

Chemistry at high pressures also has many technological applications. Chemistry in supercritical fluids, for example, is drawing increasing attention for the possibility of replacing organic solvents in synthetic, purification, and separation processes.<sup>12</sup> Extremely high pressure (20–40 GPa)<sup>13</sup> and temperature (3000–4000 K)<sup>14</sup> transients are experienced in the detonation of energetic materials. The study of the chemistry in the detonation front of explosives is an area where experimental research<sup>15</sup> and novel computer simulations (see Chap. 11 of this volume by White) are underway to understand the real time effects on energy transfer and chemical processes. On a microscopic scale, extremely high local pressures can be created at the interface where two materials slide across one another. The pressures produced at the junction where asperities come in contact can reach 1 GPa, exceeding the critical stresses beyond which the materials deform or fracture.<sup>16</sup> A satisfactory understanding and picture of all of these processes will likely rely on the development of reliable simulation methods, developed and validated in close collaboration with experiment.

Another classification of environments that can be considered extreme are highly chemically reactive environments. The sparse but reactive environment of space, the technologically important realm of plasma processing, and chemical laser systems fit into this category. A number of these situations are discussed by Minton (see Chap. 9 in this volume) who looks at the reactions of oxygen atoms with the low-earth orbital translational energy of 5 eV as they collide with spacecraft materials, and Heaven (see Chap. 4 of this volume) who discusses dynamics in chemical laser systems. Again, experiment and theory together must provide a well-grounded, fundamental understanding of the dynamics of these systems if a reliable predictive capability of the macroscopic observables is to be developed.

## **2. Chemistry at High Temperatures and Pressures**

The drive to model the chemistry in flames, in other combustion systems, and in high enthalpy air flows has motivated many studies of chemistry at high temperatures and pressures. Many studies of elementary processes under these conditions have been performed in shock tubes, typically at temperatures in the range 1000 to 2000 K, but temperatures up to 5000 K can be achieved in these devices. In a typical shock tube experiment, a driver gas is stored at high pressure behind a diaphragm, separating it from the sample residing in the length of the tube. When the diaphragm

is ruptured, a shock wave travels down the tube, and measurements are often made near the end wall of the tube behind the reflected shock where relatively constant, elevated temperatures can be maintained for hundreds of microseconds. Shock tube work has been reviewed periodically and extensively.<sup>17–19</sup> In fact, much of the existing high temperature rate data frequently used in models of combustion chemistry and other high temperature gas-phase systems has been obtained in shock tubes.<sup>20</sup>

Alternative approaches to measuring reaction rates and dynamical processes at high temperatures have been pursued. Measurements in flames using laser diagnostics<sup>21</sup> and molecular beam mass-spectrometric sampling have been carried out.<sup>22</sup> Direct laser heating of molecules in the gas-phase or heating of an absorbing gas to create a heated channel of gas far from surfaces have been used to obtain mechanistic information and quantitative Arrhenius parameters for homogeneous reactions in the gas-phase.<sup>23,24</sup> The high heating and cooling rates obtained by pulsed-laser-driven heating can produce temperatures in excess of 1000 K that last for only several microseconds. Thus, products of the initial high temperature reaction are often rapidly cooled and thermally stabilized relative to experiments at constant high temperatures. This permits analysis of primary dissociation products that can themselves often thermally dissociate.<sup>25</sup>

Novel methods are now being developed to generate shock waves that rapidly produce extreme environments of high pressure and temperatures in solid materials. Shock wave generation, propagation, and their effects on the chemistry of the material are particularly important in energetic materials, where a shock wave, initiated by a physical impact, could lead to detonation. Studies have been performed in which gas guns are used to propel a large impact plate into a sample, generating pressures of up to 200 GPa. The shocked sample can then be spectroscopically probed in single shot experiments,<sup>14,26</sup> with these spectroscopic studies usually performed in the tens of GPa pressure region. But ultrafast time resolution and precise control of the timing between shock and probe is required to unravel the initial physical and chemical changes and vibrational energy redistribution in condensed-phase materials and to study their evolution following passage of a shock front. New methods have recently been developed to probe these properties in real time, and are providing new insights into the behavior of these materials that directly impact their chemical reactivity.<sup>15</sup>

