New Recombination Mechanism: Tidal Termolecular Ionic Recombination

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The measured rate coefficient α for $Xe_2^+ + Cl^- \rightarrow XeCl^* + 2Xe$ (and similar processes) is far higher than had been expected. The exciting experimental results are reminiscent of assisted mutual neutralization, but this cannot occur. A Monte Carlo simulation that allows for the $Cl^- - Xe^+$, $Cl^- - Xe$, and $Xe^+ - Xe$ forces shows that the rotational and vibrational modes of Xe_2^+ tend to be excited by the passage of Cl^- through perihelion. Because of this electrostatic tidal action the orbit contracts and the internal energy of Xe_2^+ increases, leading to dissociation. The measured values of α are reproduced satisfactorily.

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The study of termolecular ionic recombination in an ambient gas

$$A^+ + B^- + M \rightarrow AB + M \qquad (1)$$

has been under way for almost a century, the earliest paper on the subject having been published in 1896 by Thomson and Rutherford.[1] Since then there have been a succession of eras in which the research of lasting value has been mainly theoretical or in which it has been mainly experimental.[2,3]

In 1903 Langevin[4] gave an accurate expression for the recombination coefficient α in the high ambient-gas density limit, where the drift of oppositely charged ions towards each other is rate limiting. Recombination at moderate and low gas densities is harder to treat. In 1924 Thomson[5] delineated the physics of the process. One of a pair of ions that have approached each other along an open orbit may experience a collision with a gas molecule, which may reduce the energy of relative motion of the ions by enough to render the orbit closed. Subsequent collisions may either reduce the energy further or increase it. Clearly α is determined by the average effect of many collisions. In order to avoid having to carry out the averaging mathematically, Thomson boldly proposed a simplified model in which an approximation to α in the low-density region is expressed in terms of the probability that either ion experiences a collision when within a certain distance $2e^2/3kT$ of the other.

The measurement of α in the laboratory is difficult and more than a decade passed before fairly reliable results became available due to the work of Sayers,[6] Gardner,[7] McGowan,[8] and others (see Massey and Gilbody[9]). In accord with theory it was found that, as the ambient-gas density N is raised, α first increases linearly, then passes through a maximum and decreases monotonically becoming inversely proportional to N in the high ambient-gas density limit. At 300 K the maximum typically occurs near 2×10^3 Torr and is around 2×10^{-6} cm^{3}s^{-1}. Mass analysis of the ions was not carried out so that accurate comparisons with Thomson's predictions could not be made. As far as can be judged, however, the agreement is reasonable.

With the advent of fast computers the research balance swung in favor of theory because, in so far as the ions may be regarded as structureless particles, the problem is exactly soluble for a given ion-neutral interaction. In the $N \rightarrow 0$ limit it reduces to solving a set of linear equations that define the steady-state internal energy distribution of the bound ion pairs followed by an integration that gives the down flow in energy space. This limit has been thoroughly investigated.[10-16] One result[17] is noteworthy in the present context. If, instead of being monatomic, the ions and neutrals are diatomic, the interchange of translational and rotational energy in collisions affects α by only about 10% at most. Most, if not all,[18,19] of the "exact" calculations at nonzero N have been done by determining the fates of a large number of ion pairs by tracing their histories using a Monte Carlo simulation.[20-22] From the well-tabulated $N \rightarrow 0$ limit to α and the simple Langevin formula,[4] all Monte Carlo results pertaining to a particular type of ion-molecule interaction (for example, ion-induced dipole) may be scaled so that they may be represented by one universal curve.[23] Such comparisons as could be made with the results of the measurements mentioned in the preceding paragraph on the recombination of ions like O_4^+ and O_2^- and with later measurements[24] on the recombination of complex ions like $NH_4^+(NH_3)_n$ and $Cl^-(NH_3)_p$ in ammonia provided no indication of any real difference between theory and experiment.

Although laboratory evidence suggesting a need to take into account that the ions have structure had not been obtained, the effect of the mutual neutralization channel

$$A^+ + B^- + M \to A + B + M \qquad (2)$$

was investigated by carrying out Monte Carlo simulations that incorporated the possibility of a transition occurring during a traversal of a pseudocrossing of the potential-energy curves.[20,21,25-28] It was discovered that the inclusion of channel (2) may enhance α by an amount $\Delta\alpha$ that is much greater than α_2^0, the *in vacuo* binary recombination coefficient. The explanation for the enhancement is that the ambient gas increases the frequency of the traversals. At 300 K, $\Delta\alpha$ peaks when N is as low as around 2×10^2 Torr. Assisted mutual neutralization, as process (2) is called, explains discrepancies that prior to its discovery had been found between calculated values of α_2^0 and values that had been inferred[29] from measurements in flames. Making allowance for it in the Monte Carlo simulation has led to the observed recombination coefficient between small ions in the troposphere and lower stratosphere being reproduced satisfactorily.[30] Evidence for assisted mutual neutralization would be expected to show at the lower gas densities in some of the laboratory studies mentioned. None does. Conceivably it is obscured by a change in the complexity of the ions as the gas density is reduced, but further measurements are needed.

