

## Tidal termolecular ionic recombination

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**Abstract.** Measurements by Mezyk and co-workers have shown that the rate coefficient for  $\text{Xe}_2^+ + \text{Cl}^- + \text{Xe} \rightarrow \text{XeCl}^+ + 2\text{Xe}$  is enhanced relative to that given by the universal curve that describes termolecular recombination of structureless atomic ions. This is attributed to  $\text{Cl}^-$  exciting internal modes of  $\text{Xe}_2^+$  during passage through the perihelion part of the orbit. The electrostatic tidal effect is simulated by the Monte Carlo technique, excellent agreement with the data of Mezyk *et al* being obtained. It is reasoned that the tidal action cannot enhance the rate of termolecular recombination of small valence-bound ions like  $\text{O}_2^+$  and  $\text{O}_2^-$  appreciably. However its influence is pervasive because complex ions are commonly present when the ambient gas density is enough for termolecular recombination to be of interest: for example,  $\text{O}_4^+$  is the main positive ion if the ambient gas is pure oxygen. Enhanced mutual neutralization may obscure the experimental evidence. It may be disregarded in the case of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n + \text{NO}_3^- + \{\text{He}, \text{Ar}\} \rightarrow \text{neutrals}$ . Experimental research by Lee and Johnsen has shown that the rates of these two processes are enhanced relative to the universal curve. The only possible explanation for the enhancement seems to be tidal action.

### 1. Introduction

The physics of termolecular ionic recombination



was established in the first quarter of the present century (see Flannery 1976). Thus Langevin (1903) recognized that when  $[\text{M}]$  is very high the recombination coefficient  $\alpha$  is determined by the rate at which oppositely charged ions drift together under the influence of their mutual attraction and proved that it is given by

$$\alpha = 4\pi e(K^+ + K^-) \quad (2)$$

where  $K^+$  and  $K^-$  are the mobilities of the of the positive and negative ions so that the variation of  $\alpha$  with  $[\text{M}]$  is as

$$\alpha = B/[\text{M}] \quad (3)$$

$B$  being a constant. Again Thomson (1924) showed that when the mobility drift is not rate limiting  $\alpha$  is determined by the collisions which  $\text{X}^+$  and  $\text{Y}^-$  make with  $\text{M}$

in that these collisions convert the initial hyperbolic  $X^+ - Y^-$  relative motion into elliptical relative motion. He demonstrated that in the low  $[M]$  limit

$$\alpha = A[M] \quad (4)$$

where  $A$  is another constant and devised a simple model to represent the complicated sequence of collisions leading to recombination and allows  $A$  to be calculated approximately.

With the advent of fast computers the theory could be advanced seemingly to completion because for a given ion-neutral interaction (say ion-induced dipole) the problem presented is exactly soluble in so far as the ions may be regarded as structureless particles.

Attention was first directed to the low  $[M]$  limit and the main cases were treated: symmetrical charge transfer resonance collisions (Bates and Moffett 1966, Flannery 1981); hard sphere core with polarization tail (Bates and Flannery 1968); pure polarization (Bates and Mendaš 1982a). To a sufficient approximation the constant  $A$  of equation (4) may be taken to be the sum of a term arising from  $X^+ + M$  collisions and a term arising from  $Y^- + M$  collisions. As well as being functionally dependent on a parameter describing the ion-neutral collision and on the reduced mass of the ion-neutral pair, each of these terms is numerically dependent on a certain mass ratio. Tabulations have been published with this mass ratio as the independent variable, the best being that of Flannery and Mansky (1988). Consequently  $A$  may easily be obtained for any ions in any ambient gas. Simple formulae are available for the mobilities  $K^+$  and  $K^-$  on which  $B$  of equation (3) depends (cf Dalgarno *et al* 1958).

