PRODUCTION, QUENCHING AND REACTION OF VIBRATIONALLY EXCITED IONS IN COLLISIONS WITH NEUTRALS IN DRIFT TUBES

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1. INTRODUCTION

The Flowing Afterglow Technique (Ferguson et al., 1969) provided the first chemically versatile method for measuring ion-molecule reactions at room temperature, later extended from 80K to 900K (Lindinger et al., 1974). Positive and negative ions of great variety can be studied, including metal ions, heavily solvated ions, doubly charged positive ions, electronically excited ions and now vibrationally excited ions. A variety of neutrals including H, O, atoms, OH radicals, O₃, H₂O₂, HNO₃, H₂SO₄ and N₂O₅ have been reacted with ions in the Flowing Afterglow. Reactions of ions with vibrationally excited N₂ (Schmeltekopf et al., 1968) and H₂ (Jones et al., 1986) have been carried out. The chemical versatility is unmatched by any other technique.

The subsequent Flow Drift technique (McFarland et al., 1973) allowed an extension of the energy range from thermal to several electron volts relative kinetic energy, bridging the gap between thermal energy and higher energies accessible to beam experiments. An inherent problem with drift tube measurements, in which kinetic energy is supplied to the ions by means of an applied electric field, is that the energetic ions do not have Maxwellian distributions of velocities. Thus one does not obtain true thermal rate constants. This problem has been solved for atomic ions in atomic buffer gases (Lin and Bardsley, 1977; Viehland and Mason, 1977) so that cross sections have been deduced from ~ 0.04 to 2 eV for several O⁺ and O⁻ reactions, carried out in helium buffer gas. The measured mobilities of the ions in the buffer gas supply sufficient information about the ion-neutral interaction to allow either a deduction of the ion velocity distribution from which reaction cross-sections can be derived from experimental rate constants (Lin and Bardsley, 1977), or they allow measured rate constants to be corrected to thermal ones (Viehland and Mason, 1977). The velocity distribution problem has not yet been solved for either molecular ions or molecular buffer gases because of the complexity added by the internal degrees of freedom, which are
excited in collisions.

Another aspect of drift tube measurements is that the internal degrees of freedom of molecular ions may not be in equilibrium with translation; in general they are not. Usually rotational excitation is equilibrated with translation but vibrations are not, depending on the buffer gas, the ion, the drift tube length, the pressure and the applied electric field strength. Recently theory has shown that molecular ion internal excitation in atomic buffer gases will be in equilibrium with translation at steady state (Viehland et al., 1981). In practice, particularly with He buffer gas, steady state is not usually reached in conventional drift tubes involving \(-10^3\) collisions between the molecular ions and the He buffer gas.

This situation must of course be reckoned with; it can be either an advantage or a disadvantage. If one is simply interested in thermodynamic rate constants (as one often is) then it is clearly a disadvantage. On the other hand, it does offer an experimental possibility of separating the contributions of kinetic energy and vibrational energy to reaction rate constants, i.e. the possibility of a certain limited amount of state-to-state chemistry. It is this aspect of flow drift tubes that is addressed in this discussion, namely the manner in which vibrational excitation and deexcitation rate constants may be obtained, and demonstrations of specific effects on reaction rate constants due to ion vibrational excitation. Such studies offer insight into molecular reaction mechanisms and dynamics and into the nature of molecular potential surfaces.

2. VIBRATIONAL EXCITATION

A clear indication of ion vibrational excitation in drift tubes has been given by the finding of quite different rate constants versus energy for many ion neutral reactions carried out in different buffer gases. The most usual experience has been to find that a reaction rate constant is larger in Ar buffer than in He buffer. This kind of result could also be due to the differing velocity distribution of the ions in the two buffer gases. However, the effect of different velocity distributions is quantitatively very much less and is only significant for a very steeply increasing rate constant with energy, in which case the velocity distribution with the greatest high energy tail will produce the largest rate constant. This situation has been worked out in detail for the reaction \(O^+ + N_2 \rightarrow NO^+ + N\), for which the rate constant increases by a factor of \(\sim 40\) between thermal energy and \(\sim 1\text{eV}\) (Albritton et al., 1977). This is about as extreme a case as can be encountered for velocity distribution effects, and yet is quite small compared to commonly observed vibrational enhancement effects. A convincing proof of the vibrational nature of many enhancements has often been obtained by vibrationally quenching the reactant ion by addition of a trace of its parent neutral. The quenching by charge-transfer normally occurs near the collision rate, while the velocity distribution would be scarcely perturbed by trace gas addition. Large rate constant changes due to added trace quantities of ion reactant