William Klemperer

SOME SPECTROSCOPIC REMINISCENCES

William Klemperer

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

ABSTRACT

We review a number of essentially spectroscopic problems in this personal account. The structure of high-temperature species remains a topic of considerable broad interest. The binary fluorides of essentially every element are stable as the isolated gas-phase molecular species. As such they provide a means of comparing bonding with the entire periodic table. The structural characterization of the binary fluorides, although still incomplete, has provided a considerable insight into a variety of bonding types.

The formation of molecules in the interstellar medium has been a model for abiotic synthesis of complex species. A kinetic model based upon ion-molecule reactions as the predominant reaction class appears to fit many of the observations, such as the polyatomic ion HCO^+. The high abundance of carbon-chain compounds is attributed to the efficient formation of C^+ by the reaction $CO + He^+ \rightarrow C^+ + O + He$.

The spectroscopic characterization of weakly bonded species has led to a detailed knowledge of intermolecular potentials. The dynamics of molecular complexes has been frequently novel. In particular the concurrent breaking and making of weak bonds is observed in many species.

Introduction

The rapid growth of physical chemistry that has occurred during my scientific period has dramatically changed how we look at the subject of chemistry. At the outset of this myopic discourse, I note that I was

1

extremely fortunate to have studied with George Pimentel during my exciting Berkeley graduate work. George Pimentel was an extremely enthusiastic scientist. He believed in action, both in science and in societal responsibility. Throughout my lifetime contact with George, I never saw him urge others into activities that he was not willing to perform himself. This good fortune continued to hold when I joined the Harvard faculty and conversed with Bright Wilson on an almost daily basis, a tremendous fringe benefit. Bright remains the model scientist—always totally rational, with a sharp critical judgment; totally unselfish; and the least egotistical. Both George and Bright continue to greatly impact chemistry through their large number of students and research associates.

The strong academic emphasis on the inorganic chemistry of aqueous solutions has virtually disappeared, and I think this is for the better. To one who taught analytical chemistry, it was noteworthy that the aqueous solubility of the silver halides steadily decrease from AgCl to AgBr to AgI, with the latter truly insoluble. I found the fundamentality of this frequently cited phenomena questionable, upon learning that the order of solubility reversed upon replacing the aqueous solvent with liquid ammonia (1). The predominance of the experimental study of bulk properties, either static or transport, has been supplanted by essentially molecular studies. The language of chemists is molecular. This change is well exemplified by how physical chemistry is taught. Increasingly the subject is introduced by the study of quantum chemistry of atoms and molecules. Perhaps in our quest to harness academia for research applied to national needs, we will return to the heuristic memorization of macroscopic chemical behavior. I hope not, since the analytic molecular approach has been fun. Although, undoubtedly, there are vast arrays of topics in which complexity is integral and the molecular approach either irrelevant or impotent, there has been much satisfaction gained from the understanding and control afforded in simple molecular systems.

High-Temperature Species

In our systematic quest for a practical understanding of the behavior of systems, a synthesis based on the understanding of the basic components comprising the system has become virtually universal. Structure of molecules has been a recurrent theme in chemistry. The widespread availability of computers has allowed the development of powerful structural tools, especially those applicable to the condensed phase, X-ray crystallography, and nuclear magnetic resonance, which provide structure determination of vast classes of molecules. These techniques, which are housed locally, are much more effective for solving real problems than those demanding national facilities, such as those for neutron diffraction.

Molecular spectroscopy allows the determination of detailed nuclear geometries for many species that are relatively unstable under the usual conditions of room temperature. The exploitation of high-resolution molecular spectroscopy for the characterization of this type of species is unique and has changed our perception of nature. In this superficial perusal of molecular spectroscopy, I sketch some topics of particular personal interest. The structure of high-temperature species (species that exist in equilibrium as isolated molecules only at high temperatures) are of broad interest, as was certainly pointed out to many of us by Leo Brewer. The vast majority of simple inorganic molecules are of this type. I greatly enjoyed a long collaboration with Warren Falconer, during the course of which we published a bibliography of structural studies of the binary fluorides (2). This topic still remains an interesting one. With the exception of helium, neon, and argon, stable binary fluorides of all the elements exist. As such, the binary fluorides offer the possibility of comparing bonding within the entire periodic table. From a molecular viewpoint the characterization of the solids is virtually irrelevant in view of the very strong interactions that obtain therein. It is therefore of considerable importance to be able to structurally characterize high-temperature species directly because the majority of the binary fluorides have appreciable vapor pressure only at high temperatures.

The diatomic fluorides provide the basic information for the M-F bond: its strength, length, and stiffness. In addition modern high-resolution spectroscopy provides hyperfine structure as well as the electric dipole moment, virtually the only moment of the charge distribution that is measured. The wonderful plan initiated by Norman Ramsey (3) and fully exploited by Bill Flygare (4a,b) to determine the quadrupole moment of molecules by the equivalent determination of the anisotropy of magnetic susceptibility has unfortunately not been actively pursued. This type of measurement, however, produced a sensation when applied to the determination of the sign of the electric dipole moment of CO (5). Robert Mulliken (private communication) pointed out (humorously) that the dipole moment of carbon monoxide should be zero, since CO is iso-electronic to N_2. Nonetheless, although this assertion is correct in principle, in practice CO has a small, distance-dependent electric dipole moment. Charlie Townes et al (5) measured the sign of the moment, showing it to be $^-CO^+$, in contrast to both the very powerful elementary chemical intuition and the less powerful but more sophisticated electron-structure calculations of the time. Because charge distributions should be calculable within the self-consistent field approximation, a considerable discussion ensued on whether the experiment was reliable [see e.g. the excellent paper by Huo (6)]. It was. The effects of electron correlation were shown to

reverse the small 0.1 D moment. It is of considerable importance to note that Bernard Ransil (7) showed that the dipole moment of the highly heteronuclear species BF wâs both small, 1.4 D, and had a sign, $^-BF^+$, clearly opposite that of electronegativity pictures. The moment was measured a decade later (8) as 0.5 ± 0.2 D. The sign of the dipole moment of CO and, more importantly, BF is still a surprise to most students of chemistry. It is certainly a dramatic display of the power of molecular orbital theory, which was then in the hands of the school of Robert Mulliken.

The alkali halides are the simplest species illustrating bonding. The ionic model, certainly the simplest of the electrostatic models, is exceptionally effective for virtually all of the species and phases that must be considered. The Born-Mayer model for the crystal (9) has endured for half a century. The Rittner (10) model for the diatomic molecules followed it closely and provides a virtually quantitative description of the energetics and charge distribution of these species. The clustering of the alkali halides demonstrated so clearly by Polykarp Kusch from precision measurements of velocity distributions of effusive sources (11) is also nicely accounted for by the Rittner ionic model (12). The molecular beam–electric resonance method, developed of course at Columbia (see 3 for references), used alkali halides because they are efficiently detectable by surface ionization on hot tungsten. Rotational constants, hyperfine structure constants, and electric dipole moments were determined for several alkali halides. Rotational constants for the remaining halides, with the exception of some lithium halides, were measured by Townes and colleagues (14) with microwave absorption spectroscopy in an important display of high-temperature methods. Stuart Rice, Steve Berry, and I measured the infrared absorption spectra of the alkali halide molecules (15a–c).
vibrational band heads allowed us to obtain reliable and reasonably accurate vibrational frequencies for these basic species.[1] With these in hand, the repulsion parameters of the Rittner model were determined, allowing both the potential energy curve and the dipole moment function of a number of alkali halides to be determined. We did not originally see the vibrational spectrum of the alkali halide dimers and argued quite vocally and incorrectly with Kusch about their existence. This oversight was due

---

[1] Our apparatus was actually quite simple. A commercial spectrometer was cut in half so that a six-foot steel stube, heated in the center, could be located between a light source and the prism monochromator. We found that the glass reflector from automobile headlights was a more than adequate parabolic mirror. A schematic of the apparatus is shown in Figure 1 of Reference 15a.

to my failure to look in the correct spectral region (17), but it was a further lesson to pay careful attention to work of the Columbia physics group.