Clott and coworkers<sup>27,28</sup> have developed a technique to generate shock waves with fast (< 25 ps) risetimes in specially designed assemblies, that are

then probed spectroscopically. In this method, a near-infrared laser pulse is absorbed by a 2- $\mu\text{m}$  thick outer layer of a microfabricated, multilayered target array. A few nanograms of this polymer layer are rapidly ablated and a shock wave that is relatively planar, and of approximately constant velocity throughout the sample is launched into the layers below. A buffer layer delays the arrival of the shock at the sample layer as debris from the ablation is permitted to clear. The shock then impinges on the sample layer, and subsequently travels into a dissipation layer. This layered assembly is supported on a glass substrate which provides optical access for probing by coherent anti-Stokes Raman spectroscopy. This “nanoshock” method has produced transient pressures on the order of 1–5 GPa and temperature rises of several hundreds of degrees in a region about 100  $\mu\text{m}$  in diameter. Since the sample is locally destroyed by the ablation of the shock-generation layer, the sample assembly is translated before the next shot is fired, and reproducible shocks have been generated at a repetition rate of 80  $\text{s}^{-1}$ .

The “nanoshock” method allows the collection of vibrational spectra of molecular solids with time resolution of 25 ps. It has been applied to a number of energetic materials.<sup>29</sup> The rapid cooling during unloading of the shock ( $\sim 10^{11} \text{ K s}^{-1}$ ) allows little time for thermal decomposition of the sample. This method has recently been used to detect fast mechanical processes in polycrystalline films of the energetic material NTO.<sup>30</sup> The shocks induce partial orientation of the crystals with one another in only a few nanoseconds. This orientation is faster than the time scale for initiating chemical reactions in this system, and may have implications for the mechanism of the initiation of detonation of energetic materials. The importance of orientation in detonation has been previously observed in the directional dependence of shock-wave initiated detonation of single crystals of energetic materials.<sup>31</sup>

The detonation of energetic materials is also critically dependent on energy transfer in molecular solids.<sup>32</sup> Studies of vibrational energy redistribution in polyatomic molecules in the condensed-phase are being carried out on a number of systems.<sup>33,34</sup> Resonant vibrational excitation from ultra-short infrared pulses can drive molecules to effective vibrational temperatures of 4000–5000 K. Vibrational energy redistribution can then be studied by anti-Stokes Raman probing. These IR–Raman studies, with time resolution of about 1 ps, monitor the energy flow throughout almost all of the vibrational states of a polyatomic liquid. A particularly relevant case for

energetic materials is nitromethane, a model system for detonation. When the C–H stretching modes of nitromethane are excited, vibrational cooling is observed to occur in three distinctive steps.<sup>34</sup> First, the deposited energy is redistributed to all of the vibrations of the molecule in a few picoseconds. Second, the higher frequency vibrations relax to lower energy modes in a few tens of picoseconds. Finally, these lower energy modes decay to the bath in about 100 ps. The dynamics of coupling of energy into these lowest frequency modes may play a key role in determining the sensitivity of an energetic material to shock initiation.

Other novel methods are being employed to examine chemistry at extremely high temperatures and pressures. For example, Suslick and co-workers use ultrasound to initiate “sonochemistry.”<sup>35,36</sup> In this work, ultrasound is directed into a liquid creating bubbles that grow, and then implisively collapse. The rapid collapse, or cavitation, compresses and heats the gas trapped in the bubble producing hot spots with effective temperatures of  $\sim 5000$  K, pressures of  $\sim 100$  MPa, and heating and cooling rates above  $10^{10}$  K s<sup>-1</sup>. Sonoluminescence, the light that is often produced during cavitation, can provide a probe of the interior of the bubble. The intense temperatures and pressures produced during cavitation can have destructive effects, for example, when it occurs around the propeller of a ship. However, these conditions have been used for some novel chemical synthesis, with particular effect when solid surfaces or powders are in the liquid.<sup>37</sup> In these systems, solid particles are accelerated to high velocities and interparticle collisions can change surface morphology and chemical reactivity. Unique nanostructured materials and biomaterials have been synthesized by these methods.<sup>38,39</sup>

