

Electron-temperature dependence of recombination of electrons with $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ -series ions

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A microwave-afterglow mass-spectrometer apparatus has been used to determine the dependence on electron temperature T_e of the recombination coefficients α of the hydronium-series ions $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$. For $n = 1-3$, we find $\alpha(37^+) = (2.5 \pm 0.5) \times 10^{-6} [300/T_e (\text{K})]^{0.08}$, $\alpha(55^+) = (3.0 \pm 0.6) \times 10^{-6} [300/T_e (\text{K})]^{0.08}$, and $\alpha(73^+) = (3.6 \pm 0.7) \times 10^{-6} [300/T_e (\text{K})]^{0.00} \text{ cm}^3/\text{sec}$ over the range $300-400 \text{ K} \leq T_e \leq 6000-8000 \text{ K}$ and $T_{\text{gas}} = T_+ = 300-400 \text{ K}$. For $n = 4$ and 5 , $\alpha(91^+) \approx \alpha(109^+) \sim 5 \times 10^{-6} \text{ cm}^3/\text{sec}$, with no apparent dependence on T_e . These results for the higher hydrates differ somewhat from those obtained by Leu, Biondi, and Johnsen. The very weak dependence of α on T_e is quite similar to the behavior noted for the $\text{NH}_4^+ \cdot (\text{NH}_3)_n$ cluster ions.

I. INTRODUCTION

The capture of electrons by ions of the hydronium series, $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$, where $n = 1, 2, \dots$, is of interest for several reasons. These ions dominate the positive-ion composition of the lower D -region of Earth's ionosphere; thus, the rate at which they capture electrons affects the ionization levels in these regions. Also, studies over a narrow temperature range ($\sim 300-540 \text{ K}$) hinted¹ that the recombination coefficients for these cluster ions ($n \geq 1$) exhibit a very different variation with electron temperature than that observed for dissociative recombination of unclustered molecular ions.² This very weak dependence of the cluster-ion recombination coefficient α on electron temperature T_e has been demonstrated conclusively in studies³ of the ammonium-series ions, $\text{NH}_4^+ \cdot (\text{NH}_3)_n$, with $n = 1$ and 2 , over the range $300 \leq T_e \leq 3000 \text{ K}$. In order to investigate further the properties of the hydronium-series ions and to determine whether the very weak dependence of α on T_e is a general property of ions about which polar molecules are clustered, we have measured the loss of electrons by recombination with $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ ions for the cases $n = 1, 2, 3$ over the range $\sim 300 \leq T_e \leq 8000 \text{ K}$, and have also obtained some qualitative information about the behavior of the higher hydrates, $n = 4$ and 5 .

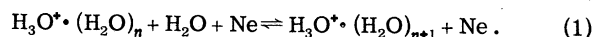
II. METHOD OF MEASUREMENT AND DATA ANALYSIS

The microwave-afterglow mass-spectrometer apparatus is the same in principle as that used in previous studies of the cluster ions^{1,3} except that a new copper and stainless-steel microwave cavity employing demountable flanges for the various windows, microwave feeds, etc., has replaced the copper cavity with silver-brazed joints. The new cylindrical cavity, which is suitable for high-temperature vacuum processing (to $\sim 500 \text{ C}$), has in-

ternal dimensions $R = 3.86 \text{ cm}$ and $H = 6.45 \text{ cm}$, yielding a fundamental diffusion length $\Lambda = 1.25 \text{ cm}$, only slightly smaller than the previous cavity's $\Lambda = 1.3 \text{ cm}$.

A microwave discharge lasting typically 1 msec and repeated at a 10-Hz rate is generated in a mixture of $\leq 0.3 \text{ mTorr}$ of vacuum distilled H_2O vapor and 13 Torr of neon (Linde ultrahigh-purity grade) which has been further purified by $\sim 12 \text{ h}$ exposure to a liquid-nitrogen-cooled zeolite trap. The "microwave-averaged" electron density $\bar{n}_{\mu\omega}$ during the afterglow is obtained from measurements of the resonant frequency shift of the high- Q TM_{010} cavity mode, while steady electron heating is achieved by application of microwave power via a low- Q ($Q = 17$) TE_{111} cavity mode. The decay curves of the various afterglow ions are determined by sampling the ions which diffuse to the cavity wall and effuse through a small orifice into a differentially pumped quadrupole mass filter.

The principal steps in the formation of the hydronium-series cluster ions are thought to be (a) electron-impact excitation of neon to a metastable state Ne^m ; (b) Penning ionization via $\text{Ne}^m + \text{H}_2\text{O} \rightarrow \text{Ne} + \text{H}_2\text{O}^+ + e^-$; (c) atom transfer, $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$; and (d) cluster-breakup reactions of the form



The gas temperature and the partial pressure of H_2O are used to regulate which cluster ions dominate the afterglow.

