Chemical physics: Molecular clouds, clusters, and corrals

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Vignettes of three frontier areas illustrate the eclectic scope of modern chemical physics. (1) Radioastronomy has revealed a profusion of organic molecules in interstellar clouds, now attributed to sequences of exoergic, bimolecular ion-molecule reactions proceeding far from thermodynamic equilibrium. The organic profusion occurs because He^+ ions react far more readily with CO than with the much more abundant H_2 molecules. (2) Molecular clusters, generated by supersonic expansions, have become a favorite medium for study of reactions and spectra. Exemplary episodes are the discovery of carbon-60 and kindred fullerene molecules and the observation of sharp rotational spectra of guest molecules in superfluid helium clusters. (3) New means to control molecular trajectories are being developed. These include spatial orientation or alignment by field-induced hybridization of rotational states, corralling (or trapping) molecules after collisional or mechanical quenching of translational kinetic energy, and laser control of photochemical reaction pathways. [S0034-6861(99)02702-6]

I. INTRODUCTION

In its modern incarnation, chemical physics as a field is generally regarded as having been born in 1933, along with the *The Journal of Chemical Physics*. Its first editor, H. C. Urey, declared that "the boundary…has been completely bridged…chemists and physicists have become equally serious students of atoms and molecules" (Urey, 1933). Among other evangelical founders were P. Debye, H. Eyring, G. B. Kistiakowsky, I. Langmuir, G. N. Lewis, L. Pauling, K. S. Pitzer, J. C. Slater, J. H. Van Vleck, and E. B. Wilson, Jr. Actually, Urey's bridge was still rickety and had to stretch over a wide cultural gulf (Nye, 1993).[1] A major impetus for the new journal was the fact that *The Journal of Physical Chemistry* refused to accept any purely theoretical paper (and continued to do so for another two decades). By 1939, however, Slater had published his *Introduction to Chemical Physics*, and by 1942 Wilson and Van Vleck had established at Harvard the first Ph.D. program in chemical physics. Over the next 50 years, means of elucidating molecular structure and dynamics developed enormously, by virtue of pervasive applications of quantum theory and experimental tools provided by physics, especially myriad spectroscopic methods.

Chemical physics and physical chemistry no longer differ appreciably, either in research journals or in academic programs, now that computers and lasers have become ubiquitous. Yet creative tension persists at the interface of chemistry and physics. The chemist wants above all to understand why one substance behaves differently from another; the physicist wants to find disembodied principles that transcend the specific substances. A chemical physicist thus sometimes stands awkwardly astride a widening intellectual abyss. However, often the duality of outlook provokes invigorating perspectives. This article takes a brief look at three frontier areas that offer such perspectives. Necessarily, these vignettes are idiosyncratic and impressionistic; only a few leading references and reviews can be cited, and many other fruitful areas are left out altogether. The chief aim is to exemplify the characteristic eclectic style of chemical physics, coupling theory and experiment, probing structural and dynamical aspects, and ranging from *ab initio* rigor to heuristic extrapolation.

II. CHEMISTRY IN INTERSTELLAR MOLECULAR CLOUDS

Over the past 30 years, radioastronomy has revealed a rich variety of molecular species in the interstellar medium of our galaxy and even others. Well over 100 molecules have now been identified in the interstellar gas or in circumstellar shells (Thaddeus *et al.*, 1998). These include H_2, OH, H_2O, NH_3, and a few other small inorganic species, but most are organic molecules, many with sizable carbon chains involving double or triple bonds. To appreciate how surprising this proliferation of organic molecules is, we need to review some aspects of the interstellar environment.

A. Uniform radiation, multiform chemistry

As early as 1941, optical absorption lines of the CN molecule were observed in an interstellar cloud that fronted a bright star, which served as the light source. The intensity ratio of lines originating from the ground level and first excited rotational levels provided the first evidence for the 3 °K cosmic background radiation, although not recognized as such until 25 years later (Thaddeus, 1972). This background contains roughly 99% of the electromagnetic energy in the known universe. It is now established as isotropic, blackbody radiation and

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[1] Nye concludes that chemistry, as a discipline, preceded and aided the establishment of physics as an academic and laboratory discipline. She points out that the term "chemical physics" often appears in the titles and chapters of textbooks in the latter half of the 19th century. These treated heat, light, and electricity as chemical agents, topics regarded as prefatory to the core of chemistry dealing with properties and reactions of inorganic and organic substances.

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attributed to a frigid whimper of radiation, still in thermal equilibrium, from a primordial inferno, the Big Bang.

The cosmic abundance of the elements is drastically nonuniform. Hydrogen comprises over 92%, helium over 6%; next come oxygen at 0.07%, carbon at 0.04%, and nitrogen at 0.009%. The average density within our galaxy is only about one H atom per cubic centimeter. Yet the density is about a hundredfold higher in what are called diffuse interstellar clouds and up to a millionfold higher in dark clouds. In diffuse clouds, such as those in which the CN rotational states were found to be in thermal equilibrium with the 3 °K background radiation, a molecule collides with another (H_2 or He) only once every two months or so. This led, in the early days of radioastronomy, to the expectation that emission spectra from rotational levels of any polar molecules in the interstellar medium would be unobservable, because collisions were much too infrequent to alter the rotational temperature.

