

have observed very interesting behavior in the vibrational lifetime, T_1 , as a function of density and temperature near the critical points. In these experiments, a CO stretching vibration in $W(\text{CO})_6$ was excited to $v = 1$, and its lifetime was measured using picosecond infrared lasers. In supercritical CO_2 , just above the critical temperature, the vibrational lifetime decreased from over 900 ps to about 700 ps as the density increased from about 2 to 5 mol L^{-1} . The lifetime then reached a plateau, and remained constant in the density range 7 to 12 mol L^{-1} , before beginning to decrease again at higher densities.^{51,52} At constant, near-critical density, vibrational lifetimes were studied as a function of temperature.^{53,54} Temperature regimes were found in supercritical ethane and fluoroform where the vibrational lifetime increases with increasing temperature. In supercritical CO_2 , however, the lifetime decreased approximately linearly with temperature. These interesting and carefully collected data are providing some nonintuitive results that are challenging tests for theories to describe the intermolecular interactions near the critical point.

3. High Temperature Chemistry in the Atmosphere

The earth's upper atmosphere possesses a collection of extreme environments. For example, at altitudes between 100 and 400 km, the temperature of the atmosphere rises from 200 K to 2000 K. In this region of the ionosphere, the dominant ions are O_2^+ , NO^+ , and O^+ , having concentrations between 10^4 and 10^5 cm^{-3} .⁵⁵ Until recently, it has not been possible to measure reaction rates for these species throughout the range of temperatures characteristic of the ionosphere. The need to validate rate constants for use in computational models of the ionosphere has spurred the development of instruments to obtain this data.

Viggiano, Morris, and coworkers have developed a high temperature flowing afterglow that they have used for studying ion-molecule reactions at temperatures from 300 K to 1800 K.⁵⁶ The high temperature capability enables the observation of the onset of higher energy reaction channels, and combined with data from previous studies, provides insights into the role of internal energy in promoting reactivity. Examples of this are the reactions of O^+ with N_2 and O_2 ,⁵⁷ where prior work in drift tubes had been used to selectively enhance translational energy.⁵⁸ Comparing the rate constants obtained using pure thermal excitation with those from nonthermal, translational excitation, it was determined that rotational energy plays a

minimal role in controlling reactivity, while vibrational excitation has a much greater, enhancing effect.⁵⁷ In the case of the reaction of O^+ with O_2 , thermally exciting vibrations increased the reaction rate constant a factor of 5 over the same energy obtained by pure translational excitation. For O^+ with N_2 , it was found that thermally exciting N_2 to $v = 2$ increased the reaction rate constant by a factor of 40 relative to the $N_2(v = 0)$ rate constant, in agreement with earlier observations of Schmeltekopf *et al.*^{59,60} The role of vibrational excitation in enhancing reactivity has recently also been observed in the reactions of N^+ and N_2^+ with O_2 ⁶¹ and in the reactions of O^+ with CH_4 ,⁶² where new product channels were seen to open as CH_4 became vibrationally excited due to high thermal excitation. Wodtke and coworkers⁶³ have also recently reported that vibrational excitation can promote surface chemistry. They observed that NO molecules excited to $v = 13$ and 15 react (via dissociative adsorption) with a copper surface with a reaction probability more than one thousand times greater than for ground state NO.

Ion beam experiments involving high temperature vapors are also being carried out. Levandier *et al.*⁶⁴ have developed a high temperature guided-ion beam apparatus in which reaction cross sections can be measured at selected translational energies and target vapor temperatures up to 800 K. While the instrument was originally designed for metal vapor studies, it has also been used to investigate the change in threshold behavior when low-frequency modes of a molecular target are thermally excited.⁶⁵ Studies in this system related to meteor chemistry are discussed in more detail in Chap. 6 by Dressler and Murad in this volume.

Another example of a chemically interesting property of the upper atmosphere is nonlocal thermodynamic equilibrium (NLTE). Rotational NLTE has been demonstrated by the observation of pure rotational emission^{66–68} from high N levels of OH, NO, and CO in the upper mesosphere/lower thermosphere (85 to 95 km) where pressures are about 5 Pa. For OH ($X^2\Pi$, $v = 0-3$), emission from rotational levels up to $N = 33$ were observed in the airglow in the CIRRIS 1A experiment conducted on the space shuttle.⁶⁶ Holtzclaw *et al.*⁶⁹ have studied the rotational relaxation of high N states of OH ($X^2\Pi$, $v = 1-3$) by O_2 in a cryogenically-cooled chamber called LABCEDE at 100 K to assess the processes that affect the rotational distribution of OH in the upper atmosphere. They found that rotational relaxation occurred at a gas-kinetic rate, predominantly by single-quantum steps within each vibrational manifold.