In a recombination-dominated afterglow in which several species of positive ions are present, the rate of change of electron concentration $n_e(\vec{r}, t)$ is given by

$$\frac{\partial n_e(\vec{r}, t)}{\partial t} = -(\alpha_1 n_1 + \alpha_2 n_2 + \dots + \alpha_N n_N) n_e, \quad (2)$$

where α_j and n_j are the recombination coefficient

and concentration of the j th positive-ion species, respectively. Using the quasineutrality condition for the afterglow plasma $n_e \approx \sum_{j=1}^N n_j$ and introducing the fractional concentration $f_k \equiv n_k / \sum_{j=1}^N n_j$, Eq. (2) simplifies to

$$\frac{\partial n_e(\vec{r}, t)}{\partial t} \approx -\alpha_{\text{eff}} n_e^2, \quad (3)$$

where α_{eff} , the effective recombination coefficient, is given by

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

In these cluster-ion afterglows it is often found that the fractional concentration of each ion does not vary significantly with time, so that α_{eff} is time independent and the solution of Eq. (3) is

$$1/n_e(\vec{r}, t) = 1/n_e(\vec{r}, 0) + \alpha_{\text{eff}} t, \quad (5)$$

which is identical to the "recombination decay" form when a single ion dominates the afterglow. Further, the ambipolar diffusion coefficients D_a of the ions in the buffer gas (here neon) should be sufficiently close in value^{4,5} that the more complete electron continuity equation can be written in a form analogous to that of the single-ion case, namely,

$$\frac{\partial n_e(\vec{r}, t)}{\partial t} \approx -\alpha_{\text{eff}} n_e^2 + D_a \nabla^2 n_e. \quad (6)$$

A point-by-point computer solution⁶ of Eq. (6) yields the predicted spatial and temporal variation of the electron density.

The measurements of the microwave cavity's resonant-frequency shift during the afterglow yield values of the microwave-averaged electron density,⁷ $\bar{n}_{\mu w}(t)$. In order to determine α_{eff} from these measurements one either obtains a best fit to the data of curves of $\bar{n}_{\mu w}(t)$ computed from Eq. (6), treating α_{eff} as a parameter and using estimated^{4,5} values of $D_a = D_+(1 + T_e/T_+)$, or one employs calculated correction factors⁸ S to the measured early-time slopes of recombination decay curves of the form

$$1/\bar{n}_{\mu w}(t) = 1/\bar{n}_{\mu w}(0) + (S\alpha_{\text{eff}})t. \quad (7)$$

Both methods have been used in the present study, the former being deemed more accurate.

The deduction of the recombination coefficients for individual ion species from the α_{eff} determinations is simplest when only two species are important in the afterglow, since in this case $f_1 = 1 - f_2$ and

$$\alpha_{\text{eff}} = \alpha_1 + (\alpha_2 - \alpha_1)f_2. \quad (8)$$

Extrapolation of the straight line representing α_{eff} vs f_2 to $f_2 = 0$ and $f_2 = 1$ yields α_1 and α_2 , respectively. Since two, and sometimes three,

adjacent members of the cluster-ion series $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ are present in significant concentrations during the afterglow, determination of the dependence on electron temperature of each of the recombination coefficients often requires iteration of the analysis to achieve the final result, which consequently has substantially larger uncertainties than that for a single-ion dominated afterglow.

III. RESULTS

An example of the variation of the electron density decays with electron temperature is given in Fig. 1 for a case in which 73° and 55° are the principal afterglow ions, with 37° the only other significant ion. The near-constant concentration ratios among the ions during the afterglow are illustrated in Fig. 2 for the $T_e = 2080$ K data of Fig. 1. It will be seen that all ions decay together and satisfactorily track with the renormalized $\bar{n}_{\mu w}$ values (dashed lines).