Such pessimistic anticipation was dispelled by the discovery of molecular rotational emissions from dark clouds (Rank *et al.*, 1971). This discovery showed that the gas density in many interstellar regions was actually high enough to enable the population of rotational levels to be governed more strongly by collisions than by the background radiation. However, the observed molecular abundances departed enormously from estimates derived by assuming chemical equilibrium. For instance, next to H_2, carbon monoxide is the most abundant interstellar molecule (although typically down by a factor of 10^{-4} or more). But thermodynamic calculations predict that under typical dark cloud conditions (20 °K, density of $H_2 \sim 10^5\ \mathrm{cm}^{-3}$) at chemical equilibrium there would be fewer than one CO molecule in the volume ($10^{84}\ \mathrm{cm}^3$) of the observable universe. Likewise, the prevalence of organic molecules containing many carbon atoms and relatively little hydrogen is inexplicable by thermodynamics.

B. Synthesis of interstellar molecules

This situation led Klemperer (1995, 1997) to propose a nonequilibrium kinetic scheme for the synthesis of interstellar molecules, to show how "chemistry can, in the absence of biological direction, achieve complexity and specificity." The scheme invokes sequences of exoergic, bimolecular ion-molecule reactions. Extensive laboratory experiments have shown that these processes are typically quite facile and uninhibited by activation energy barriers, unlike most gas-phase chemical reactions not involving ions. Uninhibited reactions in two-body collisions are the only plausible candidates for gas-phase chemistry at the low density and temperature of an interstellar cloud. The clouds also contain dust particles of unknown composition. Formation of hydrogen molecules from atoms is probably catalyzed on the surface of dust particles, but the host of other molecules seem more likely to be produced by nonequilibrium gas-phase kinetics.

The dark clouds where most interstellar molecules have been seen are immense, typically comprised of hydrogen and helium with a million times the mass of our Sun. In our galaxy such clouds loom as huge dark blotches obscuring regions of the Milky Way. Ionization by the pervasive flux of 100-MeV cosmic rays seeds the clouds with a little H_2^+ and He^+ (about one ion per 500 cm^3), from which sprout many reaction sequences.

The H_2^+ rapidly reacts with H_2 to form H_3^+ which, as known from laboratory studies, itself readily transfers a proton to many other molecular species. Most of the H_3^+ is converted to HCO^+, a very stable species. This prediction was a triumph for Klemperer's model. Soon thereafter interstellar emission from a species dubbed Xogen, which had not yet been seen on earth, was shown to come from the HCO^+ ion. It has proved to be the most abundant ion in dark clouds and has even been observed in several distant galaxies.

Much else offers support for the kinetic model. For instance, proton transfer from H_3^+ to nonpolar molecules such N_2 and CO_2 converts them to polar species HN_2^+ and $HOCO^+$, which are capable of emitting rotational spectra. Again, laboratory observation of these spectra (Saykally and Woods, 1981) confirmed the detection of interstellar emissions from these species.

Most striking are offspring of the He^+ ions, which exemplify how chemical kinetics can produce paradoxical results. The extraction by He^+ of a hydrogen atom from H_2, the most abundant molecule in interstellar clouds, would be very exoergic. Yet, for reasons described below, that reaction does not occur. Instead, He^+ reacts with CO, the second most abundant molecule, to form C^+ and O. The ionization of helium is almost quantitatively transferred to C^+, enhancing its concentration a thousandfold (by the He/CO abundance ratio). In turn, the C^+ ion reacts only feebly with H_2 (via radiative association), but reacts avidly with methane, CH_4, and acetylene, C_2H_2, to launch sequences that build up many organic compounds, including chains punctuated with double and triple bonds. The paradoxical irony is that the mutual distaste of the simplest inorganic species, He^+ and H_2, gives rise to the proliferation of complex organic molecules in the cold interstellar clouds.

C. Electronic structure and reaction specificity

The three-electron system involving only helium and two hydrogen atoms offers a prototypical example for interpretation of chemical dynamics in terms of electronic structure (Mahan, 1975). As shown in ion-beam scattering experiments, the reaction $He + H_2^+ \rightarrow HeH^+ + H$ is endoergic by 0.8 eV, but occurs readily if at least that amount of energy is supplied, either as relative kinetic energy of the collision partners or as vibrational excitation of H_2^+. In contrast, the reaction $He^+ + H_2 \rightarrow HeH^+ + H$ is exoergic by 8.3 eV, but appears not to occur at all; the less exoergic pathway to form $He + H^+ + H$ has been observed, but its reaction rate is four orders of magnitude smaller than for comparable exoergic ion-molecule reactions.

