

Recombination of electrons with $\text{NH}_4^+ \cdot (\text{NH}_3)_n$ -series ions

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The recombination coefficients α of $\text{NH}_4^+ \cdot (\text{NH}_3)_n$ series ions for $n = 0$ to 4 have been determined using a microwave afterglow-mass-spectrometer apparatus. For NH_4^+ ions, under conditions where the electron, ion, and neutral temperatures are equal ($T_e = T_+ = T_n$), $\alpha(18^+) = (2.5 \pm 1)$, (1.5 ± 0.3) and $(1.3 \pm 0.2) \times 10^{-6}$ cm³/sec at 200, 300, and 410 K, respectively. The electron-temperature dependences of the recombination coefficients for the first and second cluster ions are found to be (in cm³/sec) $\alpha(35^+) = 2.82 \times 10^{-6} [300/T_e(\text{K})]^{0.147}$ and $\alpha(52^+) = 2.68 \times 10^{-6} [300/T_e(\text{K})]^{0.050}$, accurate to $\pm 10\%$ over the range $300 \leq T_e \leq 3000$ K. At 200 K, the third and fourth clusters yield $\alpha(69^+) = \alpha(86^+) = (3 \pm 1) \times 10^{-6}$ cm³/sec. A new recombination mechanism, cluster-detachment recombination, is postulated to account for the very weak variation of α with electron temperature observed for the (35^+) and (52^+) ions.

I. INTRODUCTION

We have undertaken studies of the recombination of electrons with ammonium-series cluster ions, $\text{NH}_4^+ \cdot (\text{NH}_3)_n$, for two reasons: (i) NH_4^+ may be a significant ion in the lower atmospheres of Earth¹ and possibly of the outer planets. (ii) We wish to investigate further the weak temperature dependence of the cluster ion's recombination coefficient which was first noted² for the hydronium-series cluster ion, $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_2$. The present paper describes determinations of the recombination coefficients for the first five members of the ammonium series, (18^+) through (86^+) ,^{2a} at temperatures between 200 and 410 K. In addition, the electron temperature dependence of the recombination coefficient α has been determined for (35^+) and (52^+) , the $n=1$ and 2 cluster ions, over the range $300 \leq T_e \leq 3000$ K.

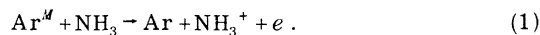
II. METHOD OF MEASUREMENT AND DATA ANALYSIS

The microwave afterglow mass-spectrometer apparatus and the method of data analysis used in these studies have been described in detail previously.²⁻⁴ The decay of the electron concentration during the afterglow following a ~ 1 msec discharge (repeated once per second) is determined from the change in resonant frequency of a high- Q TM_{010} mode of the resonant cavity containing the plasma. The electron temperature is elevated above the neutral and ion temperatures by controlled microwave heating using a broadband (low- Q) TE_{111} mode of the cavity. The decay curves of the various ion species in the afterglow are obtained by sampling the ions which diffuse to the wall of the cavity and effuse through a small orifice into a differentially pumped quadrupole mass filter.

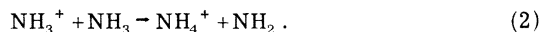
The plasma is generated in a mixture of typically 0.2 to 50 mTorr of NH_3 (Linde ultrahigh pur-

ity grade) in ~ 12 Torr of Ar buffer gas (Matheson ultrahigh purity grade). Before being admitted to the cavity the argon gas is further purified in the medium pressure (~ 3 atm) gas feed line by passing through a dry-ice-cooled zeolite trap.

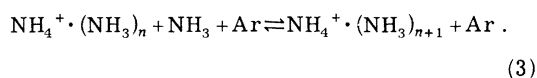
The principal steps leading to the formation of the ammonium series ions in the plasma afterglow are electron impact excitation of argon to a metastable state, followed by Penning ionization,



The NH_3^+ is rapidly converted to NH_4^+ by the fast two-body ion-molecule reaction⁵



Subsequent cluster ion formation proceeds by a sequence of reactions of the type



When several ion species are of importance in the afterglow, the decay of electron concentration under recombination controlled conditions is governed by the equation

$$\frac{\partial n_e}{\partial t} = -\alpha_1 n_1 n_e - \alpha_2 n_2 n_e \cdots - \alpha_j n_j n_e \cdots, \quad (4)$$

where the α_j and n_j represent the recombination coefficient and concentration, respectively, of the j th species of positive ion.

