composition $(S)^+$ alone. These three peaks are mentioned by Aston.[9] As he found, so it was found here that there is no evidence of peaks at $m/e=35$ or 36, which, if existent, would indicate isotopes of sulphur at $m/e=33$ or 34, respectively. No $(S_2)^+$ ions were observed.

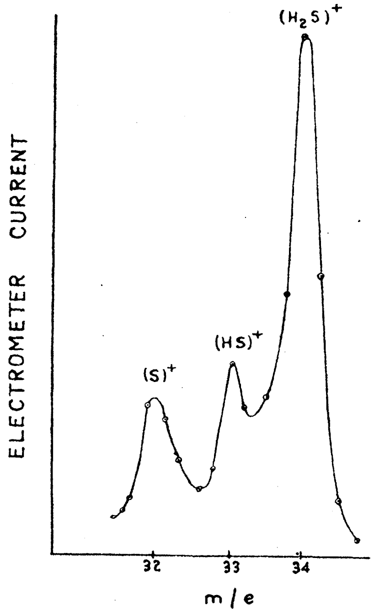

Fig. 5. Mass spectrum of ions produced by electron impact in H_2S.

A definite ionization potential was found for each of the three types of ion. That for $(H_2S)^+$, the weighted mean of fourteen observations is 11.1 ± 1.5 volts, in approximate agreement with the value given by Mackay,[4] who concluded that there was a discontinuity at 10.4 volts due to $(H_2S)^+$, the identification of the ion involved being confirmed here. The discrepancy may be due either to uncertainty in the electron speeds or to chemical reaction with the grid, which might affect the field somewhat. The results here obtained indicate that dissociation processes due to the electron impacts occur. There is positive evidence of an $(HS)^+$ peak with an ionization potential of 17.6 ± 1.5 volts (the weighted mean of ten observations). The range of Mackay's measurements just falls short of this and may explain our disagreement with his conclusion as to the non-existence of dissociation products due to electron impacts. The thermal dissociation does not become of any importance, however, in affecting our results, since hardly any hydrogen ions (and no negative ions) were observed, and the ionization potential of $(S)^+$, namely 16.5 ± 1.5 volts (the weighted mean of twelve observations), indicates that it arises from H_2S by electron impact, rather than from a sulphur atom. Since Mackay's work on H_2S was done with an apparatus designed primarily

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[9] Aston, Isotopes (1924) p. 79.

for the measurement of ionization potentials, it seems best to adopt his value of 10.4 volts as a calibration of the absolute voltage scale, so that the corrected values of ionization potentials are (1) for $(H_2S)^+$, 10.4 volts, (2) for $(HS)^+$, about 16.9 volts, and (3) for $(S)^+$, about 15.8 volts.

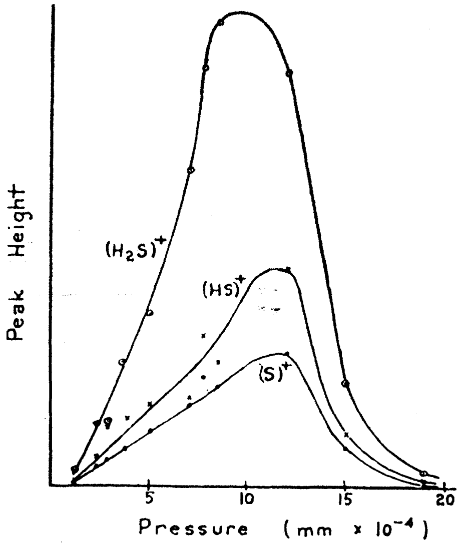

Fig. 6. Relative proportions of different types of ions as a function of pressure.

The characteristic curves of pressure variation are shown in Fig. 6. It is seen that there is no evidence of any secondary process taking place and that the relative proportions of the different types of ion remain sensibly constant as the pressure is increased. From this and from the existence of distinct ionization potentials, it is to be concluded that the three types of ion are all due to the primary process of electron impact with molecules of hydrogen sulphide.

DISCUSSION

As in previous cases, so it is found here that the principal molecular ions, namely $(NH_3)^+$ and $(H_2S)^+$, are formed by the primary process of electron impact. In addition, other such "primary"[1] ions are found, namely $(NH_2)^+$, $(HS)^+$, and $(S)^+$. It seems to the writer that very little can be said with any degree of certainty about the way in which the latter ions are formed, in view of the very incomplete knowledge[10, 11] of the molecular structure as found to date from the band spectrum data. The conjecture[5] that the $(NH_2)^+$ and $(NH)^+$ ions are more stable toward collisions than the $(NH_3)^+$ ion finds support in the results given here. The fact that the ammonia and hydrogen sulphide molecules are easily dissociated thermally indicates a weak binding and would lead one to believe that these molecules might also be dissociated by electron impact. This view likewise finds support in the present results.

In conclusion, the writer wishes to express his appreciation to Dr. H. A. Barton and Professors E. C. Kemble and P. W. Bridgman for many helpful suggestions, and to Mr. H. W. Leighton for material assistance in glassblowing. (This work was carried out at the Jefferson Physical Laboratory of Harvard University.)

INSTITUT FÜR THEORETISCHE PHYSIK,
LEIPZIG,
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[10] From the symmetry characters of a possible model, the type of NH_3 spectrum to be expected has been predicted by F. Hund, Zeits. f. Physik **43**, 823 (1927).

[11] See also for NH_3, R. M. Badger, Nature **121**, 942 (1928), and B. J. Spence, Jour. Opt. Soc. Amer. **10**, 127 (1925). See also Robertson and Fox, Proc. Roy. Soc. **A120**, 189 (1928).