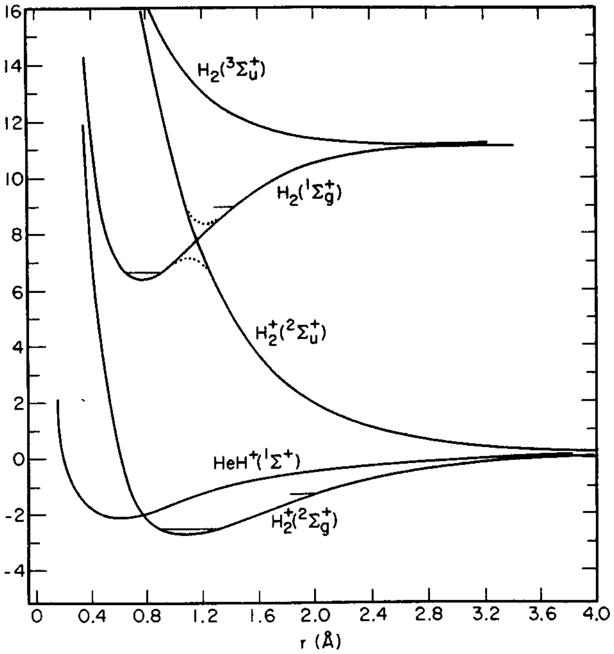

FIG. 1. Potential-energy curves for the diatoms in the asymptotic reactant and product regions of the $(He\text{-}H_2)^+$ system. Since the energies of He and He^+ are included, here the ground $^1\Sigma_{g^+}$ state of H_2 lies above the states of H_2^+. Note the crossing of the curves for H_2 $(^1\Sigma_{g^+})$ and H_2^+ $(^2\Sigma_{u^+})$, which occurs in the reactant region of $He^+ + H_2$, but which becomes an avoided intersection (indicated by dashes) when all three atoms are close to each other. From Mahan, 1975.

Figure 1 provides an explanation, due to Mahan (1975), for the drastic difference in reactivity of $He + H_2^+$ and $He^+ + H_2$. Plotted are diatomic potential-energy curves for the reactants and products; these represent cuts through the triatomic potential-energy surfaces in the asymptotic entrance and exit channels. Consider first the lowest-lying trio of separated atoms, $He + H^+ + H$. Since both the reactants $He + H_2^+$ and the products $HeH^+ + H$ correlate adiabatically to $He + H^+ + H$, the reaction can be expected to proceed on a single triatomic potential-energy surface.

However, for the upper trio of atoms, $He^+ + H + H$, this does not hold. The ground-state H_2 diatomic potential curve; $^1\Sigma_{g^+}$, which arises from bringing together two H atoms with antiparallel spins, represents a cut in the asymptotic reactant region through the potential surface for $He^+ + H_2$ collisions. The corresponding cut in the product region, generated by bringing together $He^+ + H$, yields an excited singlet state that is totally repulsive, according to electronic structure calculations. Likewise, the accompanying excited triplet state with parallel spins is at best only very weakly bound. Accordingly, colliding $He^+ + H_2$ is very unlikely to form a stable HeH^+ molecule.

As can be seen in Fig. 1, in the asymptotic reactant region, the ground-state $H_2(^1\Sigma_{g^+})$ potential curve crosses at about 1.1 Å that for $H_2^+(^2\Sigma_{u^+})$, a strongly repulsive state. When He^+ approaches H_2, however, the resulting interaction induces these states to mix, as both then acquire the same symmetry (A' under the C_S point group). The crossing thus evolves into an avoided intersection (indicated schematically by dashes). If electron transfer occurs, the adiabatically formed products initially are $He + H_2^+(^2\Sigma_{u^+})$, which dissociate directly to $He + H^+ + H$.

Exemplary of chemical physics, the profusion of organic molecules tumbling in the heavens is linked to devilish details that govern an electron hopping between helium and hydrogen.

III. MOLECULAR CLUSTERS, SUPERSTRONG OR SUPERFLUID

The properties and interactions of molecules are often much influenced by the company they keep. Molecular clusters, generated by supersonic expansion of gas into a vacuum apparatus, have now become a favorite medium for the study of reactions and spectra. Such clusters, composed of from two to up to a billion molecules, offer means for interpolating between gaseous and condensed phases or solution chemistry (Castleman and Bowen, 1996). Before considering two examples from this cornucopian field, we describe the key experimental tool that made it possible, the supersonic nozzle.

A. The versatile supersonic beam

The canonical physics literature on molecular beams, going back to Otto Stern and I. I. Rabi, stressed that the pressure within the source chamber should be kept low enough so that molecules, as they emerged from the exit orifice, did not collide with each other. In this realm of effusive or molecular flow, the emergent beam provides a true random sample of the gas within the source, undistorted by collisions. Chemical physicists, in desperate need of intensity for studies of reactions in crossed beams, violated the canonical ideal by using much higher source pressures. Collisions within the orifice then produced hydrodynamic, supersonic flow. This realm, avidly explored by chemical engineers (Fenn, 1996), proved to offer many advantages.

When a gas expands isentropically into a vacuum through a pinhole nozzle, the pressure and temperature both drop abruptly. The nozzle imposes collisional communication that brings the gas molecules to nearly the same direction and velocity. It also efficiently relaxes thermal excitation of molecular rotation and (less so) vibration. Thus not only is the intensity of a supersonic beam far higher than that from an effusive source, but the spreads in velocity and rotational states are markedly narrowed. The effective temperature for relative motion of molecules within such a beam is typically only a few °K. Moreover, by seeding heavy molecules in a large excess of light diluent gas, one can accelerate the heavy molecules to the exit velocity of the light gas. Translational energies much higher than are feasible with an effusive source can thereby be obtained, up to a few eV.

Within the markedly nonequilibrium environment of a supersonic expansion, chemical interactions are liberated from thermodynamic constraints. In effect, in the free energy, $\Delta H\text{-}T\Delta S$, the entropy term ΔS is suppressed by the low internal temperature within the beam. Even a weakly favorable enthalpy term ΔH can then suffice to produce large yields of molecular clusters.