Since the plasma afterglow is essentially neutral, $n_e \approx \sum_j n_j$. Introducing the fractional ion concentrations $f_j \equiv n_j / \sum_j n_j$, we have $\sum_j f_j = 1$. Equation (4) may thus be simplified to

$$\frac{\partial n_e}{\partial t} \approx - \left(\sum_j f_j \alpha_j \right) n_e^2. \quad (5)$$

If, as is sometimes found, the fractional ion concentrations f_j do not vary with time, we have a

simple solution for the electron decay

$$1/n_e(t) = 1/n_e(0) + \alpha_{\text{eff}} t, \quad (6)$$

where we have introduced the effective recombination coefficient, $\alpha_{\text{eff}} \equiv \sum_j f_j \alpha_j$. Equation (6) has the same "recombination decay" form found when a single positive ion species is present in the afterglow. The recombination coefficient α_{eff} is determined from the slope of the linear portion of a $1/\bar{n}_{\mu w}$ vs afterglow time recombination plot^{2,3} ($\bar{n}_{\mu w}$ is the "microwave-averaged" electron density determined from the cavity resonant frequency shift).

In the simple case where only two ion species are of importance, the effective recombination coefficient is given by

$$\alpha_{\text{eff}} = \alpha_1 + \Delta\alpha f_2, \quad (7)$$

where $\Delta\alpha = \alpha_2 - \alpha_1$. We have used this method of data analysis to determine the recombination coefficients for the members of the clustered-ion series. As in the earlier studies of the hydronium-series ions,² we calculate the fractional concentrations f_j of the ions directly from the relative strengths of the mass-analyzed ion signals.

III. RESULTS

A. NH_4^+

By heating the cavity to 410 K and using a rather low partial pressure of ammonia ($\sim 2 \times 10^{-4}$ Torr) the unclustered ammonium ion (18^+) was made dominant throughout the early afterglow, as may be seen from the left-hand side of Fig. 1, which shows the time dependences of the various ion signals. Although the electron loss is determined

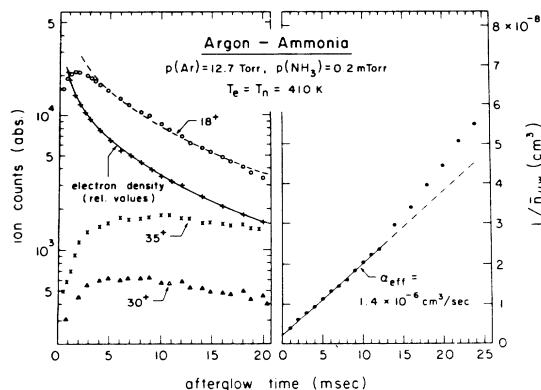


FIG. 1. Left: Comparison of electron density and ion wall current signals under conditions where the ion 18^+ dominates the ion composition. The dashed line represents the electron density curve normalized to the 18^+ curve at 5 msec. Right: Recombination plot of the electron density decay, whose slope yields α_{eff} .

primarily by recombination with 18^+ ions, the recombination coefficient determined from the slope of the $1/\bar{n}_{\mu w}$ curve at the right of Fig. 1 has been corrected² for the small effect of the 35^+ ($\text{NH}_4^+\cdot\text{NH}_3$) and 30^+ (probably NO^+) ions by use of the known values of α for these ions [see Sec. III B for the $\alpha(35^+)$ determination]. The value $\alpha(\text{NH}_4^+) = (1.3 \pm 0.2) \times 10^{-6}$ cm^3/sec is obtained at 410 K.