In this case we have used the computer solutions of Eq. (6) to fit the data, as indicated by the solid lines in Fig. 1, and so obtain α_{eff} vs T_e for the 0.46:0.46:0.08 concentration ratio of [73°]:[55°]:[37°]. The results are shown in the middle portion of Fig. 3, together with results at other concentration ratios. Data of this type were used to evaluate the coefficients $\alpha(55^\circ)$ and $\alpha(73^\circ)$, with the small perturbing effect of the 37° ions removed by using trial values of $\alpha(37^\circ)$ obtained from 37° and 55° dominated afterglows and then iterating to ob-

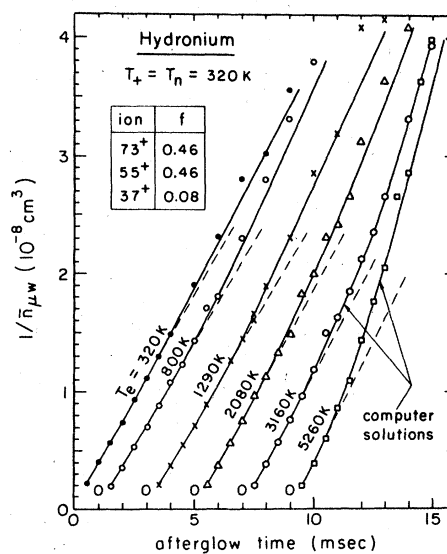


FIG. 1. $1/\bar{n}_{\mu w}$ vs time "recombination decay" plots for $T_e = T_n = 320$ K at $p(\text{Ne}) = 13$ Torr and $p(\text{H}_2\text{O}) \sim 0.2$ mTorr. (The afterglow time origins are displaced for clarity.) The solid lines represent best-fit computer solutions of Eq. (6) to the electron density data.

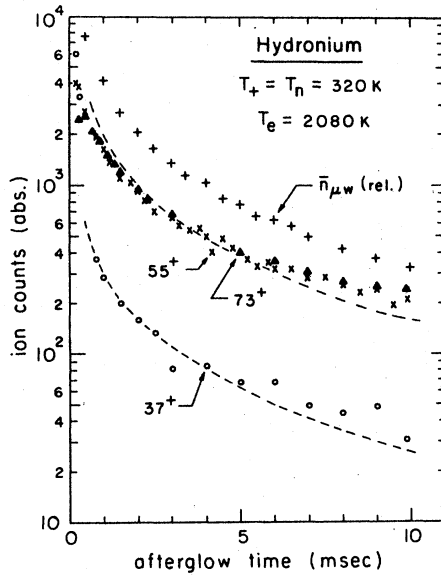


FIG. 2. Comparative decays of volume electron density and ion wall currents at $T_e = 2080$ K, $T_+ = T_n = 320$ K, and $p(\text{Ne}) = 13$ Torr and $p(\text{H}_2\text{O}) \sim 0.2$ mTorr. The dashed lines represent normalized volume electron density decays.

tain corrected values of all three recombination coefficients.

An example of the α_{eff} vs f analysis for the unheated case $T_e = T_n$ is given in Fig. 4. The solid lines are least-square fits of Eq. (8) to the data for the $37^+ - 55^+$ and the $55^+ - 73^+$ cases. It will be seen that the two analyses lead to values of $\alpha(55^+)$ which agree within 10%. The overall results of the studies can be represented by the following expres-

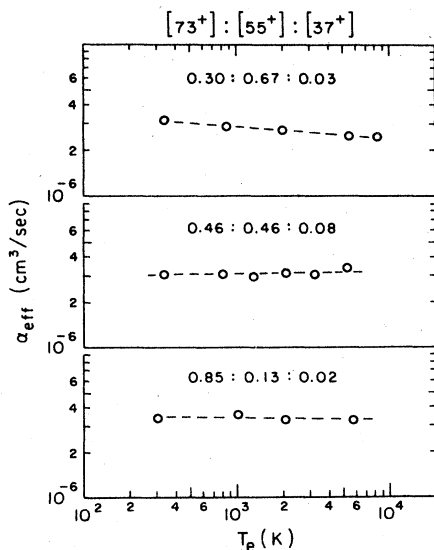


FIG. 3. Variation of α_{eff} with electron temperature at three ratios of the $73^+ : 55^+ : 37^+$ ion signals.

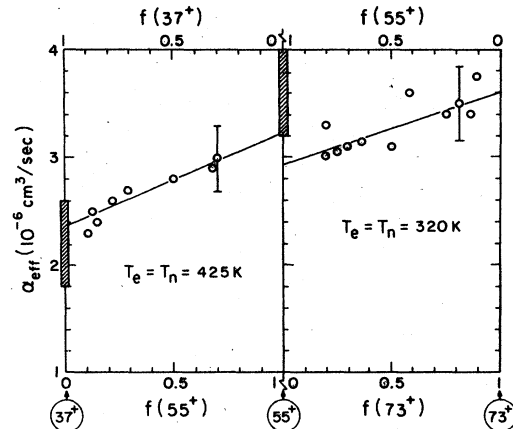


FIG. 4. Variation of α_{eff} for the 37^+ , 55^+ , and 73^+ ions as functions of $f(37^+)$, $f(55^+)$, and $f(73^+)$. The vertical bars represent typical overall errors in the α_{eff} determinations. The solid lines represent least-square fits of Eq. (8) to the data. The crosshatched symbols on the vertical axes represent the results of Leu, Biondi, and Johnsen.