Molecular Beams

The power and beauty of molecular beams methods was quite apparent simply from reading the papers. I greatly enjoyed spending a sabbatical leave in the laboratory of Norman Ramsey, across Oxford Street from my department, learning beams methods. One of the most pleasant experiments Dudley Herschbach and I conducted in Norman's laboratory was to measure the rate at which alkali ions came off a heated tungsten filament when a chopped beam of alkali halide struck the wire. When the wire was very hot, the signal was a square wave. With a cool filament the signal was dc. It was a revelation, in 1956, to see chemical kinetics displayed directly on an oscilloscope. We never published this work because we knew the surface was dirty and the vacuum was only 10^{-6} torr. We did publish an enjoyable paper showing that the difference in vibrational frequency of LiCl measured by vibrational spectroscopy and that obtained by John Trischka (19) from the intensity of rotational transitions in molecular beams detected by tungsten surface ionization could readily be explained as due to a vibrational dependence in the rate of surface ionization reaction (20a,b). Trischka turned the tables on us by showing his vibrational frequency was incorrect, probably owing to an incorrect oven temperature (21).

A precision data base for the structure of diatomic molecules is extremely useful. The bond lengths of polyatomic molecules may be estimated. Len Wharton had measured the lowest rotational transition for LiF (22) by using the molecular beam–electric resonance spectrometer he designed and built. This provided the Li-F bond length of 1.54 Å. Bond lengths of valence-bonded species have rarely produced much excitement among chemists. For example, the carbon-carbon bond is summarizable as $1.4 \text{ Å} \pm 15\%$. Geometrically chemistry is angles; of these the H-O-H angle of water, at 104.5° has been stressed as one of the fundamental structural constants. Its explanation, always purportedly general, is centered upon oxygen and includes hybridization, valence shell electron pair repulsion, etc. The discovery of the very open angle of 145° in disiloxane (23a--c), $(SiH_3)_2O$, prompted us to investigate the structure of compounds of oxygen with simple highly electropositive elements. Using electrostatic deflection of molecular beams, Buchler et al (24) found Li_2O to be nonpolar. Previous electron diffraction studies had shown Li_2O to have an angle near that of H_2O as well as an Li-O bond length of 1.82 Å. Because the M-F and M-O bond lengths are always quite close, and LiF had been established by high-precision spectroscopy, the origin of the discrepancy

of 0.3 Å was sought. It was observed that when the effluent from a heated molybdenum oven filled with Li_2O was mass spectrometrically examined, the major species is Li_2MoO_4, the structure of which almost certainly contains a tetrahedral MoO_4 unit with lithium bridge bonding. In the crystal the Mo-O bond length is determined by X-ray crystallography to be 1.82 Å. Since this time (24), the rotational spectrum of a number of alkali metal hydroxides have been measured (25a-c). The species are linear, with low bending frequencies. Interestingly, these structural studies have had virtually no impact upon the presentation of theories of bonding and molecular geometry at the freshman level.

Molecular beams are fun for a chemist. They give one a sense of power. The beam operator can push molecules around with electric or magnetic fields and change their state with coherent radiation at resonant frequencies. For high-temperature species, a small heated source is a great advantage. As has become clear over the years, however, beam detection as a means of monitoring resonances is not necessarily the preferable approach. An increasing number of spectroscopic measurements utilizing molecular beams detect radiation rather than molecules. The fantastic progress that has occurred through the use of laser vaporization (26) has entirely changed high-temperature chemistry; in particular, the container problem has disappeared.

High-temperature species present considerable challenges for structural characterization. We were infatuated with electric deflection for the simple characterization of the polarity of species. A multipole focuser—quadrupole, hexapole, or octapole—has the characteristic that the magnitude of the electric field is null at the center and therefore must increase radially outward. Such a system will act as a focusing lens or, better, a gathering system for molecules in quantum states that increase in energy with increasing electric field. It will conversely throw out molecules in states that have the opposite or negative Stark effect. It is possible then to determine whether a molecule has an electric dipole moment. The power of this method was demonstrated by Len Wharton (27), who showed that approximately half the alkaline earth dihalides were polar and therefore could not have the centrosymmetric linear arrangement that everyone knew they had. These halides were textbook examples of linear molecules and were so readily explained in term of hybrid sp orbitals. It is interesting that they indeed have disappeared from the elementary textbooks and been replaced, in order to display sp hybridization, by the perfect example of a linear centrosymmetric species, BeH_2, a species never observed.

Electric deflection of high-temperature molecular beams was soon found to be plagued with lack of clarity. Nonpolar forms, which do not possess inversion symmetry, have polar-excited vibrational states. Thus species

such as TiF_4 appear very polar (CCl_4 appears slightly polar). Is this a consequence of an irregular tetrahedral geometry, such as is observed in SF_4, or simply the presence of highly polar degenerate excited vibrational states? Although electric deflection methods may readily be applied to high-temperature species, the meaning of their results is frequently unclear. This has been further noted. When a clearly polar species such as tritertiary butyl amine is examined by electric deflection, it appears nonpolar. This puzzle was resolved by Fraser & Pate this past year (28). They demonstrated the Stark effect of a complex system in which the interacting levels show a multiplicity of avoided crossings, leading to the force on a molecule in such a state being essentially zero. Although these problems are, in principle, surmountable by cooling techniques, they have not been seriously pursued.

Cooling techniques for molecular beams were suggested very early on by Kantrowitz & Grey (29). George Kistiakowsky, an experimental virtuoso, realized the great value of high-intensity beam sources for chemical kinetics. Bill Slichter had the ambitious task of producing high-intensity supersonic beams for his PhD thesis (30). The pumping system he had at his disposal was the standard small, glass mercury-diffusion pump. This required him to use liquid nitrogen traps and a condensable gas, NH_3. For many years George Kistiakowsky would apply extremely obscene expletives to any suggestions of the value of molecular beams for scientific studies.

The widespread availability of high-speed metal-diffusion pumps allowed beams to enter chemistry departments. The molecular beam–electric resonance spectrometer that Len Wharton designed and built had as its aim the measurement of the radiofrequency spectrum of lithium hydride. Of particular interest to us was the determination of the electric dipole moment of LiH, the simplest stable heteronuclear molecule. There was a considerable amount of electron structure theory for this species. LiH is not an easy species to study by molecular beams techniques. Although its optical and infrared spectrum was well studied by absorption spectroscopy, producing beams of it required a high-speed pumping system to allow for the large overpressure of hydrogen required for stability. This is a good example of the difference between hydrides and fluorides. In general, one never needs an overpressure of fluorine to stabilize the M-F bond. Wharton measured the dipole moment of several vibrational states of LiH and LiD; the hyperfine structure was also measured and, most importantly, so were the nuclear quadrupole coupling constants (31a,b). The beauty of molecular beam–radiofrequency spectroscopy was clearly evident. The measurements, made for the first time, had an accuracy that really needed little reconfirmation. The value of 6 D for the electric dipole

moment agreed excellently with theoretical calculations, as was pointed out by Al Matsen (32). Earlier I had estimated the dipole moment to be 4 D from infrared intensity measurements (33). The measurement was important in showing that fully ab initio calculations on simple systems could produce reliable charge distributions. The measurements delighted the theorists.[2] These measurements were also on the simplest lithium compound and allowed a determination of the nuclear quadrupole moment (35) of both ^{7}Li and ^{6}Li by combining accurate theoretical values of the field gradient at the nucleus with the experimental hyperfine structure constant. This determination is probably unique for lithium, where the small nuclear quadrupole moment made it unmeasurable in the atomic 2p state owing to radiative lifetime broadening. I think the willingness to utilize these measurements also separated chemists from physicists. The latter only accepted atomic measurements. (Norman Ramsey is of course unique in being completely at home with atoms, molecules, or elementary particles.)