At $T_n = 300$ K it was not possible to make 18^+ the dominant afterglow ion, since at lower partial pressures of NH_3 the parent NH_3^+ ions converted too slowly to NH_4^+ by reaction (2). However, at $p(\text{NH}_3) \sim 2 \times 10^{-4}$ Torr, 18^+ and 35^+ were the only important afterglow ions, and they decayed in apparent equilibrium. From plots of α_{eff} vs $f(35^+)$ values of $\alpha(18^+)$ and $\alpha(35^+)$ have been obtained at 300 K by use of Eq. (7). The value $\alpha(18^+) = (1.5 \pm 0.3) \times 10^{-6}$ cm^3/sec is obtained at $T_e = T_n = 300$ K. The value of $\alpha(35^+)$ agrees very well with the value determined in Sec. III B.

At $T_n = 200$ K, owing to the increasing abundance of cluster ions in the afterglow, only a rough value of $\alpha(18^+)$ has been obtained, $(2.5 \pm 1) \times 10^{-6}$ cm^3/sec .

B. $\text{NH}_4^+\cdot\text{NH}_3$ and $\text{NH}_4^+(\text{NH}_3)_2$

At $T_n \sim 300$ K and $p(\text{NH}_3) \sim 2$ mTorr the ions 35^+ and 52^+ were the only important afterglow ions, and they decayed in apparent equilibrium, as may be seen from Figs. 2 and 3. These conditions proved suitable for the electron temperature-dependence studies, and the effect of electron heating on the electron-concentration decay is shown in these figures for $T_e = 300$ and 2000 K.

Data were taken as a function of electron temperature at a fixed partial pressure of NH_3 , yielding the electron temperature dependence of α_{eff}

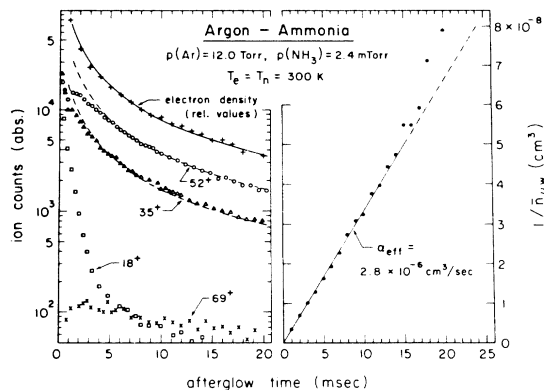


FIG. 2. No microwave heating. Left: Comparison of electron density and ion signal decays when the principal ions 35^+ and 52^+ decay together in apparent equilibrium. Right: Recombination plot of the electron-density decay.

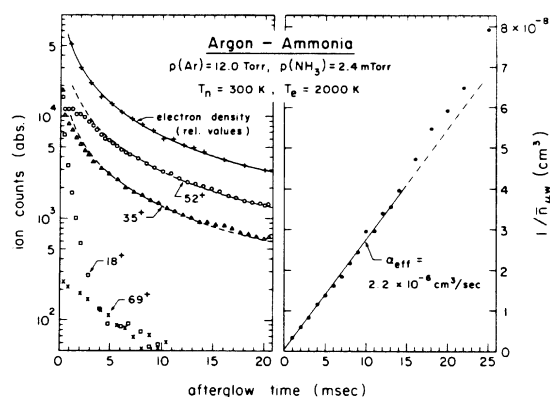


FIG. 3. Microwave heating data. Same format as Fig. 2.

at a particular value of $f(52^+)$. For the case $f(52^+) = 0.65$ illustrated in Figs. 2 and 3, the results are indicated in Fig. 4. By taking similar data at a number of partial pressures of NH_3 , a family of curves was generated for various $f(52^+)$ values.

The values of $\alpha(35^+)$ and $\alpha(52^+)$ at various electron temperatures have been obtained from plots of α_{eff} vs $f(52^+)$, as shown in Fig. 5. From Eq. (7), $\alpha(35^+)$ is obtained by extrapolation to $f(52^+) = 0$ and $\alpha(52^+)$ by extrapolation to $f(52^+) = 1$. The solid lines in Fig. 5 indicate the least-squares fits of Eq. (7) to the data, and the fits yield slightly different temperature dependences for $\alpha(35^+)$ and $\alpha(52^+)$, as shown in Fig. 6.