B. Balls and tubes of carbon

The discovery of carbon-60 and kindred fullerene molecules ranks among the most important achievements of chemical physics (Dresselhaus *et al.*, 1996; Baum, 1997). It also affirms the value of fostering eclectic collaborations and the playful pursuit of curious observations. The crucial ingredient was a technique, devised by Richard Smalley, to generate clusters from solid samples. This procedure uses a laser to vaporize material, enabling it to be entrained in a supersonic gas flow. In the early 1980s, several laboratories had adopted this technique, chiefly to study clusters of metals or semiconductor materials, of interest for catalysis or microelectronics. Among many curious results were features of a mass spectrum of carbon clusters from laser-vaporized graphite, published by a group at the Exxon laboratory as part of an Edisonian survey (Rohlfing *et al.*, 1984). For C_{40} and larger clusters, only those with an even number of carbon atoms appeared, in a broad distribution extending above C_{100}. Especially prominent in the mass spectrum was the C_{60} peak, about twice as tall as its neighbors.

What is now justly regarded as the discovery of C_{60} did not come until nearly a year later. Smalley's group at Rice University was visited by Harry Kroto from Sussex, who had long pursued work on carbon-containing interstellar molecules. Kroto wanted to examine carbon clusters and their reactions with other molecules, in hopes of identifying candidates for unassigned interstellar spectra. Smalley was reluctant to interrupt other work, particularly since vaporizing carbon would make the apparatus very dirty. Fortunately, hospitality and willing graduate students prevailed. On repeating the Exxon work, the Rice group found that, when conditions were varied, the C_{60} peak became far more prominent. That result led them to play with models and propose as an explanation the celebrated soccer-ball structure, dubbed Buckminsterfullerene. It contains 12 pentagonal and 20 hexagonal carbon rings, with all 60 atoms symmetrically equivalent and linked to three neighbors by two single bonds and one double bond. Soon other fullerene cage molecules were recognized, differing from C_{60} by the addition or subtraction of hexagonal rings, in accord with a theorem proved in the 18th century by Euler.

These elegant structures, postulated to account for cluster mass spectra, remained unconfirmed for five years. Then, in 1990, it was not chemists but astrophysicists who found a way to extract C_{60} in quantity from soot produced in an electric arc discharge. As well as enabling structural proofs, that discovery opened up to synthetic chemistry and materials science a vast new domain of molecular structures, built with a form of carbon that has 60 valences rather than just four. It is striking, however, that despite the great stability of C_{60} and its self-assembly after laser ablation or arc discharge of graphite, as yet all efforts to synthesize C_{60} by conventional chemical means have failed. Such means, which operate under thermodynamic equilibrium conditions, evidently cannot access facile reaction pathways.

Among the burgeoning families akin to fullerene molecules are carbon nanotubes, first discovered by Sumio Iijima at NEC Fundamental Research Laboratories in Tsukuba, Japan. Particularly intriguing is a single-walled nanotube (designated 10,10) of the same diameter as C_{60} (7.1 Å). In principle, its chicken-wire pattern of hexagons can be extended indefinitely; in practice, nanotubes of this kind have now been made that contain millions of carbon atoms in a single molecule. The electrical conductivity of this hollow carbon tube is comparable to copper, and it forms fibers 100 times stronger than steel but with only only one-sixth the weight. Already carbon nanotubes have provided much enhanced performance as probe tips in atomic force microscopy. Chemically modifying the nanotube tips has even been shown to create the capability of chemical and biological discrimination at the molecular level, in effect directly reading molecular braille (Wong *et al.*, 1998). A host of other applications is in prospect.

C. Reactions and spectra in clusters

Much current work examines the effect of solvation on reaction dynamics or spectra by depositing solute reactants or ''guests'' on a cluster of solvent or ''host'' molecules, bound by van der Waals forces or by hydrogen bonds (Mestdagh *et al.*, 1997). Often photoinduced reactions, particularly those involving electron or proton transfer, are studied in this way, as are processes involving ion-molecule reactions within clusters (Castleman and Bowen, 1996), including ''cage'' effects due to the solvent. Among many variants is work in which high-velocity clusters are made to collide with metal or crystal surfaces. Such collisions can induce even guest species that are ordinarily inhibited by a high activation barrier to react (Raz and Levine, 1995). Here we consider a quite different special realm, employing spectra of a guest molecule to study clusters that are finite quantum fluids.

In the prototype experiment, shown in Fig. 2, a supersonic expansion generates large He or Ar clusters, each with 10^3 to 10^5 atoms. In flight these clusters pick up one or more small guest molecules while passing through a gas cell, without suffering appreciable attenuation or deflection. The cluster beam is probed downstream by a laser, coaxial or transverse to the flight path, and spectroscopic transitions of the guest molecule are detected by laser-induced fluorescence or by beam depletion. This pickup technique, originally developed by Giacinto Scoles (Lehmann and Scoles, 1998), is well suited to the study of unstable or highly reactive chemical species. Indeed, these may be synthesized *in situ* by using more