The molecular beam spectrometer we used at this time was beautifully engineered, and it had high pumping speed. When Myron Kaufman built an electron impact ionizer and mass analyzer, we (stealing the words of my colleague Dudley Herschbach) moved out of the alkali age. The universal detector allowed the spectroscopic study of any species. In deflection studies we showed that for every alkaline earth difluoride, the polarity of the isoelectronic dioxide was identical (36). For example, SiO_2 was nonpolar and therefore linear centrosymmetric, as was MgF_2. As a thrill seeker, I always wanted new molecules and was unenthusiastic about precision remeasurements of standard molecules. Thus when Bill Kaiser wanted to learn resonance methods on hydrogen chloride, I offered little support. His precision measurement of the electric dipole moment and chlorine nuclear quadrupole coupling in several vibrational levels of HCl and DCl was a great example of the breakdown of the Born-Oppenheimer approximation (37).

The measurement of the dipole moment of SiO (38) had exciting consequences. The radio astronomers had observed the λ doubling transitions of OH. We were urged to measure the corresponding doublets of CH in the laboratory so that an interstellar search could be made. There has been a great tradition of organic synthesis at Harvard. It would appear that the

---

[2] At a subsequent Gordon conference on theoretical chemistry, devoted entirely to electron structure calculations, I was the captive experimentalist. It was amusing to note that in virtually every lecture, the speaker would be interrupted by three comments at the same point. These were always "It's wrong," "It's obvious," "I did it first." Only the order of these remarks varied.

synthesis of CH should be child's play for those who could whip out quinine, chlorophyll, or prostoglandins. This was not the case, however, and we resorted to elementary but exciting original methods, such as mixing O_2 and HCCH and attempting partial oxidations or reacting Cl_3CH with lots of potassium vapor. Although these methods never produced radio spectra of CH, the combustion of acetylene did get us a very large laboratory. Initially George Thomasevich—an extremely bright, fast, and fearless scientist—worked in a small corner of a large laboratory that housed several departmental facilities, such as mass spectrometers and optical spectrophotometers. After numerous explosions that resulted in the fragmentation of mercury manometers, not many people wanted to share this facility with us. Thus we had it all to ourselves. It now houses many of our present spectrometers and has taught me that the talents of students are useful in a variety of unforeseen ways.

The SiO molecule was my entry into astronomy. I had asked my friend Pat Thaddeus where I should spend a sabbatical year learning astronomy, and he suggested Cambridge with Professor Martin Ryle. Although I did go to Cambridge, it was under the wing of Dennis Sciama. This was indeed fortunate. Dennis Sciama is a great intellect and a great person with an uncommon breadth of knowledge and interests. Among his former students are some of the very brightest cosmologists, such as Martin Rees and Stephen Hawkings.

I presented our work on the dipole moment of SiO at my first astronomy conference in Holland. This measurement was the standard, relatively unimportant laboratory astrophysics; a measurement was made for some purpose and then pumped up in cosmic importance. The conference on molecular astronomy was interesting because it probably was the worst science I had heard. In 1968 the topic of interest was the unsolved problem of the identification of the diffuse interstellar bands.[3] These were then approximately forty visible spectral features with erratic frequency distribution, width, and intensity. Their carrier was sought by pouring virtually any aromatic species into a spectrophotometer.

Astronomy—Interstellar Chemistry

Interstellar chemistry, the chemistry of the diffuse matter between the stars of the galaxy, is certainly one of the most challenging areas of science. The history of it is intimately linked to molecular spectroscopy. We know what we can see. Our comprehension of our universe is shaped by our

---

[3] The diffuse interstellar bands are the oldest interstellar absorption features. They have eluded carrier indentification for almost one century. Herbig (39, 39a) has written a wonderful review.

interpretation of the radiation reaching us. Simple questions, such as those regarding density and temperature, are not readily answered and indeed have radically altered in the past 25 years. Hydrogen and helium are 99% of the universe. The understanding that hydrogen is molecular in the denser regions, molecular clouds, was the outgrowth of molecular radio astronomy. The increase in knowledge from three species—CH, CH$^+$ and CN—to the present approximately one hundred species has been entirely the result of rotational spectroscopy.

It is important to note that even looking for rotational transitions of polar molecules is not a good idea. The average density within our galaxy is one atom of hydrogen per cubic centimeter. At this or even a much higher density, 10^4 molecules cm^{-3} of H$_2$, the rotational energy levels of a polar molecule are coupled to the background radiation field. Thus no specific emission will occur. The discovery of emission by the ammonia inversion spectrum (40) in the galactic center showed that the gas density was high enough that the rotational levels were more strongly coupled to the kinetic collisions than to the three-degree background radiation. The heterogeneity of density is much greater than had been expected. The density in these large spatial regions will never be high enough to pressure broaden spectral lines.

The chemistry of the interstellar medium provides a specific example of a general problem. The abundances of the observed species is far from that predicted by equilibrium considerations. Relatively large species, e.g. HC$_{13}$N, have been observed. Because hydrogen is three orders of magnitude more abundant than carbon, the high degree of unsaturation is unexpected, yet the preponderance of carbon species are unsaturated. Were the ubiquitous catalyst to exist, the molecular abundances would be proportional to the elemental cosmic abundance.

The synthesis of large specific species by inanimate, uncatalyzed processes is important because it illustrates that chemistry can, in the absence of biological direction, achieve complexity and specificity. It is just this specificity that makes interstellar chemistries so fascinating. The devising of kinetic schemes has always resembled an art form rather than the meticulous pedantry associated with spectroscopy. I, of course, have been extremely fortunate in watching the van Goghs of kinetics: first George Kistiakowsky, then Dudley Herschbach. These impressionists produced works that were quite unbelievable when first presented but that proved true in time.

The kinetics applicable to the interstellar medium are those of a low-density ultra-cold region. Thus all processes must be exothermic and cannot have activation energies. In addition to the gas phase, a solid phase is present that is seen readily in the dark lanes of the Milky Way, the plane

of our galaxy. The nature of the chemistry can therefore be complex. What the solid is, what its catalytic properties are, is unknown. Although there is every reason to accept that the production (synthesis is too strong a word) of molecular hydrogen from atomic hydrogen occurs on the surface, there is little specific evidence of any other particular species being synthesized and released to the gas for microwave detection by surface reactions.

The synthetic schemes that Phil Solomon and Eric Herbst and I proposed are ion-molecule processes, as the dominant production mechanism of molecules. Eric Herbst worked out the detailed picture for the production of the polyatomic molecules found in the dense molecular clouds. There were some exciting observations that almost directly showed the importance of ion molecule processes. Of these, the observation of HCO^+ by Buhl and Lew Snyder (40a,b) was dominant. In our modeling it was hard to avoid production of HCO^+; thus when Snyder (40a,b) presented the discovery of the terrestrially unknown transition at 89.6 GHz of the species he designated as Xogen at an International Astronomical Union conference in Brighton I was very excited because this frequency fit well with that expected for HCO^+. This species is isoelectronic to HCN, so the deduction of its structure was very straightforward. One of the many beauties of radio astronomy is that it is coupled so directly to molecular geometry, or structural chemistry. In addition the very high spectral resolution allows hyperfine structure to be resolved. Thus new species can be detected without previous terrestrial observation. The magnificent work of Claude Woods, Rich Saykally, and Tom Dixon (40c,d) in observing the laboratory spectrum of both HCO^+ and HN_2^+ was essential in establishing the ion molecule kinetic scheme for the synthesis of molecules in the interstellar medium (40e).