C. $\text{NH}_4^+(\text{NH}_3)_3$ and $\text{NH}_4^+(\text{NH}_3)_4$

At $T_n \sim 200$ K the abundance of ions with large cluster numbers increased, and it was not possible

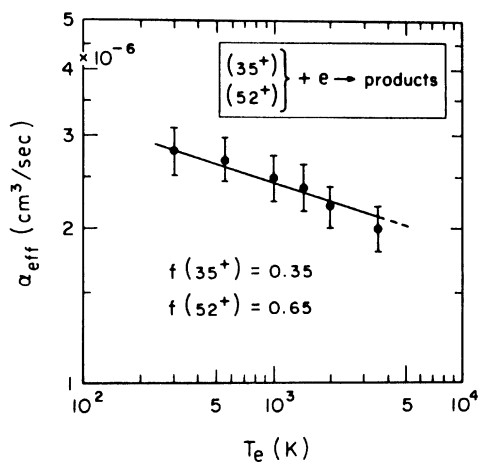


FIG. 4. Variation of α_{eff} with electron temperature at a fixed ratio of 35^+ to 52^+ ion signals. The error bars provide an estimate of the random and systematic errors associated with the α_{eff} determinations.

to attain conditions where only one or two ion species dominated the afterglow. With $p(\text{NH}_3)$ in the range 2–50 mTorr the important cluster species were those with cluster numbers $n=1$ to 4, and all species decayed in apparent equilibrium during the afterglow. Thus, as was the case in the hydronium-series studies,² it was possible to determine α_{eff} for various fractional concentrations of the cluster ions from the slopes of the $1/\bar{n}_{\text{mw}}$ -vs- t curves. For these conditions, Eq. (5) yields

$$\alpha_{\text{eff}} = \sum_{j=1}^4 f_j \alpha_j. \quad (8)$$

Approximate values of $\alpha(69^+)$ and $\alpha(86^+)$ have been obtained at $T_n \sim 200$ K by obtaining α_{eff} values for many different partial pressures of NH_3 , yielding a large range of concentration ratios of the four cluster ions. Combining these measurements with the extrapolated values $\alpha(35^+) \approx 3.0 \times 10^{-6}$ and $\alpha(52^+) \approx 2.7 \times 10^{-6}$ cm^3/sec at $T_n = 200$ K (from the curves in Fig. 6), we obtain the values

$$\alpha(69^+) \approx \alpha(86^+) = (3 \pm 1) \times 10^{-6} \text{ cm}^3/\text{sec} \quad (9)$$

and a more accurate determination of the sum of the coefficients

$$\alpha(69^+) + \alpha(86^+) = (6 \pm 0.5) \times 10^{-6} \text{ cm}^3/\text{sec} \quad (10)$$

at 200 K.

IV. DISCUSSION AND CONCLUSIONS

The recombination coefficients of the ammonium-series ions, measured under conditions where $T_e = T_n = T_w$, are given in Table I. The temperature variation for the unclustered NH_4^+ ion (18^+) suggests a behavior similar to that observed for O_2^+ and NO^+ ions,^{4,6,7} that is, a sharper rise with decreasing temperature between 200–300 K than at temperatures above 300 K. This behavior has been attributed to the increasing importance of the indirect dissociative capture process compared to the direct process as the temperature is lowered.⁸ It has not been possible to isolate the NH_4^+ ion for studies of the electron temperature dependence of $\alpha(18^+)$ over a wide range; however, the data between 300 and 410 K suggest the $T_e^{-1/2}$ variation predicted theoretically for the direct dissociative process and found experimentally to be approximated for various unclustered ions.⁸

Considering the clustered ions, the variation of α with cluster size n for the ammonium-series ions, $\text{NH}_4^+(\text{NH}_3)_n$, differs strikingly from that noted² for the hydronium-series ions, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$. At a fixed temperature, the hydronium ions show an increase in α by a factor of ~ 3 in going from $n=1$ to $n=4$, while for the ammonium ions little if any change in α is found over