Studies at extremely high static pressure can be carried out in diamond anvil cells.<sup>40</sup> Studies of chemical dynamics in gem anvil cells are beginning to be carried out,<sup>41</sup> and some unique chemical synthesis can also occur at these high pressures. For example, a high pressure polymerized phase of carbon monoxide was recently reported to be synthesized using visible laser light to irradiate a carbon monoxide sample at pressures of over 5 GPa in a diamond anvil cell.<sup>42</sup>

Another class of extreme environments being used for synthetic applications are near critical and supercritical fluids. A number of reviews have looked at reactions in supercritical water.<sup>43,44</sup> Brill and coworkers have developed experimental devices in which to perform infrared and Raman

spectroscopic studies of hydrothermal reactions at temperatures up to 700 K and pressures of 35 MPa,<sup>45,46</sup> above the critical point of water (647 K, 22.1 MPa).<sup>47</sup> These studies have elucidated the kinetics and reaction pathways of numerous systems under hydrothermal conditions.

Studies of solvation and energy transfer in supercritical fluids provide an important way to bridge our understanding of dynamics in the gas-phase and liquid phase.<sup>48</sup> Troe and coworkers have performed studies in supercritical fluids to test the applicability of the Isolated Binary Collision (IBC) model of energy transfer over a wide range of density and temperature, spanning the transition from gas-phase to liquid phase.<sup>49,50</sup> In these experiments, subpicosecond lasers were used to excite azulene with about  $20\,000\text{ cm}^{-1}$  of energy to its first excited singlet state,  $S_1$ . This state rapidly underwent internal conversion producing highly vibrationally excited levels of the ground electronic state,  $S_0^*$ . Deactivation of the vibrationally excited azulene by collision partners (Xe,  $\text{CO}_2$ , ethane, propane, *n*-pentane, *n*-octane) was monitored by transient absorption in the ultraviolet on the  $S_3 \leftarrow S_0$  transition. These experiments, coupled with Monte Carlo simulations, demonstrated that an IBC model of energy transfer proved applicable from densities that spanned the gas-phase to the liquid phase if the collision frequency was expressed in terms of the radial distribution function around the azulene solute molecule, assumed to be a hard sphere in a Lennard–Jones fluid.<sup>50</sup> The radial distribution function accounts for the local cluster formation or solvation that dynamically occurs in supercritical fluids. This clustering increases the local density of the solvent around the solute with respect to the bulk and could be thought of as shielding the excited molecule. This model implies that while the collision frequency varies with density, the average energy transferred per collision  $\langle \Delta E \rangle$  remains constant as a function of density, and should be transferable from gases to liquids.<sup>50</sup>

Another probe of the local environment around the azulene solute molecule was the shift of the frequency of the  $S_3 \leftarrow S_0$  absorption band, as a function of density.<sup>50</sup> This solvachromic shift, or stabilization of the electronic states of the solute in the presence of the solvent, was accurately described using the same radial distribution function used to reproduce the collisional deactivation rates. The applicability of the same radial distribution function to treat collisional deactivation and solvachromic frequency shifts suggests that both have a similar dependence on local density.

Fayer and coworkers have studied the vibrational dynamics of molecules excited in solvents that were in or near supercritical conditions.<sup>51–54</sup> They

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  $\text{CO}_2$ , 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  $\text{L}^{-1}$ . The lifetime then reached a plateau, and remained constant in the density range 7 to 12 mol  $\text{L}^{-1}$ , before beginning to decrease again at higher densities.<sup>51,52</sup> At constant, near-critical density, vibrational lifetimes were studied as a function of temperature.<sup>53,54</sup> Temperature regimes were found in supercritical ethane and fluoroform where the vibrational lifetime increases with increasing temperature. In supercritical  $\text{CO}_2$ , 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  $\text{O}_2^+$ ,  $\text{NO}^+$ , and  $\text{O}^+$ , having concentrations between  $10^4$  and  $10^5$   $\text{cm}^{-3}$ .<sup>55</sup> 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.<sup>56</sup> 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  $\text{O}^+$  with  $\text{N}_2$  and  $\text{O}_2$ ,<sup>57</sup> where prior work in drift tubes had been used to selectively enhance translational energy.<sup>58</sup> Comparing the rate constants obtained using pure thermal excitation with those from nonthermal, translational excitation, it was determined that rotational energy plays a