The chemistry of the interstellar medium is fascinating in that the vast majority of polyatomic species are unsaturated organic species. The synthetic scheme must be efficient. The production of organic chains proceeds through the addition of the atomic carbon ion to smaller chains. It is the efficient production of C^+ that is so important and so unique. In the dense molecular clouds, volume ionization is produced by high-energy cosmic rays. The most abundant carbon species is carbon monoxide. The abundance of CO is typically 10^{-4} of H_2 and 10^{-3} of He. Ionization by 100 MeV particles is totally unselective with respect to species. Ionization of H_2 produces the ion H_2^+, which rapidly reacts with H_2, forming H_3^+. He^+, similarly produced by 100 MeV cosmic rays, does not react with H_2. This was pointed out to Herbst and me by the master of ion-molecule chemistry, Eldon Ferguson. Because He^+ does not react with the most abundant species, it does react with the second most abundant species, CO, forming

C^+ and O. Thus C^+ is the reactive species leading to the formation of the unsaturated chains. The efficiency of the process is that the ionization of He is transferred quantitatively to C^+ formation, with a gain of the ratio of abundances of He to CO. Thus the abundance of organic molecules in the interstellar medium may be said to be a result of helium chemistry.

Radio astronomy and its molecular interpretation has changed our perception of the universe from one of stars and atoms to a rich highly heterogeneous cosmos. The molecular probes provide insight into the physical conditions prevalent. It is well known that the universal 3 K temperature had been observed by the rotational population of CN in the optical spectrum in 1940 (although not understood at that time) (40f). The infrared region allows new exploration (see e.g. 41). Of particular excitement is the molecular hydrogen quadrupole emission spectrum, which has shown large energy-rich regions. Our desire to understand our universe by analysis of the radiation reaching us has been the route to much of the deepest physical understanding.

As noted above, the spectroscopy of isolated high-temperature species remains a challenge. The perforce large partition function of the species in its native habitat generally leads to broad spectral transitions with low information content. There have been a variety of techniques designed to meet this challenge. George Pimentel provided a solution to the problem by the invention of the matrix isolation method. The importance of isolating reactive species so that they could be structurally characterized by vibrational spectroscopy was the motivation of this research. It was an immediate success, coupling so well to the long wavelengths of infrared radiation. The scattering or low optical quality of the matrix was least important in this region. Vibrational spectroscopy had a well-developed empirical basis for structure characterization. The experiments are quick as is the analysis. The extension of this technique to other spectral regions was simultaneous. Wilse Robinson produced optical spectra of species such as NO_2 at the same time.

I_2 and NO_2

NO_2 has been a molecular siren in its allure for spectroscopists. There have been few realistic counts of the human years invested in the analysis of its visible spectrum. The reason is obvious. It has a visible fluorescence spectrum. In principle this should allow the study of the polyatomic molecule at the same level of detail as has been achieved for diatomic molecules by the study of molecular iodine. An inordinate number of spectroscopic discoveries have been made by the study of the I_2 B-X band system. Rotation-vibration energy transfer within molecular collisions was first discussed by R W Wood (42a,b) for the changes in the I_2 fluorescence

spectrum pumped by the Hg green line ($\lambda = 5460$ Å, $v = 25$, $J' = 34$) (43). The Franck-Condon principle was invented to explain the intensity distribution for the bands of the B-X system. Stimulated emission pumping was invented on the B-X system as a means of preparing specific rotation-vibration levels (44) of ground-state I_2. Hyperfine-induced predissociation was observed in this system (45). The cage effect is readily studied in this system.[4] It is possible to continue on the I_2 B-X system almost forever. It is also extremely interesting commentary that quantitative electron structure theory has played no role in these developments (47). To the physical chemist hoping to enter the real world, a polyatomic version of I_2 would be the Rosetta stone. Herein lies the infinitely seductive charm of NO_2. Its visible bands fluoresce. Thus simply putting vibrational and rotational labels on the spectral lines will allow everything done on I_2 to be extended into the real chemical world.

Perhaps the most important simplifying assumption in physical chemistry is the Born-Oppenheimer approximation and with it the concept of (isolated) potential energy surfaces. The history of I_2 is of course a monument to the success of the Born-Oppenheimer approximation. (It seems that the term approximation in a theory holding so well for isolated ground-state potential energy surfaces is almost hypocritical; a much better term would be Born-Oppenheimer Truth.) In the I_2 B-X system where there are no observed frequency perturbations, a picture of isolated non-interacting excited states, the B state, works well. NO_2 is then the system for which the picture of isolated excited state works badly, very badly.

The cooling of NO_2 in an argon matrix at 1.5 K left a complex spectrum (48). This, I believe, was an intrinsic weakness in the method of matrix isolation. If something was hard to understand it could be attributed to matrix effects, of which there were many. Bill Weltner has repeatedly shown that this last remark is to be taken with a very large grain of salt, because in his hands both in electron-spin resonance and optical spectroscopy, matrix-isolation methods work extremely well (see e.g. 49). Nonetheless the quest to understand the complexity of NO_2 persist, and more powerful methods appear to be required.

Supersonic Jets and Molecular Complexes

The supersonic jet source (50) was the solution to many spectroscopic problems. It allowed cooling of species to extremely low temperatures, and it provided a convenient tool for the clustering of molecules, allowing

---

[4] The concept of the cage effect starts, of course, in the condensed phase. It is also seen in the gas phase.

the synthesis of virtually any binary cluster. Because it was a source for a molecular beams spectrometer, one could have everything, high intensity and low temperatures, while maintaining gas-phase isolated molecule conditions, under which the theory of energy levels so well established held rigorously. It was a tool to have fun with. Our first observation using this source was, of course, the obvious; given an essentially monoenergetic beam, all species had the same dwell time in the resonance region. Under these conditions the transition probability given by Rabi for the two-level system held in a particularly simple form, with all of the periodic oscillations displayed (51). Everyone who has seen the two level formula displayed is overwhelmed. It must have been published a thousand times. Much more exciting to us was the ability to form and study new molecules in a controllable manner.

The hydrogen-fluoride dimer is probably the simplest example of a hydrogen-bonded species. This was easily made by expansion, and its microwave spectrum was readily observed by Tom Dyke and Brian Howard (52). Because the moment of inertia is determined essentially by the heavy atom separation, the rotational transitions were predictable. The lowest rotational transition is $J = 1 - J = 0$. This was predicted near 14 GHz, and a transition was observed. All was well except for one small detail: The Stark effect of the observed transition was much more complicated than the one line predicted for the $J = 1 - J = 0$ transition. As more transitions were observed, nothing fit the simple picture of rigid rotor transitions. Much time passed until a set of transitions near 20 GHz was observed. This we knew was the frequency at which NH_3 inverted its pyramid or changed the direction of its electric dipole moment. Clearly HF-HF was inverting to FH-FH, changing the dipole moment direction. The spectrum we were observing was a rotation inversion, rather than pure rotation spectrum. The levels were soon fitted with an inversion frequency three times the rotational constant. Two further displays of the inversion were the large change (factor of fifteen decrease) in the inversion frequency but not the rotational constant (a 5% decrease) in $(DF)_2$ and the total quenching of inversion in the mixed dimer HFDF. This, at that time, unique motion became quite typical for homomolecular dimers that did not possess a center of symmetry. Molecular beams spectroscopy is a high-resolution method. Line widths can typically be the flight time through the resonance region, which in Wharton's spectrometer is about 10^{-3} s. Thus precision dipole moments as well as deuteron quadrupole coupling constants were readily determined.[5] In addition to the study of $(HF)_2$, we saw

---

[5] From recent conversations with Tom Dyke, it is clear that we both remember the 14-GHz transition well, but the line is not listed in either of our compilations, or those of others.

in the mass spectrometry of the beam the ions $(HF)_nH^+$, $n = 1$–6. These were simplistically attributed to the neutral parents $(HF)_{n+1}$. The polarity of these polymeric species was examined by electric deflection. Only the dimer $(HF)_2$ was found polar. The remaining species were cyclic rings. We noted that the polymerization appeared to be continuous. The previous view of the polymerization of the hydrogen-fluoride system, from analysis of vapor density, was monomer, dimer, hexamer. It was interesting that we found a paucity of hexamer, in complete accord with a just-published electron structure calculation by Del Bene & Pople (54).