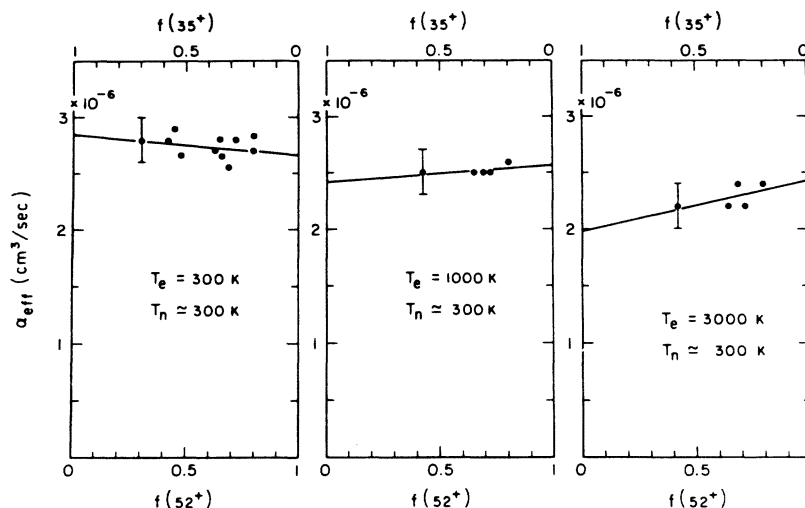


FIG. 5. Variation of α_{eff} for the 35^+ and 52^+ ions as a function of $f(52^+)$ and $f(35^+)$ at three electron temperatures. The vertical bars present typical values for the overall errors in the α_{eff} determinations. The solid lines represent least-squares fitting of Eq. (7) to the data.

the same cluster-size range. (We have used the weak dependence of α on T noted for the cluster ions to extrapolate values to a common temperature in each case.) At the present time we cannot explain why, at moderate temperatures, 200–400 K $\alpha[\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n]$ increases monotonically with n (observations were made for $1 \leq n \leq 6$), while $\alpha[\text{NH}_4^+ \cdot (\text{NH}_3)_n]$ does not change appreciably with n ($1 \leq n \leq 4$).

A principal aim of the present study has been to examine, over as wide a T_e range as possible, the variation of α for the clustered ammonium series ions, since the $n=2$ cluster of the hydronium ion, $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_2$, exhibits little, if any, dependence on temperature over the range 300–540 K.² Because of the unavoidable presence of more than one clustered ion during the afterglow, successful electron temperature studies have been achieved only for

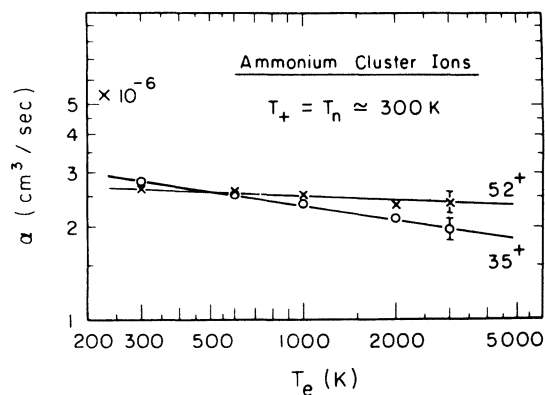


FIG. 6. Variations of $\alpha(35^+)$ and $\alpha(52^+)$ with electron temperature. The vertical bars represent estimates of typical overall errors in the determinations of α . The solid lines represent least-squares fits of T_e^{-x} dependences to the data.

the first and second clusters of the ammonium ion, (35^+) and (52^+). In spite of the uncertainties in an individual determination of α_{eff} for these ions, see Fig. 5, the least-squares fitting procedure yields the weak, slightly different T_e dependences illustrated in Fig. 6. It will be seen from the error bars that the observed difference between the two curves is slightly greater than possible systematic errors in the determinations.

The deduced electron temperature dependences over the range $300 \leq T_e \leq 3000$ K may be represented by

$$\alpha(35^+) = 2.82 \times 10^{-6} [300/T_e(\text{K})]^{0.147} \text{ cm}^3/\text{sec} \quad (11)$$

and

$$\alpha(52^+) = 2.68 \times 10^{-6} [300/T_e(\text{K})]^{0.050} \text{ cm}^3/\text{sec} . \quad (12)$$

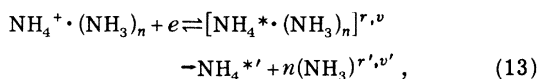
The finding of an extremely weak temperature dependence for the $n=2$ ammonium cluster ion (52^+) is consistent with the apparent lack of temperature dependence noted² for the $n=2$ hydronium cluster ion (55^+).