For intermediate  $[M]$   $\alpha$  may be evaluated by using the Monte Carlo method to follow the lives of a very large number of ion pairs (cf Bates and Mendaš 1978, Bardsley and Wadehra 1980). Representing the ion-neutral interaction by that between the ion and the induced dipole on the neutral and choosing the temperature to be 300 K Bates and Mendaš (1982b) carried out Monte Carlo calculations on a particular recombination process. Affixing  $s$  as a subscript to all symbols for entities relating to this standard case they showed from dimensional considerations that a plot of  $\alpha_s$  against  $[M_s]$  is a universal curve. The curve covers any other recombination process  $x$  at temperature  $T$  because scaling parameters  $\lambda$  and  $\eta$  exist such that the curve

$$(T/300)^{3/2} \lambda \alpha_x - (300/T)^{3/2} \eta [M_x]$$

coincides with it. Their values are:

$$\lambda = (A_s B_s / A_x B_x)^{1/2} \quad (5)$$

$$\eta = (A_x B_s / A_s B_x)^{1/2}. \quad (6)$$

An important check on theory has been provided by measurements that Lee and Johnsen (1990) have made on



in which the asterisk indicates that the XeF formed is in the excited state that is formed when the ions approach adiabatically. The helium was at a temperature of about 300 K and at pressures from 140 to 500 Torr. Lee and Johnsen obtained satisfactory agreement with the calculations of Bates and Mendaš (1982a) and of Morgan *et al* (1982).

If any of the species participating in process (1) is molecular the collisions may be inelastic. The effect has been investigated by the Monte Carlo method (Bates 1981). It was found that the increase in  $\alpha$  is insubstantial. This is as would be expected since the main change that a collision with a neutral molecule makes in the energy of relative motion of an ion pair is due to the deflection of the ion involved in the collision.

#### Mutual neutralization

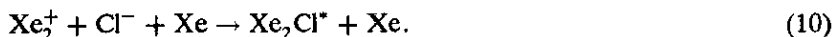


may occur if there is a suitable avoided crossing of the potential energy curves. In the absence of an ambient gas the rate coefficient for mutual neutralization is typically some  $2 \times 10^{-7} (300/T)^{1/2} \text{ cm}^3 \text{ s}^{-1}$  or less (Bates and Boyd 1956, Aberth and Peterson 1970). At 300 K it is hence less than the rate coefficient for termolecular ionic recombination over much of the [M] range normally of interest. However Monte Carlo calculations (Bates and Mendaš 1978) have revealed that the rate of mutual neutralization is enhanced by the presence of an ambient gas. This enhancement is accompanied by a diminution in the rate of termolecular ionic recombination but the total recombination rate is increased by a mutual neutralization channel (cf Bates 1980, 1983, 1985, Whitten *et al* 1982, 1983). The increase may be by a considerable factor. Because of this it has been natural to seek to invoke mutual neutralization when trying to explain a measured ionic recombination coefficient that is greater than the predicted termolecular ionic recombination coefficient.

In the context of research on inert-gas halide lasers Mezyk *et al* (1989, 1991) have carried out measurements on the rate coefficients of processes of the type

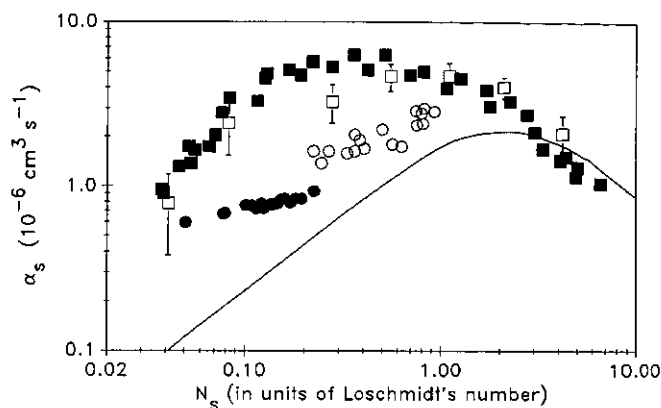


by monitoring the emission from the electronically excited molecule. Their investigation did not include



The value of  $\alpha$  that Mezyk *et al* (1991) obtained for process (9) is much larger than the predicted termolecular ionic recombination coefficient except in the high [Xe] region where there is fair agreement (see figure 1).

Mutual neutralization cannot be invoked since the reactants and products lie on the same potential energy surface with the Cl retaining its excess electron (see Huestis 1982, figure 4). Noting that the equilibrium internuclear distance  $r_e$  for  $\text{Xe}_2^+$  is as great as  $6.18 a_0$  and that the spectroscopic constants  $B_e$  and  $\omega_e$  are only  $0.0239$  and  $112 \text{ cm}^{-1}$  (Wadt 1978) so that neighbouring rotational and vibrational levels are so close together that they may be regarded as forming a continuum, Bates and Morgan (1990) in a preliminary note suggested that the observed behaviour stems from *electrostatic tides* being raised in  $\text{Xe}_2^+$  when  $\text{Cl}^-$  is near perihelion. These tides occur because the field of force that  $\text{Cl}^-$  exerts on  $\text{Xe}_2^+$  differs from the force between two point charges.