The easy production of virtually any binary complex in an adiabatic expansion source allowed study of intermolecular interactions in relatively simple systems using extremely high resolution methods. Harry Welsh and colleagues (55a,b) exploited low-temperature long path length infrared absorption for the study of complexes of hydrogen. Roy Gordon and colleagues (56) had treated the rotation-vibration spectra of the hydrogen dimer, obtaining a representation of the intermolecular potential. Of particular interest was the anisotropy, and this problem remains today. The interaction of argon with hydrogen chloride had been a classic system for the experimental determination of anisotropic intermolecular potentials. Both vibration-rotation spectra of HCl in argon and nuclear magnetic resonance had been measured. David Rank and coworkers (57) had observed spectral features in the Ar + HCl system that they attributed to the rotation-valence vibration spectrum of Ar-HCl. The Amsterdam group had examined the far-infrared spectrum (see 58 for references to earlier work) of the Ar + HCl system, attributing features in the 30–50 cm^{-1} region to the rotation–soft mode vibration spectrum of Ar-HCl. The complexity of the spectra in both regions prohibited a complete analysis and structure characterization.

Roy Gordon urged us to measure the rotational spectrum by molecular beams resonance. Stewart Novick and coworkers (59) prepared the species by the now-standard two-step synthesis: buy the components and expand. This method depends upon detection of resonance by changes in beam intensity. The species ArHCl was detected as the parent ion ArHCl$^+$; thus as opposed to the vibration rotation spectra, there was no interference from either monomeric constituent. The spectra were readily observed for both hydrogen and chlorine isotopomers (a word uniformly disliked). The species showed large-amplitude oscillation, as noted from the dipole moments and quadrupole coupling constants. The spectral resolution was high. It was clear that one could determine rotational spectra of these extremely weakly bound species with at least the same resolution as used for standard stable molecules. From just looking at the lines of the rotational spectra, there was little evidence that the binding energy of the

species was small. Rotational transitions of bound states appear quite similar. Because the rotational transitions are for a specific vibrational state, generally the lowest state, the effects of zero-point oscillation must be considered if one is to draw structural conclusions. van der Waals molecules, and ArHCl certainly is one, have large-amplitude zero-point motions. The linear Ar-HCl equilibrium configuration shows the greatest distortion resulting from zero-point oscillation, since this geometry is an extremum (with zero volume), i.e. bending makes the system nonlinear. In Ar-HCl the average angle that the HCl makes with the line connecting the Ar to the HCl center of mass is near 45°. It changes to 33° in Ar-DCl in agreement with expectation for a linear equilibrium configuration.

The Ar + HCl system has remained a target of opportunity for the study of anisotropic interactions with the steady development of new spectroscopic techniques,[6] as well as theoretical modeling (61a,b). However, the theoretical simplicity of Ar + HF has made this system also attractive. Multiple Ar binding to the HX moiety has been studied both in the microwave region (62a,b) and in the infrared (63). These studies will no doubt provide a precision data base upon which theories of many-body forces may be tested (64a,b).

The rotational spectroscopy of molecular complexes by molecular beam–electric resonance appeared to be a particularly powerful technique. In addition to the high spectral resolution of Doppler-free spectroscopy, positive species identification by mass spectroscopy appeared to be essential. The molecular species had bizarre spectra, owing to their nonrigidity; thus it was extremely useful to know what species was being studied before one started the spectroscopy. Secondly it was important to know that all the lines observed had the same carrier. Mass spectrometry is virtually the only self-calibrating analytical tool. Although superficially this sounded great, it was obvious that fragmentation during electron impact ionization required consideration; for example, spectral transitions in $(HF)_2$, the first molecular complex studied, were detected by monitoring the fragment ion. Nonetheless this method produced rotational spectra and definitive structural characterization of a number of molecular complexes that remain interesting today. The structure of the dimer of water was determined by Dyke & Muenter (65a,b). $(H_2O)_2$, with four protons and only one hydrogen bond, exhibits a myriad of proton interchange tunneling motions, whose complete characterization has been accomplished over an almost two-decade interval of dedicated spectroscopic research (66).

Of particular interest are the structures of the halogen-inert gas

---

[6] ArHCl was the first van der Waals molecule to which far infrared jet spectroscopy was applied.

complexes. Warren Falconer worked with Stewart Novick to produce beams and spectra of XeF. This species is of singular interest because it has a short but weak bond. The question of electron sharing would be answered by both electric dipole and electron spin hyperfine structure determination for the gas-phase species. With the ability to produce any species by adiabatic expansion, we thermally dissociated F_2 in a Xe-Ar mixture using a nickel tube. The container problem for high-temperature species is an interesting one. Nickel is stable with respect to attack by fluorine, as a consequence of the impermeability of nickel fluoride. Unfortunately just at temperatures where F_2 is well dissociated to atoms, NiF_2 sublimes. We had no difficulty seeing intense XeF^+ signals; however, these signals were due to XeF_2, the chemically bonded species discovered a decade earlier by Neil Bartlett and colleagues (see 67). It was interesting to us to see how easily noble-gas fluorides could be prepared when one knew they existed. The rotational spectrum XeF remains today as an interesting problem in both valence-state preparation and more generally in the question of short but weak bonds (68).[7]

After not producing XeF, we attempted the van der Waals complex Xe-F_2 to compare with valance-bonded XeF_2. The species was not polar enough to focus by the inhomogeneous electric fields of our quadrupole-state selector (69a,b). Because ClF is just as reactive as F_2, it appeared to essentially be a very convenient slightly polar form of fluorine. The structure of ArClF, a linear complex with atomic arrangement as written, is important because it clearly shows that a simple model of intermolecular interactions as a sum of atom-atom central forces is incorrect. Dudley Herschbach explained to us that indeed the lowest unoccupied molecular orbital of ClF was the antibonding σ orbital with composition primarily $p\sigma$ Cl. The picture of the structure of all complexes as simply related by isoelectronic rules was particularly attractive to us. This structural simplicity was soon questioned by contrary empirical evidence.

The strong cooling in inert-gas adiabatic expansions was most effectively coupled to laser-induced fluorescence by Don Levy, Len Wharton & Rick Smalley (69c). They obtained the visible excitation spectrum of NO_2 at very low temperatures, showing that the spectrum consists of a large number of bands even when rotations are frozen out. The complexity observed earlier by Robinson & McCarty (48) was intrinsic and not a result of matrix interactions. They further showed, by laser-induced fluorescence, that the visible B-X bands of inert-gas complexes of I_2 were analyzable in

---

[7] The measurement of hyperfine structure and the dipole moment of the species requires the high spectral resolution of rotational spectroscopy.

terms of a T-shaped complex (69d). This of course was in striking contrast to the previous linear structure of ArClF. The T-shaped structure was appealing because it was at once analyzable, for both electronic states, in terms of additive atom-atom central forces.

Laser-induced fluorescence is an extremely powerful technique, as has been shown from the early high-resolution spectra of I_2, which reveals hyperfine structure. Dick Zare (69e,f) exploited this method for the determination of the quantum-state distribution of products of reactions. Coupling laser excitation to the seeded jets provides a powerful methodology for the study of a wide variety of species, especially for those readily detected by fluorescence of the excited state.