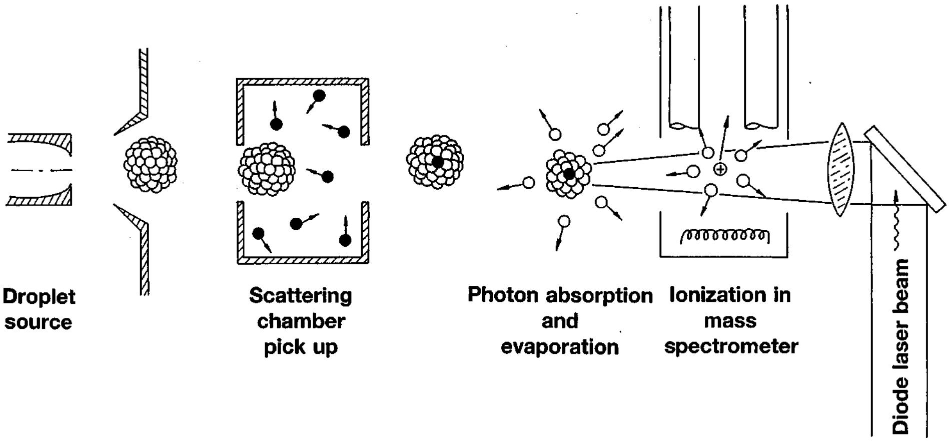

FIG. 2. Schematic diagram (omitting vacuum pumps) of molecular-beam apparatus for depletion spectroscopy of molecules embedded in helium clusters. The large clusters or droplets of He, formed in a supersonic nozzle, pick up a guest molecule while passing thorough a scattering chamber. En route to the mass spectrometric detector, the cluster is irradiated by a tunable, coaxial laser. When the laser is in resonance with the guest molecule, the absorbed energy induces evaporation from the cluster and a depletion in the mass spectrometer signal. From Hartmann *et al.*, 1996.

than one pickup cell, or by introducing into the cell species generated in a discharge or pyrolytic decomposition. Instead, a stable guest molecule can serve to probe the environment within its solvent cluster. In this way, the group of Peter Toennies at Göttingen (Hartmann *et al.*, 1996; Grebenev *et al.*, 1998) has recently obtained striking results for superfluid helium clusters.

These ^{4}He clusters are produced by a strong supersonic expansion (e.g., He at 5-bar pressure and 6.6 °K behind a 5-μm nozzle), which drops the internal temperature to about 0.4 °K, well below the transition temperature for superfluidity ($T_\lambda = 2.12$ °K). When a hot guest molecule comes aboard (from the pickup cell at 10^{-5} mbar and ~300 °K), the cluster rapidly evaporates away a few hundred He atoms, thereby cooling itself and the guest to the original internal temperature (in about 10^{-6} sec). In the process, the guest molecule also migrates from the surface to the center of the cluster (as deduced from mass spectroscopic experiments and predicted by theory). For a variety of guest species, among them the linear triatomic molecule OCS, the Göttingen group found spectra with well-resolved rotational structure. This indicates the guest molecules are rotating freely within the clusters, although with an effective moment of inertia larger (by a factor of 2.7 for OCS) than that for an isolated, gas-phase molecule.

In normal liquids, rotational structure in spectroscopic transitions is destroyed by diffusional and librational processes; free rotation is seen only for light, weakly interacting molecules such as H_2 or CH_4. Free rotation within the ^{4}He clusters thus can plausibly be attributed to superfluidity, but it might instead result from the exceptionally cool and feeble guest-host interactions, further blurred by the large zero-point oscillations of the helium atoms.

As a diagnostic test for the role of superfluidity, the experiments were repeated using ^{3}He clusters. These have lower density, so are more weakly interacting and somewhat colder (about 0.15 °K), although far above the superfluid range ($T_\lambda = 3\times10^{-3}$ °K). Indeed, in ^{3}He clusters the OCS spectrum showed no rotational structure, but rather had the broad, featureless form typical for heavy molecules in normal liquids. A further elegant test was obtained in a series of runs made with increasing amounts of ^{4}He added to the OCS vapor in the pickup cell. Because of their high diffusivity and lower zero-point energy, the ^{4}He atoms entering a ^{3}He cluster gathered around the guest molecule. The average number of such friendly ^{4}He atoms that were picked up was estimated from a Poisson distribution. When this number reached about 60, the rotational structure in the OCS spectrum had again grown in, just as sharp as for pure ^{4}He clusters.

Thus, in the pure, nonsuperfluid ^{3}He clusters, the guest molecule does not rotate freely, but it does so in pure, superfluid ^{4}He clusters or when surrounded by about 60 atoms of ^{4}He, enough to form about two shells around the OCS molecule. Rough estimates suggest the increase in effective moment of inertia may be due chiefly to dragging along the vestigial normal-fluid component of these shells. The Göttingen experiments offer strong evidence that a sharp guest rotational spectrum is diagnostic of superfluidity and it can occur even in ^{4}He clusters with as few as 60 atoms.

IV. CORRALLING MOLECULES, CONTROLLING REACTIONS

Under ordinary experimental conditions, gas molecules careen about in all directions with a broad range of thermal velocities and also tumble erratically with random spatial orientations. Taming that molecular wildness has been a major odyssey of chemical physics, still unfolding. It is part of a modern alchemical quest to exploit molecular dynamics in developing means to control the outcome of chemical reactions. We review some recent advances, including efforts towards achieving spatial trapping of molecules and utilizing lasers as the philosopher's stone.

A. Pendular orientation and alignment

Although supersonic beams have long served to subdue the translational wildness of molecules, until a few years ago there was no generally applicable technique for constraining the spatial orientation of a molecular axis. Without that capability, major directional features of collisional interactions were averaged out by molecular rotation. The only previous method for producing beams of oriented molecules, developed in the late 1960s, used inhomogeneous electric focusing fields to select intrinsically oriented rotational states in which the molecular axis precessed rather than tumbled. This is an excellent method; it has made possible incisive studies of "head vs tail" reaction probabilities in collisions with both gas molecules and surfaces. However, the method requires an elaborate apparatus and is only applicable to low rotational states of symmetric top molecules (or equivalent) that exhibit a first-order Stark effect.