The current theory of termolecular ionic recombination has been outlined to make the assumptions on which it depends clear and to show how fully it has been developed. This provides a firm base for considering some unexpected and exciting results obtained in recent experiments.[31-33]

The experiments arose in part because of interest in rare-gas halide lasers initiated[34,35] by processes like

$$Xe_2^+ + Cl^- + Xe \to XeCl^* + 2Xe, \qquad (3)$$
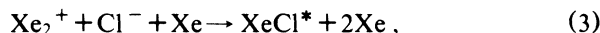
where the asterisk indicates that the molecule is in the excited lasing state. By monitoring the emission from $XeCl^*$, Mezyk, Cooper, and Sherwell[33] determined the rate coefficient α_3 for this recombination channel but did not determine the rate coefficient α_4 for the alternative channel

$$Xe_2^+ + Cl^- + Xe \to Xe_2Cl^* + Xe. \qquad (4)$$
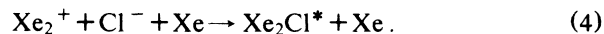
They found that α_3 increases very sharply with pressure reaching a broad maximum of about 4×10^{-6} cm^{3}s^{-1} centered around 200 Torr (Fig. 1). As may be seen, the discrepancy between experiment and theory is great. At 20 Torr the measured α_3 is some 13 times the value read from the universal curve.[23]

The form of the experimental α_3 curve is suggestive of assisted mutual neutralization. However, there is no possibility of this process because $XeCl^*$ is an ionic
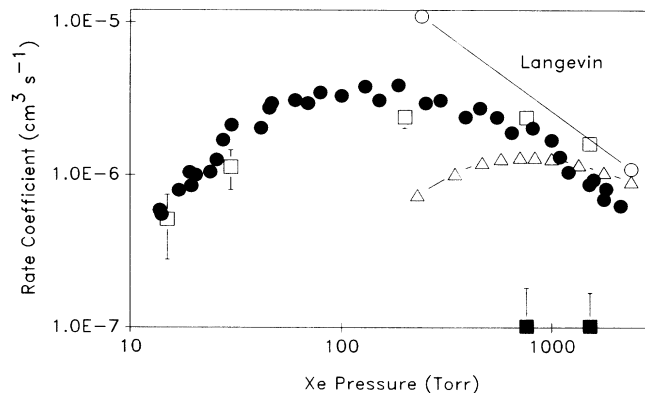

FIG. 1. Comparison of calculated rate coefficients with experimental values ($\bullet$) of Mezyk, Cooper, and Sherwell (Ref. 33). Calculated results for simple theory (that is assuming the ions can be treated as atomic) are represented by $\triangle$; calculated results for the tidal theory are represented by $\square$ for the formation of $XeCl^*$ and by $\blacksquare$ for the formation of Xe_2Cl^*. Note that the Langevin (Ref. 4) curve represents an upper limit to the rate coefficient.

$(Xe^+\text{-}Cl^-)$ state. The reactants and products are on the same potential-energy surface. Channel (3) does not entail an electronic transition (cf. Huestis,[34] Fig. 4).

The sole respect in which the universal curve (or the equivalent Monte Carlo simulation) is not exact is that it depends on the validity of the assumption that Xe_2^+ may be treated as a monatomic ion. Earlier calculations[17] already mentioned show that the recombination coefficient is scarcely affected by whether the ion-neutral collisions involve monatomic or diatomic ions.

Now the equilibrium internuclear separation r_e for Xe_2^+ is as great as $6.18a_0$ and the spectroscopic constants B_e and ω_e are only 0.0239 and 112 cm^{-1}, respectively,[36] so that neighboring rotational and neighboring vibrational levels are close enough together to be regarded as forming a continuum. We therefore speculated that in the perihelion region (say, when Cl^- is at a distance of $50a_0$) the difference between the resultant force on Xe^+ and that on Xe is sufficient to cause significant Xe_2^+ internal energy excitation; and that this electrostatic tidal effect is the key to explaining the observed very high values of α_3 at low pressures. In order to test the speculation, realistic representations of the Cl^--Xe^+, Cl^--Xe, and Xe^+-Xe forces were adopted and the Monte Carlo simulation program was refined[37] so as to take the three forces fully into account.

The tidal effect was found to be important. Because of it the orbit of Cl^- relative to Xe_2^+ tends to contract during a passage through perihelion. The Xe_2^+ internal energy tends to increase correspondingly and to become finally so great that dissociation occurs as in channel (3). The calculated and measured values of α_3 are in excellent agreement (Fig. 1).

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