Among the new weakly bound species observed, the inert-gas complexes of I_2 provided a wealth of dynamical information by analysis of the B-X emission of I_2, which had been produced by vibrational predissociation of the complex. This provides a great advantage in simplicity of analysis over earlier collisional energy-transfer experiments. In collisions there is no control over the impact parameter; however, in these half-collision experiments one can select the rotation-vibration level of the complex in the preparation step. These experiments showed a propensity rule of minimum change in the vibrational state of I_2, the minimum being set by the strength of the $Rg-I_2$ bond. In some ways these observations are similar to the early collision experiment with I_2 prepared in a particular rotation-vibration level of the B state. There the vibrational propensity rule was minimum change in vibration. The power of laser-induced fluorescence was dramatically displayed by Levy, Wharton & Smalley (69g–i) in their study of HeI_2. Helium does not quench the fluorescence of the B state of I_2. Thus a detailed picture of the flow of energy from the high-frequency valence vibration of the I_2 into the soft van der Waals bond was readily observed from the dispersed fluorescence. A vast number of laser fluorescence studies of molecular complexes followed this work (70).

The explanation of these observations was given by Joshua Jortner & Alberto Beswick (70a,b), who used essentially Fermi Golden Rule arguments. A nice physical picture was put forth by George Ewing (70c,d). These pictures explain the difficulty in converting vibrational energy into translation in weakly coupled systems. The nature of energy flow in polyatomic species remains a topic of intense activity.

The temperature of a jet is generally 10 K or less. It would appear unlikely that anything but the lowest-energy isomeric structure could be observed. This seemingly foolproof argument was used by us to rule out the possibility that the structure characterized by rotational spectroscopy was anything but the minimum energy configuration. Electronic spectroscopy first revealed isomeric forms.

Many new spectroscopic methods have been developed to exploit the power of the adiabatic expansion source. Bill Flygare developed an extremely powerful method of rotational spectroscopy by exploiting time-domain methods, so popular in magnetic resonance. The observation of free induction decay in a high-Q cavity provides an effective means of executing high-resolution beam spectroscopy. The spectrometer is well coupled to a pulsed beam source. This method showed clearly that species identification by mass spectroscopy was not mandatory. Working in the time domain, digitizing the signal allows excellent signal averaging. Fourier transform methods are dependent upon efficient computers.

As these techniques became available, transform methods came into their own. As an aside on this point, it was interesting to follow infrared spectroscopy, as presented at the yearly Ohio State University symposium on molecular structure and molecular spectroscopy. In the 1950s there were innumerable papers showing the theoretical advantage of inter-ferometric methods in an energy-limited regime. At the same time all the high-quality, high-resolution spectra of interesting systems were produced with grating spectrometers. It was only when Pierre Connes showed the spectrum of methane in the atmosphere of Venus with a better quality than any previous terrestrial spectrum that believers were created. The rapid development of low-cost digital computers totally changed spectroscopy.

Rotational spectroscopy of molecular complexes provided an excellent data base for theories of intermolecular forces. It did not, however, provide reliable values for, perhaps, the first quantity desired—the interaction strength. This quantity was only reliably determined from either electronic or vibrational spectroscopy, and even there with some difficulty. The question of what determines the interaction strength is clearly a question of general importance. A very popular model is that of atom-atom central interactions. This immediately permits a two-parameter potential energy function for simple systems. Consider the linear Ar-BC complex. In this complex a typical potential would be taken to be the Lennard-Jones 6–12, namely $V(R) = -A/R^6 + B/R^{12}$. As such, only two measurements are required for parameter specification. Because the rotational constant and the centrifugal distortion provide this, the problem is solved. The only problem appears to be what is R? Here a large element of arbitrariness enters. For heavy-atom systems such as Ar-ClF, R is the Ar-Cl distance, but for hydrides such as Ar-HCl, R is also the Ar-Cl distance. This point is probably important because molecular mechanics packages rely heavily on atom-atom interactions for simplicity of computation.

The development of the vibrational spectra of molecular complexes took several routes. Alan Pine (70e) observed $(HF)_2$ and ArHF in a cooled

long path length cell. This work showed clearly that the line widths for the two HF stretching vibrations, which are separated by 80 cm^{-1}, are quite different. The hydrogen-bonded HF stretching vibration is broader. In addition the tunneling frequency that now involves the switching of the excitation as well as the positions of the two HF units is reduced by about a factor of three. In addition to observing the absorption spectrum at the Doppler or predissociation limit of resolution, this technique provided an estimate of the dissociation energy, D_0, from the ratio of concentration of $(HF)_2$ to HF, which is readily obtained by using the free HF vibration of the dimer. This mode does not suffer an intensity enhancement upon H-bond formation.

It is interesting to note how little fuss was made over the infrared spectrum of $(HF)_2$. The literature of hydrogen bonding is filled with the mysteries of the intensification and breadth of hydrogen-bonded systems. The hydrogen-fluoride dimer was studied at high spectral resolution, so all the details of the spectrum are observed. Other than the small effects of inversion, the spectrum is perfectly normal. There is an undramatic intensification of the H-bonded HF stretching vibration by a factor of two. The trimer of hydrogen fluoride has been observed as a broad spectrum but certainly understandable.

The dissociation of $(HF)_2$ has been a classic problem. Originally we thought that the mechanism for the efficient vibrational relaxation of HF $v = 1$ by HF $v = 0$, which occurs in 1 in 80 gas kinetic encounters, could be related to the vibrational predissociation. If relaxation proceeds through a collision complex, then the above efficiency is simply the ratio of vibrational predissociation time to the collision complex lifetime (71). Our simplistic idea leads to a single lifetime for both $v = 1$ levels of $(HF)_2$. Because they differ by a factor of 30, it is clear that a statistical energy-sharing complex cannot be appropriate for this system.

The understanding of the dynamics of the $(HF)_2$ system has come from the measurement of the angular distribution of photodissociation products by Roger Miller and colleagues (71a). They have shown that the energy is primarily in product rotation with very asymmetric rotational distribution. Using aligned $(HF)_2$ the high rotational HF comes from the hydrogen-bonded HF. This was well predicted from simple dynamical models. There is a considerable advantage in theoretical simplicity in studying photo-dissociation on the ground electronic potential energy surface. The $(HF)_2$ dimer shows this clearly. Good agreement between experiment and dynamics executed on a fully ab initio potential has been demonstrated.

The spectroscopic study of species bound by intermolecular rather than valence interactions has been extended in many ways. Of considerable value has been direct measurement of the soft modes that fall in the far

infrared, 10–200 cm^{-1}. This has been a particularly difficult spectral region due primarily to the lack of moderately intense coherent sources. Although an early study of the π bending state of ArHCl found a few transitions by using Stark tuning and molecular beam detection (72), this was an awkward method. Ken Evenson et al (72a) showed several methods for generating tunable radiation in this region. These methods derived from the intense CO_2 laser, either by frequency difference generation or by Raman type processes together with microwave mixing in a Schottky barrier diode. The power output is adequate for absorption methods but not for saturation as beam-flop methods require.

The advantages of power detection of the absorption signal were shown in a series of studies by Rich Saykally and coworkers (73a,b). The far infrared provides direct measurement of the soft mode excitations. The resolution is sub-Doppler because slit jets are used as the source, providing hyperfine structure as well as rotational fine structure. These measurements provide data for a set of vibrational states, with nuclear density encompassing a large set of intermolecular coordinates, most interestingly the angular ones. As noted, chemists have much more interest in angles than in distances; thus in general, a clearer picture of the anisotropy in intermolecular potentials has emerged from these studies.

We were hindered in our study of complexes of ammonia by the use of the mass spectrometer for species detection. I had believed that argon, our primary inert gas, always behaved like a weak Lewis base. Thus when $ArNH_3$ was not detected by the parent ion $ArNH_3^+$, I accepted this negative result as positive evidence for its lack of formation, which resulted from the very feeble binding between a weak base and a strong base. When Gerry Fraser showed that all NH_3 complexes fragment upon electron impact ionization and that the ion generally observed is NH_3^+ (except in complexes allowing the formation of NH_4^+), spectroscopy of ammonia complexes became very doable. Fraser, Ken Leopold, and David Nelson (73c,d) obtained the rotational spectra of a number of these complexes.