**Figure 1.** The full line is the universal curve of Bates and Mendaš (1982b) for termolecular recombination between structureless atomic ions. The data points scaled by the factors  $\lambda$  and  $\eta$  of equations (5) and (6) are as follows:  $\blacksquare$ , measurements of Mezyk *et al* (1991) and  $\square$ , calculations, both for  $\text{Xe}_2^+ + \text{Cl}^- + \text{Xe} \rightarrow \text{XeCl}^+ + 2\text{Xe}$ ;  $\bullet$  and  $\circ$ , measurements of Lee and Johnsen (1989) on  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n + \text{NO}_3^- + \text{M} \rightarrow \text{neutrals}$  where M is He and Ar respectively.

## 2. Calculations

### 2.1. Models

Our simulations of ionic recombination were performed using a modification of the Monte Carlo method developed by Bardsley and Wadehra (1980) in which random numbers determine entities such as the times when collisions with ambient gas atoms occur. We begin with an ion pair a distance  $r_0$ , say 1000–2000  $a_0$ , apart with initial velocities chosen from a Maxwellian distribution. The positive ion and the negative ion, which initially are not bound, follow a hyperbolic trajectory until one of them collides with an ambient gas atom. Until this moment the calculation is performed as a two-body central force problem in the centre-of-mass reference frame. If the  $\text{Xe}_2^+$  and  $\text{Cl}^-$  are bound after a collision between one of them and an ambient gas atom occurs, the simulation is then continued to completion by solving the nine coupled equations of motion for the three atoms involved: the two Xe atoms comprising the  $\text{Xe}_2^+$  ion and the  $\text{Cl}^-$  ion. An adaptive stepsize fourth-order Runge-Kutta algorithm (Press *et al* 1986) is used for the numerical integration. The three atoms are assumed to interact with additive pair potentials. The two atoms comprising the  $\text{Xe}_2^+$  are bound by a Morse potential having parameters that were determined by Wadt (1978). The collisions between the ions and the ambient gas atoms are treated in the constant collision frequency approximation (i.e., ion-induced dipole potential). When the total orbital energy of the ion pair is  $-kT$  there is about one collision per orbit at 200 Torr. The collision dynamics are performed such that the energy loss to or energy gain from the ambient gas atom is properly accounted for. Owing to  $\text{Xe}_2^+$  being very massive relative to  $\text{Cl}^-$  its kinetic energy is not increased appreciably by the orbital motion of the ion pair. To be specific, on denoting the masses, 263 amu and 35 amu, of  $\text{Xe}_2^+$  and  $\text{Cl}^-$  by  $M_1$  and  $M_2$  it may be seen that when the kinetic energy of the relative motion is say  $\xi$  the kinetic energy of  $\text{Xe}_2^+$  in the centre-of-mass frame is

$\xi M_2/(M_1 + M_2)$ , which is only  $0.12\xi$ . Similarly the kinetic energy of relative motion is changed by only  $0.12\xi$  if the kinetic energy of  $\text{Xe}_2^+$  is changed by amount  $\xi$  in a deactivating collision. Since the energy of relative motion is not affected materially by a deactivating collision neither is the total recombination coefficient for channels (9) and (10) together.

Because the two atoms of the  $\text{Xe}_2^+$  ion are indistinguishable the charge is generally shared by them. To represent the interaction with  $\text{Cl}^-$  we adopted the simple model of placing charge  $e/2$  on each Xe and found it to be remarkably successful. The success probably stems from a path towards recombination being set by a few rather distant encounters between the ions.

## 2.2. Results

There are four possible outcomes for a given computer experiment:

- (i) the  $\text{Xe}_2^+$  and  $\text{Cl}^-$  separate again on open orbits;
- (ii) the  $\text{Xe}_2^+$  is dissociated by tidal effects but recombination does not occur;
- (iii) the  $\text{Xe}_2^+$  is dissociated and recombination takes place forming  $\text{XeCl}^*$ ;
- (iv) recombination occurs without dissociation and  $\text{Xe}_2\text{Cl}^*$  is formed.