A different method, much wider in chemical scope and far simpler to implement, exploits the low rotational temperatures attainable in supersonic beams. This method, introduced in 1990, uses a strong homogeneous electric or magnetic field to create oriented or aligned states of polar or paramagnetic molecules (Loesch, 1995; Friedrich and Herschbach, 1996). In the presence of the field, the eigenstates become coherent linear superpositions or hybrids of the field-free rotational states. These hybrids coincide with the familiar Stark or Zeeman states when the dipole and/or the moment of inertia is small or the field is weak; then the molecule continues to tumble like a pinwheel. When the interaction is sufficiently strong, however, the hybrids become librational; then the molecule swings to and fro about the field direction like a pendulum. Such pendular states can be produced for linear or asymmetric rotors as well as for symmetric tops. The magnetic version produces alignment rather than orientation,[2] but is applicable to many molecules not accessible to the electric version; this includes paramagnetic nonpolar molecules and molecular ions (which would just crash into an electrode if subjected to an electric field). Either version requires that the interaction of the molecular dipole with the external field exceed the kinetic energy of tumbling; hence the key role of drastic rotational cooling by a supersonic expansion.

The experimental simplification is major because a focusing field (typically a meter long and expensive to fabricate) is not needed. Instead, the molecular beam is merely sent between the plates of a small condenser (usually about 1 cm^2 in area and a few mm apart) or between the pole pieces of a compact magnet. The uniform field which creates the hybrid eigenstates need only extend over the small region in which the beam actually interacts with its target.

A kindred variety of pendular states can be produced by utilizing the induced dipole moment created by nonresonant interaction of intense laser radiation with the molecular polarizability (Friedrich and Herschbach, 1995a, 1995b). This can produce alignment whether the molecule is polar, paramagnetic, or neither, as long as the polarizability is anisotropic. That is generally the case; for example, for a linear molecule the polarizability is typically about twice as large along the axis as transverse to it. Although the electric field of the laser rapidly switches direction, since the interaction with the induced dipole is governed by the square of the field strength, the direction of the aligning force experienced by the molecule remains the same. Experimental evidence for strong alignment arising from the polarizability interaction has been found in nonlinear Raman spectra (Kim and Felker, 1997).

Pendular states make accessible many stereodynamical properties. Studies of steric effects in inelastic collisions or chemical reactions are a chief application (Loesch, 1995). The ability to turn the molecular orientation on or off makes possible modulation of angular distributions and other collision properties, thereby revealing anisotropic interactions not otherwise observable. In photodissociation of oriented molecules (Wu *et al.*, 1994), pendular hybridization renders the laboratory photofragment distributions much more informative. For all applications, the spectroscopy of pendular states has an important role, as the field dependence of suitable transitions reveals the extent of molecular orientation or alignment. Other features arising from the hybrid character of pendular states also prove valuable in spectroscopy, including the ability to tune transitions over a wide frequency range and to access states forbidden by the field-free selection rules.

B. Towards trapping molecules

The advent of powerful methods for cooling, trapping, and manipulating neutral atoms has led to dramatic achievements, including Bose-Einstein condensation of atomic vapor, an atom laser, atom interferometry, and atom lithography. Molecular physics yearns to follow suit. However, many optical manipulation methods that are effective for atoms fail for molecules because of the complexity of the energy-level structure, with its myriad vibrational and rotational components. Here we merely note some promising approaches to manipulating or trapping molecules, most not yet demonstrated experimentally.

In addition to its utility for molecular alignment, the polarizability interaction with an intense, directional laser field provides a lensing effect acting on the translational motion of molecules. Seideman (1996, 1997) has given a theoretical analysis showing how this arises. The interaction with the field produces molecular states,

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[2] As usual, here axial anisotropy is designated *orientation* if it behaves like a single-headed arrow and *alignment* if it behaves like a double-headed arrow.

"high-field seekers," whose energy levels decrease as the field increases. This generates a force that moves the molecule towards the spatial region of highest laser intensity. Thereby focusing occurs, subject to dynamics and dependent on the ratio between the molecular translational kinetic energy and the maximum attractive field-induced potential. In the strong-interaction limit, where that ratio becomes much less than unity, the molecules can become trapped in the laser field (Friedrich and Herschbach, 1995a, 1995b).

An electrostatic storage ring for polar molecules has also been proposed (Katz, 1997), modeled on a neutron storage ring. This would employ an inhomogeneous hexapolar toroidal field, within which molecules in "low-field seeking" states would be confined and follow orbits determined by their rotational state and translational velocity. Design calculations limited to practical parameters indicate that storage lifetimes of the order of 10^3-10^4 s can be expected. However, since the molecular trajectories must bend to stay in the ring, only molecules with low translational kinetic energy can be stored.