Although the structural characterization of almost every molecular complex has proven interesting, the dimer of ammonia has, in my view, been among the most interesting, and argumentative. Every chemist is taught that the hydrides of the first row—HF, H_2O, and NH_3—are hydrogen bonded. This has been the classic explanation of the unobvious observation that their boiling points are higher than the corresponding second-row hydrides—HCl, H_2S, PH_3. The spectroscopy of $(HF)_2$ and $(H_2O)_2$ immediately established the dimeric structures as hydrogen bonded. The hydrogen bond in both of these species is quite close to a X-H-X angle of 180°. From the outset the ammonia dimer was quite different than either chemical

intuition or electron structure calculations predicted. There is little evidence for a strong, highly directional, nearly linear hydrogen bond. The most rigid of the several $(NH_3)_2$ dimers has a small dipole moment, less than half of that of ammonia monomer, which is in distinct contrast to $(HF)_2$ and $(H_2O)_2$, whose moments are nearly twice that of their monomers. The minimum energy configuration is still argumentative, since the angular geometry is strongly distance dependent. The nature of vibrational averaging is complex (74a,b).

The complexes of ammonia with Lewis acids are structurally simple. The bonding always connects the nitrogen lone pair with the acidic center. The complexes of ammonia with Lewis bases show complex structures, e.g. $(NH_3)_2$. The complex with CO is puzzling (75a,b). The orientation of the NH_3 unit has, based on the nitrogen quadrupole coupling constant and the change in rotational constant with ND_3, its nitrogen end pointing toward the CO unit. HF-CO and H_2O-CO have linear and near-linear hydrogen bonded structures to the carbon end of CO. The orientation of the CO in NH_3-CO appears to be perpendicular with respect to the line connecting the centers of mass of the units. The spectra show indications of considerable nonrigidity.

We tried hard but unsuccessfully to force NH_3 to donate hydrogens to a proton acceptor. The complex with formic acid was thought to be ideal. The OH-N linkage would then be augmented by the NH-OC bond. Unfortunately we were never successful in forming the complex and measuring its rotational spectrum. David Pratt (76) has indeed seen indications of ammonia forming a hydrogen bond in a closely related system following the alteration of the internal rotational motion.

The precision study of intermolecular potentials by using the spectroscopy of the bound and metastable states has proven to be a gold mine. Our understanding of binary interactions has become quite sophisticated compared to the prespectroscopic age.[8] There are now an increasing number of studies attempting to measure the nonadditivity of interaction potentials. In addition to the characterization of intermolecular of forces, there has been a steady increase in the study of the coupling between valence and soft modes (78a,b).

Vibrational Overtones and Photodissociation

Kevin Lehmann introduced me to overtone spectroscopy. After wasting about two years of our time trying to use Stark modulation spectroscopy

---

[8] It seems that if one needs to use statistical mechanics to analyze the results of an experiment, one has misdesigned the experiment.

to gain spectral sensitivity[9] in the visible, following Bright Wilson for the microwave, reason prevailed and we used well-established photoacoustic methods, producing interesting physical results (80a,b). The ease of studying fluorescence makes energy flow in excited electronic states a very attractive methodology. There are, however, some concerns in the simple mechanical treatment. First, in general an optically bright electronic state is embedded in several other states. Secondly and somewhat related, quenching of fluorescence is a general occurrence. The observer is therefore left in some doubt as to whether the fluorescence is the remnant of a highly anisotropic quenching process. Additionally the level embedment always makes the possibility of nonadiabatic processes a further concern. The development of tunable intense infrared laser provides a variety of methods to prepare excited valence vibrational levels of jet-prepared molecular complexes (81, 82). These studies have a theoretical simplicity because all the action is within a single electronic state. The details of dissociation dynamics that have been revealed by these measurements have been powerful stimuli for dynamical modeling (83; 84a,b). The appeal of overtone spectroscopy applied to jet sources using laser-induced fluorescence as a most enjoyable type of spectroscopy was demonstrated by Huan Chang and coworkers (85a,b). This is one more example of the fact that virtually every form of spectroscopy is readily applicable to the jet source. It is remarkable that everything has worked so well and it is almost obvious that continuation of both the evolution of new methods as well as the study of new classes of species will continue unabated.

In this chapter I have mentioned a few particular studies on simple systems that have made a particular impact on me. In mentioning these I have not mentioned many others, owing to space limitations. All of the topics were curiosity driven rather than part of a grand strategic plan. The beauty and power of investigator-driven research has been made clear at many instances, perhaps the most dramatic was at the memorial service[10] for John van Vleck.

Van was a very powerful intellect who was a driving force in the creation of several important areas, such as solid-state physics and certainly magnetic phenomena. I could not help wonder if in 1930 a group of long-range planners had asked organic chemists what was the most important area to invest in for the future, would any have answered magnetism. Nuclear

---

[9] Takeshi Oka told us that he also tried Stark modulation of laser absorption and was similarly defeated by "guide noise."

[10] At the time, 1980, I was Assistant Director of the National Science Foundation for Mathematical and Physical Sciences where there was continual discussion on long-range research innovation.

magnetic resonance, with its unbelievably large number of uses, is the outgrowth of a number of powerful fundamental ideas.

Literature Cited

1. Yost DM, Russell H. 1946. *Systematic Inorganic Chemistry*. New York: Prentice-Hall
2. Hawkins DT, Bernstein LS, Falconer WE, Klemperer W. 1976. *Binary Fluorides*. New York: Plenum
3. Ramsey N. 1956. *Molecular Beams*. Oxford: Oxford Univ. Press
4a. Flygare WH, Benson RC. 1971. *Mol. Phys.* 20: 225
4b. Flygare WH. 1978. *Molecular Structure and Dynamics*. New York: Prentice-Hall
5. Rosenblum B, Nethercot AH, Townes CH. 1958. *Phys. Rev.* 109: 400
6. Huo W. 1965. *J. Chem. Phys.* 43: 624
7. Ransil BJ. 1960. *Rev. Mod. Phys.* 32: 245
8. Lovas FJ, Johnson DR. 1971. *J. Chem. Phys.* 55: 41
9. Born M, Mayer JE. 1932. *Z. Phys.* 75: 1
10. Rittner ES. 1951. *J. Chem. Phys.* 19: 1030
11. Kusch P. 1953. *J. Chem. Phys.* 21: 1424
12. Brumer P, Karplus M. 1976. *J. Chem. Phys.* 64: 5165
13. Deleted in proof
14. Honig A, Mandel M, Stitch ML, Townes CH. 1954. *Phys. Rev.* 96: 629
15a. Berry RS, Rice SA, Klemperer W. 1957. *J. Chem. Phys.* 26: 618
15b. Berry RS, Rice SA, Klemperer W. 1957. *J. Chem. Phys.* 26: 724
15c. Berry RS, Rice SA, Klemperer W. 1957. *J. Chem. Phys.* 27: 573
16. Deleted in proof
17. Klemperer W, Norris WG. 1961. *J. Chem. Phys.* 34: 1071
18. Deleted in proof
19. Marple DTF, Trischka JW. 1956. *Phys. Rev.* 103: 597
20a. Klemperer W, Herschbach D. 1957. *Proc. Natl. Acad. Sci. USA* 43: 429
20b. Herschbach DR. 1987. *Chem. Scr.* 27: 327-47
21. Moran TI, Trischka JW. 1961. *J. Chem. Phys.* 34: 923
22. Wharton L, Klemperer W, Gold LP, Strauch R, Gallagher JJ, Derr VE. 1963. *J. Chem. Phys.* 38: 1203