Frequently the  $\text{Xe}_2^+$  and  $\text{Cl}^-$  are weakly bound after the first collision with an ambient gas atom and execute several orbits exchanging energy between the orbit of  $\text{Cl}^-$  and the internal modes of  $\text{Xe}_2^+$  until, at last, the total orbital energy is positive again and the ions separate as in outcome (i). We have never observed outcome (ii) to occur in our simulations. This is expected since about 1 eV is needed to dissociate the dimer ion and the removal of so much energy from the orbital motion would ensure recombination. Outcome (iv) occurs occasionally in our calculations with a rate coefficient less than about  $5 \times 10^{-8} \text{ cm}^3\text{s}^{-1}$  at the pressures that we are concerned with. At very high pressures  $\text{Xe}_2\text{Cl}^*$  would be expected to be the dominant product because of the loss of energy from the internal modes of  $\text{Xe}_2^+$  due to frequent collisions with the ambient gas.

The dominant recombination process is outcome (iii). Because of the tidal effect, the orbit of  $\text{Cl}^-$  relative to  $\text{Xe}_2^+$  tends to contract during a passage through perihelion. The  $\text{Xe}_2^+$  internal energy tends to increase correspondingly and to become finally so great that dissociation occurs. We find that an average of 20 to 30 orbits are required to dissociate the dimer xenon ion and that the associated energy loss by the  $\text{Cl}^-$  ensures recombination. The histogram in figure 2 is typical of the distribution, approximately exponential, of the number of orbits to dissociation. The recombination rate coefficient computed by this Monte Carlo simulation is shown in figure 1 along with the experimental points of Mezyk *et al* (1991) and the theoretical termolecular rate coefficient in the absence of tidal effects (Bates and Mendaš 1982a). The tidal enhancement is apparent and the agreement between the computer simulations and the experimental points is spectacular. In view of the complexity of the recombination process being modelled the success is doubtless partly fortuitous.

The final segment of a trajectory leading to outcome (iii) is shown in figure 3. The frame of reference is that of the  $\text{Xe}_2^+$  centre of mass. Initially the  $\text{Xe}_2^+$  is rotating and vibrating in the centre of the figure. As the  $\text{Cl}^-$  comes in for a very close encounter at the perihelion of its orbit the  $\text{Xe}_2^+$  is dissociated and the  $\text{Cl}^-$  and the nearest atom of the  $\text{Xe}_2^+$ , which then becomes  $\text{Xe}^+$ , become bound as  $\text{XeCl}^*$  with the now free neutral Xe atom going off in the opposite direction in the specified frame of reference. The dissociation of  $\text{Xe}_2^+$  (with charge  $e/2$  on each Xe) is so violent that it is not affected by the arbitrary switch of charge  $e/2$  from one Xe to the other.

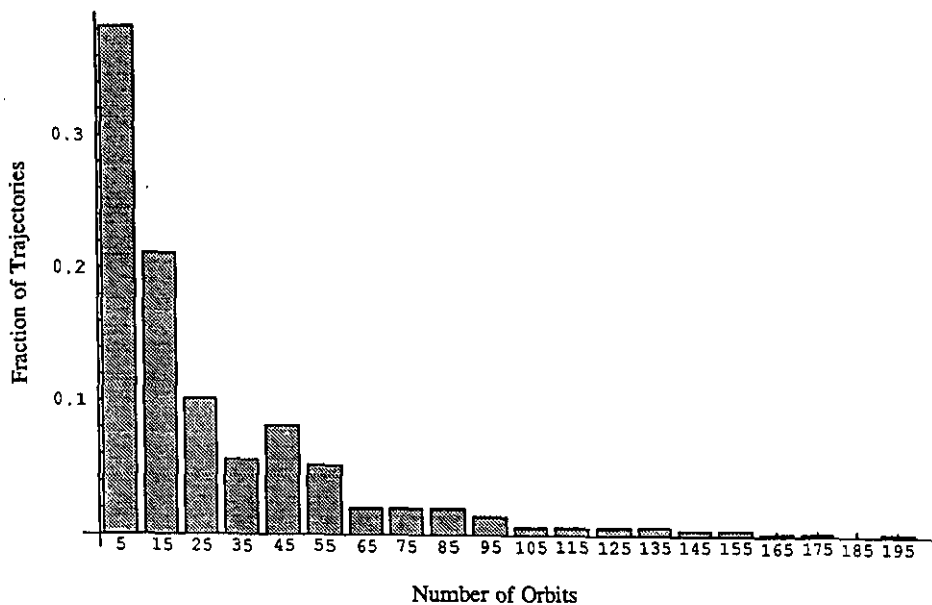


Figure 2. Histogram of number of orbits to dissociation for an ambient gas pressure of 200 Torr. The mean of the distribution is 28.6.