Whatever means are used to create an attractive potential region, molecular trapping requires a way to remove enough kinetic energy so that the molecule cannot escape from that region. Since collisions between trapped molecules can redistribute rotational or vibrational excitation into translation, those internal modes need to be quenched also. Photoassociation of trapped atoms can produce trapped diatomic molecules, but must contend with small yields and a strong propensity for vibrational excitation in forming the molecules. Collisional relaxation by means of a cold buffer gas (Doyle *et al.*, 1995) has worked well for loading atoms into a magnetic trap. Recently this technique has achieved a large yield (about 10^8) of trapped CaH molecules (Weinstein *et al.*, 1998). The best buffer gas is ^{3}He; it can be maintained by a dilution refrigerator at about 0.24 °K, where its vapor density is 5×10^{15} cm^{-3}, ample for collisional quenching. Since the helium interaction with any trap potential will be negligibly weak, it can be pumped away after cooling down the molecules. A disadvantage is that the mean lifetime of a molecule in the trap is much shorter than the time required to remove the buffer gas.

A dizzying proposal for disposing of kinetic energy involves mounting a supersonic nozzle on a high-speed rotor, in order to cancel the velocity of the emerging molecules (Herschbach, 1998a). Design calculations indicate that centrifuge action should enhance markedly the supersonic beam quality, thereby shrinking the velocity width and lowering the equivalent temperature for both relative translation and rotation to a few hundred m °K. Preliminary experiments, as yet at modest rotor speeds, confirm that gas can indeed be introduced along the rotor axis and emerge from a whirling arm in a supersonic beam, with the expected velocity subtraction. This approach, if it proves feasible, would avoid cryogenic technology and provide an intense source of molecules deprived of kinetic energy.

If a sufficient density of molecules can be confined, the temperature of the trapped ensemble can be lowered much further by evaporative cooling (Doyle *et al.*, 1991). The aim is to get to the range of a few millidegrees Kelvin or below, where the de Broglie wavelength exceeds the size of the molecule (e.g., $\Lambda_{\mathrm{de\,B}}=20$ Å for Cl_2 at 10 mK). This would give access to an exotic regime for chemical reactivity, governed by quantum tunneling and resonances (Herschbach, 1998b; Forrey *et al.*, 1998). It should be remarked that "trapping," although now a firmly established term, is ridiculously inappropriate. The tightest traps in prospect have linear dimensions at least 10^3 times larger than molecules; that is not a cage, but a roomy corral.

C. Laser control of reaction pathways

In "real world" chemistry, reaction pathways and yields have to be cajoled or conjured, by adjusting macroscopic conditions (temperature, concentrations, pH) or catalysts. Chemical physicists have sought genuine control of molecular pathways (Zare, 1998). For bimolecular reactions, this has been done by varying the collision energy, orientation, or vibrational excitation of reactant molecules or by selecting particular alignments of excited electronic orbitals of atoms. For unimolecular processes, which we consider briefly, control has been achieved by utilizing the coherence of laser light (Gordon and Rice, 1997). This enables the outcome to be governed by quantum interference arising from the phase difference between alternate routes or by the temporal shape and spectral content of ultrashort light pulses.

The method employing phase control, first proposed by Brumer and Shapiro (1986, 1997), offers a molecular analog of Young's two-slit experiment. An upper state of a molecule is simultaneously excited by two lasers, of frequencies ω_n and ω_m, absorbing n photons of one color and m of the other, with $n\omega_m=m\omega_n$. This prepares a superposition of continuum eigenstates $\Psi_n+\Psi_m$ that correlate asymptotically with different product channels. The coefficients of the components of this superposition state are determined by the relative phases and amplitudes of the two lasers. Since the wavelengths differ markedly, the light waves do not interfere, but the wave functions produced by them strongly interfere. The cross term in $|\Psi_n+\Psi_m|^2$ thus governs the product distribution, and the outcome can be controlled by varying the relative phases and amplitudes of the lasers. This scheme has received several experimental demonstrations in which product yields from two competing channels exhibit large modulations, 180° out of phase.

Another method, operating in the time domain, was introduced by Tannor and Rice (1985). This employs a sequence of ultrashort light pulses to create a wave packet of molecular eigenstates. The frequencies, amplitudes, and phases of the pulse sequence are tailored to favor a particular outcome as the wave packet evolves in time. By means of optimal control theory, the pulse shape and spectral content can be adjusted to maximize the yield of a desired product (Kosloff *et al.*, 1989; Peirce *et al.*, 1990). Moreover, with iterative feedback, the experimenter can be taught by the molecule how best to tailor the light pulses (Judson and Rabitz, 1992). The first reports of such molecular instruction, aided by a computer-controlled pulse shaper, have recently appeared (Bardeen *et al.*, 1997; Assion *et al.*, 1998). These may portend an era in which chemical physicists, like chess masters, learn of many subtle moves beyond their imagination.

V. BENEDICTION

This quick glance at a bulging family album has pointed to just a few snapshots. Anyone who looks at *Advances in Chemical Physics* or *Annual Reviews of Physical Chemistry* or the *Faraday Discussions* or many other journals will quickly learn of remarkable work in reaction dynamics, femtosecond chemistry, single-molecule spectroscopy, surface chemistry, phase transitions, protein dynamics, electronic structure theory, and a host of other vigorous domains of chemical physics. Having left unmentioned or implicit so much landmark work, I can only hope for a holographic effect, wherein even fragments convey something of the enterprising spirit of the field. In my own experience, it has been exhilarating over nearly five decades to witness what has happened on Urey's bridge. Another sentence from his preface of 65 years ago seems apt as an abiding creed or benediction for chemical physics: "New and effective methods, experimental and theoretical, for the study of these units from which massive matter is composed, have developed largely from physical discoveries which at the time did not appear to have the importance to centuries-old chemical problems that they have since assumed." (Urey, 1993).