ions (α in cm^3/sec):

$$\alpha(37^+) = (2.5 \pm 0.5) \times 10^{-6} [300/T_e (\text{K})]^{0.08}, \quad (9)$$

$$\alpha(55^+) = (3.0 \pm 0.6) \times 10^{-6} [300/T_e (\text{K})]^{0.08}, \quad (10)$$

and

$$\alpha(73^+) = (3.6 \pm 0.7) \times 10^{-6} [300/T_e (\text{K})]^{0.00}. \quad (11)$$

The electron temperature in these studies ranged from ambient (300–400 K) up to 6000–8000 K. In addition, the dependence of α on T_e for the higher clusters 91^+ and 109^+ ($n=4$ and 5) also appears to be close to T_e^0 .

IV. DISCUSSION AND CONCLUSIONS

The present results for the recombination coefficients of the first three clustered ions 37^+ , 55^+ , and 73^+ at ambient temperatures $T_e = T_n$ (no microwave heating) may be compared with the earlier work of Leu *et al.*¹ obtained with a very similar apparatus. As indicated by the crosshatched symbols in Fig. 4, the values of $\alpha(37^+)$ and $\alpha(55^+)$ of Leu *et al.* agree, within the combined experimental errors, with the present results. However, our value $\alpha(73^+) = (3.6 \pm 0.7) \times 10^{-6} \text{ cm}^3/\text{sec}$ at $T_e = T_n = 320$ K is rather smaller than Leu *et al.*'s value $(4.9 \pm 0.8) \times 10^{-6}$, and our values for the higher hydrates 91^+ and 109^+ seem to be of the order $\sim 5 \times 10^{-6} \text{ cm}^3/\text{sec}$, rather than to increase monotonically with cluster size toward $10^{-5} \text{ cm}^3/\text{sec}$, as found by Leu *et al.* We can not account for the difference between the two results, except to note that accurate inference of the recombination coefficients of the higher hydrates is made very diffi-

cult by the simultaneous presence of three or more members of the clustered-ion sequence in significant concentrations.

The present studies of recombination of hydronium-series cluster ions with electrons indicate the same very weak dependence of the recombination coefficient on electron temperature found³ for the case of the ammonium-series ions $\text{NH}_4^+ \cdot (\text{NH}_3)_n$. In the ammonium-ion paper it was suggested that a rather different process, "cluster-detachment" recombination, rather than the usual direct or indirect dissociative recombination process,² is operative when polar molecules are clustered to the molecular-ion core. We now propose that an alternative, very similar process, which is simply a somewhat more general form of indirect dissociative recombination, may also be capable of explaining the observations.

The initial electron-capture step, which is rate-limiting, is still thought to involve excitation of the rotational-vibrational degrees of the ion complex by the incoming electron, which results in

formation of a very high-lying Rydberg state of the neutral molecule associated with the core ion of the cluster complex. As a result of the large number of degrees of freedom of the complex the lifetime against autoionization (reemission of the electron) by deexcitation of the rotation-vibration is long; thus there is adequate time for interaction to lead to transfer of the system from the attractive, Rydberg state to a repulsive state which then dissociates. As noted in the previous paper³ the cross section σ_{ex} for excitation of rotation-vibration by the incoming electron should be large and may vary approximately as $u_e^{-1/2}$, where u_e is the electron energy, to account for the observed, very weak dependence of the recombination coefficients on electron temperature.

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¹M. T. Leu, M. A. Biondi, and R. Johnsen, *Phys. Rev. A* **7**, 292 (1973).

²J. N. Bardsley and M. A. Biondi, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates (Academic, New York, 1970), Vol. 6.

³C. M. Huang, M. A. Biondi, and R. Johnsen, *Phys. Rev. A* **14**, 984 (1976).

⁴I. Dotan, D. L. Albritton, W. Lindinger, and M. Pahl, *J. Chem. Phys.* **65**, 5028 (1976).

⁵I. Dotan, W. Lindinger and D. L. Albritton, *J. Chem. Phys.* **67**, 5968 (1977).

⁶L. Frommhold and M. A. Biondi, *Ann. Phys.* **48**, 407 (1968).

⁷L. Frommhold, M. A. Biondi, and F. J. Mehr, *Phys. Rev.* **165**, 44 (1968).