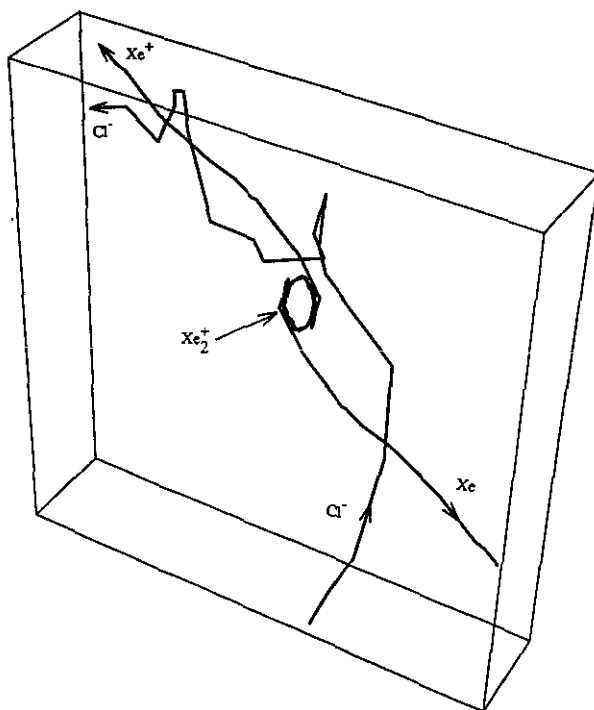
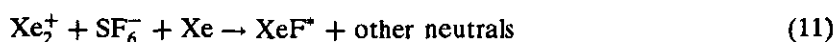


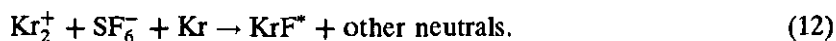
Figure 3. Representative termination of a recombination trajectory at a gas pressure of 200 Torr in the  $\text{Xe}_2^+$  centre-of-mass frame of reference. The dimensions of the box are  $70 \times 15 \times 70 a_0$ .

### 3. Prevalence of tidal termolecular ionic recombination

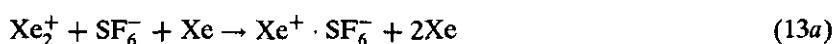
Mezyk *et al* (1989, 1991) also determined the rate coefficients of



and



Although the maxima of the measured  $\alpha$  are at above 300 Torr the results are strikingly similar to the results for process (10) and it would seem that tidal recombination is again involved. A likely sequence is the dissociation of the inert gas dimer ion followed by  $\text{F}^-$  abstraction as in



The key common feature of processes (11), (12) and (13) is that the positive ion is an inert gas dimer ion. A light valence-bound diatomic ion has different characteristics. As already noted,  $r_e$  and  $\omega_e$  for  $\text{Xe}_2^+$  are  $6.18 a_0$  and  $112 \text{ cm}^{-1}$ . In the cases, for instance, of  $\text{O}_2^+(X^2\Pi_g)$  and  $\text{O}_2^-(X^2\Pi_g)$  the corresponding values are  $2.11 a_0$  and  $1905 \text{ cm}^{-1}$  (Huber and Herzberg 1979) and  $2.53 a_0$  and  $1039 \text{ cm}^{-1}$  (Michels 1979). The slow change that occurs in the relatively weak force field during passage through perihelion could not lead to vibrational excitation. Hence the rate at which  $\text{O}_2^+$  and  $\text{O}_2^-$  ions recombine is not increased appreciably by tidal action. However the influence of tidal action is pervasive because of complex ions being common at the ambient gas densities at which termolecular recombination is of interest. For example at 300 K the main ionic recombination process that takes place in pure molecular oxygen is