REFERENCES

Assion, A., T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, and G. Gerber, 1998, Science **282**, 919.

Bardeen, C. J., V. V. Yakovlev, K. R. Wilson, S. D. Carpenter, P. M. Weber, and W. S. Warren, 1997, Chem. Phys. Lett. **289**, 151.

Baum, R., 1997, Chem. Eng. News **75**, 29.

Brumer, P., and M. Shapiro, 1986, Chem. Phys. Lett. **126**, 541.

Brumer, P., and M. Shapiro, 1997, J. Chem. Soc., Faraday Trans. **93**, 1263.

Castleman, A. W., and K. H. Bowen, 1996, J. Phys. Chem. **100**, 12911.

Doyle, J. M., J. C. Sandberg, I. A. Yu, C. L. Cesar, D. Kleppner, and T. J. Greytak, 1991, Physica B **194**, 13.

Doyle, J. M., B. Friedrich, J. Kim, and D. Patterson, 1995, Phys. Rev. A **52**, R2525.

Dresselhaus, M. S., G. Dresselhaus, and P. C. Eklund, 1996, *Science of Fullerenes and Carbon Nanotubes* (Academic, New York).

Fenn, J. B., 1996, Annu. Rev. Phys. Chem. **47**, 1.

Forrey, R. C., N. Balakrishnan, V. Kharchenko, and A. Dalgarno, 1998, Phys. Rev. A **58**, R2645.

Friedrich, B., and D. Herschbach, 1995a, Phys. Rev. Lett. **74**, 4623.

Friedrich, B., and D. Herschbach, 1995b, J. Phys. Chem. **99**, 15686.

Friedrich, B., and D. Herschbach, 1996, Int. Rev. Phys. Chem. **15**, 325.

Gordon, R. J., and S. A. Rice, 1997, Annu. Rev. Phys. Chem. **48**, 601.

Grebenev, S., J. P. Toennies, and A. F. Vilesov, 1998, Science **279**, 2083.

Hartmann, M., R. E. Miller, J. P. Toennies, and A. F. Vilesov, 1996, Science **272**, 1631.

Herschbach, D., 1998a, Nucleus (Boston) **76**(10), 37.

Herschbach, D., 1998b, in *Chemical Research—2000 and Beyond: Challenges and Visions*, edited by P. Barkan (Oxford Univ., New York).

Judson, R. S., and H. Rabitz, 1992, Phys. Rev. Lett. **68**, 1500.

Katz, D. P., 1997, J. Chem. Phys. **107**, 8491.

Kim, W., and P. M. Felker, 1997, J. Chem. Phys. **107**, 2193.

Klemperer, W., 1995, Annu. Rev. Phys. Chem. **46**, 1.

Klemperer, W., 1997, Proc. R. Institution 209.

Kosloff, R., S. A. Rice, P. Gaspard, S. Tersigni, and D. J. Tannor, 1989, Chem. Phys. **139**, 201.

Lehmann, K. K., and G. Scoles, 1998, Science **279**, 2065.

Loesch, H. J., 1995, Annu. Rev. Phys. Chem. **46**, 555.

Mahan, B. H., 1975, Acc. Chem. Res. **8**, 55.

Mestdagh, J. M., M. A. Gaveau, C. Gee, O. Sublemontier, and J. P. Visticot, 1997, Int. Rev. Phys. Chem. **16**, 215.

Nye, M. J., 1993, From Chemical Philosophy for Theoretical Chemistry: Dynamics of Matter and Dynamics of Disciplines, 1800–1950 (University of California, Berkeley).

Peirce, A. P., M. A. Dahleh, and H. Rabitz, 1988, Phys. Rev. A **37**, 4950.

Peirce, A. P., M. A. Dahleh, and H. Rabitz, 1990, Phys. Rev. A **42**, 1065.

Rank, D. M., C. H. Townes, and W. J. Welch, 1971, Science **174**, 1083.

Raz, T., and R. D. Levine, 1995, J. Phys. Chem. **99**, 7495.

Rohlfing, E. A., D. M. Cox, and A. Kaldor, 1984, J. Chem. Phys. **81**, 3322.

Saykally, R. J., and R. C. Woods, 1981, Annu. Rev. Phys. Chem. **32**, 403.

Seideman, T., 1996, J. Chem. Phys. **106**, 2881.

Seideman, T., 1997, J. Chem. Phys. **107**, 10420.

Tannor, D. J., and S. A. Rice, 1985, J. Chem. Phys. **83**, 5013.

Thaddeus, P., 1972, Annu. Rev. Astron. Astrophys. **10**, 303.

Thaddeus, P., M. C. McCarthy, M. J. Travers, C. A. Gottlieb, and W. Chen, 1998, Faraday Discuss. **109**, 1.

Urey, H. C., 1933, J. Chem. Phys. **1**, 1.

Weinstein, J. D., R. deCarvalho, T. Guillet, B. Friedrich, and J. M. Doyle, 1998, Nature (London) **395**, 148.

Wong, S. S., E. Joselevich, A. T. Woolley, C. L. Cheung, and C. M. Lieber, 1998, Nature (London) **394**, 52.

Wu, M., R. J. Bemish, and R. E. Miller, 1994, J. Chem. Phys. **101**, 9447.

Zare, R. N., 1998, Science **279**, 1875.