The fact that clustering of NH_3 molecules on the NH_4^+ ammonium-ion core markedly alters the dependence of the recombination coefficient on elec-

TABLE I. Electron-ion recombination coefficients (in units of 10^{-6} cm^3/sec) for $\text{NH}_4^+ \cdot (\text{NH}_3)_n$ -series ions and electrons under conditions where $T_e = T_+ = T_n$.

T (K)	Ion	$n=0$ (18^+)	$n=1$ (35^+)	$n=2$ (52^+)	$n=3$ (69^+)	$n=4$ (86^+)
410		1.3 ± 0.2				
300		1.5 ± 0.3	2.8 ± 0.2	2.7 ± 0.2		
200		2.5 ± 1			3 ± 1	3 ± 1

tron temperature suggests that a new electron capture process dominates the recombination with the cluster ions. It is conceivable that the recombination process is no longer a truly dissociative one, in which an unstable excited molecule, formed when the core molecular ion captures an electron, dissociates into neutral fragments. Instead, the process might involve neutralization of the core ion by capture of the incoming electron into a stable excited state through energy loss to excitation of internal modes (rotational and vibrational) of the cluster complex, followed by detachment of the cluster molecules from the excited core, i.e.,



where the superscripts *, *r*, and *v* indicate electronic, rotational and vibrational excitation, respectively. The reduced binding of the NH₃ molecules to the core following neutralization results in cluster detachment.

The rate of this "cluster detachment" recombination process depends in part on the initial capture rate, which in turn depends on the cross section for internal mode excitation of the cluster complex by the incoming electron. Rotational excitation of molecular ions by electrons, together with its effect on dissociative recombination of diatomic ions and electrons, has been considered by Stabler.^{9,10} He finds that the presence of the charge on the molecule enhances the cross section for rotational excitation compared to the neutral-molecule case. Additional enhancement of the cross section when the molecule has a strong permanent dipole moment has been predicted¹¹ and found experimentally.¹²

Initial capture of the incoming electron as a result of rotational excitation in the cluster ion may therefore occur with large probability. However, since rotational excitation involves a small energy loss, a very highly excited electronic state of the neutral core results, leading to little decrease in the binding of the polar molecules to the core. The next step in the process involves efficient *E* - *V* transfer of the electronic excitation energy of the

core molecule to vibrational excitation of the clustered molecule(s). The reduced electronic excitation reduces the cluster binding to the core and results in cluster detachment.

Using a typical rate coefficient for *E* - *V* transfer,¹³ one estimates that the NH₄^{*} will suffer substantial electronic deexcitation in $\leq 10^{-11}$ sec, leading to detachment of the NH₃ molecules and stabilization of the recombination. The reversion of the intermediate complex of reaction (13) to the initial stage should be unlikely, since the time required should be substantially longer than 10^{-11} sec, owing to the large number of degrees of freedom of the complex. Thus the initial capture rate determines the recombination rate. A recombination coefficient in the 10^{-6} cm³/sec range is projected at 300 K, if one uses an estimate of the cross section for rotational excitation of ions based on Stabler's theory.⁹

In order for the cluster-detachment recombination process to reproduce the observed weak dependence of α on *T_e*, the cross section for the initial capture step, rotational excitation of the ion complex by the incoming electron, would have to vary roughly as $E_i^{-1(0.6 \pm 0.05)}$, where *E_i* is the energy of the incident electron. While E_i^{-1} variations are predicted for rotational excitation of unclustered ions⁹ and for excitation of neutral molecules with a permanent dipole moment,¹¹ experimental measurements¹² for the latter case exhibit a weaker energy dependence. It is possible that this weaker energy dependence carries over to the case of an ion complex containing a cluster of molecules with permanent dipole moments.

The mechanism by which cluster ions capture electrons will be investigated experimentally through studies of the radiation emitted by the excited states produced by the recombination.

ACKNOWLEDGMENTS

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