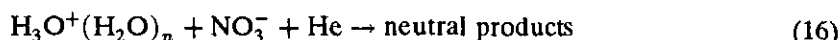
in the range

$$10^{17} \text{ cm}^{-3} < [\text{O}_2] < 10^{20} \text{ cm}^{-3} \quad (15)$$

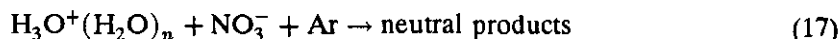
(cf Bates and Flannery 1969). The loosely bound  $\text{O}_4^+$  complex is elongated, has low bending and stretch frequencies and a dissociation energy of only 0.42 eV (Yang and Conway 1964). Internal excitation is likely in an encounter with an oppositely charged ion. As a quencher  $\text{O}_2$  is probably more effective than is an ambient inert gas atom (Ferguson 1986). Mutual neutralization channels are open. It is not at present possible to disentangle the effects of enhanced mutual neutralization and tidal termolecular ionic recombination. They are not additive in that the former process tends to suppress the latter (as it does non-tidal termolecular ionic recombination). McGowan (1967) has carried out measurements on the rate of process (14) at 300 K. In accord with expectation his values of  $\alpha$  are greater than those obtained from

the universal curve: for example at 300 Torr his value is  $1.4 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  while the universal curve value is  $0.9 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ .

Laboratory studies of



and



in which  $n$  is 2 or 3 have been made by Lee and Johnsen (1989). As they pointed out, the rate coefficients that they obtained are considerably greater than those derived from the universal curve of Bates and Mendaš (1982b). Since the proton affinity of  $\text{H}_2\text{O}$  is 7.2 eV (Radzig and Smirnov 1985) proton transfer is not feasible unless the distance between the ions is less than about 2 Å. This distance is so small that contribution of proton transfer to the recombination rate is insignificant. From the proton affinity just cited, the hydration energies of  $\text{H}_3\text{O}^+$  (Newton 1977), and the electron affinity of  $\text{NO}_3^-$  (Ferguson 1979) it is found that if  $n$  is 2 mutual neutralization is exothermic by only about 0.2 eV, which makes the relevant crossing distance much too great for its rate coefficient to be appreciable; while if  $n$  is 3 the process is endothermic. Mutual neutralization may therefore be disregarded. Only tidal effects appear to remain. The charge on  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  is dispersed amongst the  $\text{H}_2\text{O}$  molecules, which have, moreover, strong dipole moments. Hence an encounter with  $\text{NO}_3^-$  is likely to excite internal modes of the loosely bound cluster. It may be seen from figure 1 that the tidal enhancement for neither process (16) nor process (17) is as great as that for (10). A possible reason is that the ions must approach closer to raise the required electrostatic tide. Another possible reason is that excited  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  is susceptible to collisional deactivation. As already pointed out, such collisional deactivation does not affect the rate coefficient for process (9). The position is different for processes (16) and (17) since the ion that carries the excitation is not, as in the case of process (9), far more massive than is the other ion. Consequently the deactivation collision may significantly increase the orbital energy and thus significantly decrease the recombination coefficient. Comparison of the results on processes (16) and (17) provides some evidence relating to the influence of the deactivation. Were it not for tidal effects the termolecular recombination coefficients at  $[\text{He}]$  and  $[\text{Ar}]$  corresponding to the same value of the independent variable of figure 1 would be equal. The measured rate coefficient for process (16) is less than that for process (17) at the value of the independent variable where the two sets of data points overlap. This would be understandable if,

$$\beta_1(\text{He})/\beta_1(\text{Ar}) > \beta_T(\text{He})/\beta_T(\text{Ar}) \quad (18)$$

where  $\beta_1(\ )$  and  $\beta_T(\ )$  are the respective efficiencies for removal of the  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  excitation energy and for the removal of the excess energy of relative motion from the supra-thermal ions in collisions with the inert gas atom specified in the parenthesis. The masses concerned make inequality (18) reasonable. Thus the mass of  $\text{H}_2\text{O}$  is intermediate between that of He and Ar so that  $\beta_1(\text{He})$  and  $\beta_1(\text{Ar})$  would be expected to be comparable whereas  $\beta_T(\text{He})$  must be considerably less than  $\beta_T(\text{Ar})$  because the ratio of the mass of He to that of either ion is very much less than the

ratio of the mass of Ar to that of either ion. The low gradient of the plot of the data points for process (16) may also be a manifestation of collisional deactivation in ambient helium: as  $[\text{He}]$  is raised the effect of the increase in the collisional deactivation tends to reduce the recombination coefficient and hence partly offsets the increase due to the direct effect of collisions on the orbital motion.

The results on processes (16) and (17) are of special interest because polar molecules tend to cluster on ions even if the ambient gas contains only a trace of the polar gas concerned.

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