23a. Curl RF, Pitzer KS. 1958. *J. Am. Chem. Soc.* 80: 2371
23b. Aronson JR, Lord RC, Robinson DW. 1960. *J. Chem. Phys.* 33: 1004
23c. Thorsen WR, Nakagawa I. 1960. *J. Chem. Phys.* 33: 994
24. Buchler A, Stauffer J, Klemperer W, Wharton L. 1963. *J. Chem. Phys.* 39: 2299
25a. Kuczkowski RL, Lide DR, Krisher LC. 1966. *J. Chem. Phys.* 44: 3131
25b. Matsumura C, Lide DR. 1969. *J. Chem. Phys.* 50: 3080
25c. Freund SM. 1970. PhD thesis. Harvard Univ.
26. Dietz TG, Duncan MA, Powers DE, Smalley RE. 1981. *J. Chem. Phys.* 74: 6511-12
27. Wharton L, Berg RA, Klemperer W. 1963. *J. Chem. Phys.* 39: 2023
28. Fraser GT, Pate BH. 1994. *J. Chem. Phys.* 100: 6210-20
29. Kantrowtiz A, Grey J. 1951. *Rev. Sci. Instr.* 22: 328
30. Slichter WP. 1950. PhD thesis. Harvard Univ.
31a. Wharton L, Gold LP, Klemperer W. 1960. *J. Chem. Phys.* 33: 1255
31b. Wharton L, Gold LP, Klemperer W. 1962. *J. Chem. Phys.* 37: 2149
32. Matsen FA. 1962. *J. Chem. Phys.* 34: 337
33. James TC, Norris WG, Klemperer W. 1960. *J. Chem. Phys.* 32: 728
34. Deleted in proof
35. Wharton L, Gold LP, Klemperer W. 1964. *Phys. Rev. B* 133: 270
36. Kaufmann M, Muenter J, Klemperer W. 1967. *J. Chem. Phys.* 47: 3365
37. Kaiser EW. 1970. *J. Chem. Phys.* 53: 1686
38. Raymonda J, Muenter J, Klemperer W. 1967. *J. Chem. Phys.* 52: 3458
39. Herbig GH. 1975. *Astrophys. J.* 196: 129
39a. Herbig GH. 1995. *Annu. Rev. Astron. Astrophys.* 33: 19-73
40. Rank DM, Townes CH, Welch WJ. 1971. *Science* 174: 1083
40a. Snyder LE, Buhl D. 1970. *Nature* 227: 862

40b. Snyder LE, Buhl D. 1970. *Nature* 228: 267
40c. Woods RC, Dixon TA, Saykally RJ, Szanto PG. 1975. *Phys. Rev. Lett.* 29: 1269
40d. Saykally RJ, Woods RC. 1981. *Annu. Rev. Phys. Chem.* 32: 403–31
40e. Green S. 1981. *Annu. Rev. Phys. Chem.* 32: 103–38
40f. Herzberg G. 1950. *Molecular Spectra and Molecular Structure. Diatomic Molecules,* pp. 496–97. New York: van Nostrand
41. Kwok S, ed. 1993. *Future Observational Directions, Astron. Soc. Pac. Conf. Ser.,* Vol. 41. San Francisco: Astron. Soc. Pac.
42a. Franck J, Wood RW. 1911. *Philos. Mag.* 21: 314
42b. Wood RW. 1912. *Philos. Mag.* 24: 673
43. Steinfeld JI, Klemperer W. 1965. *J. Chem. Phys.* 42: 3475
44. Kittrell C, Abramson E, Kinsey JL, McDonald SA, Reisner DE, et al. 1981. *J. Chem. Phys.* 75: 2056–59
45. Vigue J, Broyer M, Lehmann JC. 1981. *J. Phys.* 42: 937–47
46. Deleted in proof
47. Mulliken RS. 1971. *J. Chem. Phys.* 55: 288
48. Robinson GW, McCarty M, Keelty MG. 1957. *Chem. Phys.* 27: 973
49. Weltner W, Van Zee RJ. 1985. In *Comparison of Ab Initio Quantum Chemistry with Experiment for Small Molecules,* ed. RJ Bartlett, pp. 1–16. Dordrecht: Reidel
50. Anderson JB, Andres RP, Fenn JB. 1966. *Adv. Chem. Phys.* 10: 275
51. Dyke TR, Thomasevich GR, Klemperer W, Falconer WE. 1972. *J. Chem. Phys.* 57: 2277
52. Dyke TR, Howard BJ, Klemperer W. 1972. *J. Chem. Phys.* 56: 2442
53. Deleted in proof
54. Del Bene JE, Pople JA. 1971. *J. Chem. Phys.* 55: 2296
55a. Kudian AK, Welsh HL, Watanabe A. 1965. *J. Chem. Phys.* 43: 3397
55b. Watanabe A, Welsh HL. 1964. *Phys. Rev. Lett.* 13: 810
56. Gordon RG, Cashion JK. 1966. *J. Chem. Phys.* 44: 1190
57. Rank DH, Rao BS, Wiggins TA. 1962. *J. Chem. Phys.* 37: 2511
58. Boom EW, Frenkel D, van der Elsken J. 1977. *J. Chem. Phys.* 66: 1826–29
59. Novick SE, Davies P, Harris SJ, Klemperer W. 1973. *J. Chem. Phys.* 59: 2273–79
60. Deleted in proof
61a. Hutson JM, Howard BJ. 1982. *Mol. Phys.* 45: 769–90

61b. Hutson JM. 1992. *J. Phys. Chem.* 96: 4237–47
62a. Gutowsky HS, Klots TD, Chuang C, Schmuttenmaer CA, Emilsson T. 1985. *J. Chem. Phys.* 83: 4817–18
62b. Gutowsky HS, Klots TD, Chuang C, Schmuttenmaer CA, Emilsson T. 1987. *J. Chem. Phys.* 86: 569–76
63. McIlroy A, Lascola R, Lovejoy CM, Nesbitt DJ. 1991. *J. Chem. Phys.* 95: 2636–44
64. Elrod MJ, Saykally RJ. 1994. *Chem. Rev.* 94: 1975
65a. Dyke TR, Muenter JS. 1974. *J. Chem. Phys.* 60: 2929
65b. Dyke TR, Muenter JS. 1977. *J. Chem. Phys.* 66: 498
66. Fraser GT. 1991. *Int. Rev. Phys. Chem.* 10: 189–206
67. Hawkins DT, Falconer WE, Bartlett N, eds. 1978. *Noble Gas Compounds, a Bibliography* 1962–1976. New York: Plenum
68. Tellinghuisen PC, Tellinghuisen J, Coxon JA, Velazco JE, Setser DW. 1978. *J. Chem. Phys.* 68: 5187
69a. Jäger W, Xu Y-J, Gerry MCL. 1993. *J. Chem. Phys.* 99: 919–27
69b. Jäger W, Xu Y-J, Gerry MCL. 1994. *J. Chem. Phys.* 100: 4147
69c. Smalley RE, Wharton L, Levy DH. 1975. *J. Chem. Phys.* 63: 4977
69d. Smalley RE, Levy DH, Wharton L. 1978. *J. Chem. Phys.* 68: 671
69e. Schulz A, Cruse HW, Zare RN. 1972. *J. Chem. Phys.* 57: 1354
69f. Kinsey JL. 1977. *Annu. Rev. Phys. Chem.* 28: 349
69g. Kim MS, Smalley RE, Wharton L, Levy DH. 1975. *J. Chem. Phys.* 65: 1216
69h. Sharfin W, Johnson KE, Wharton L, Levy DH. 1979. *J. Chem. Phys.* 71: 1292
69i. Levy DH. 1980. *Annu. Rev. Phys. Chem.* 31: 197–225
70. Janda KC, Bieler CR. 1990. In *Atomic and Molecular Clusters,* ed. E Bernstein, pp. 455–506. Amsterdam: Elsevier
70a. Beswick JA, Jortner J. 1978. *J. Chem. Phys.* 68: 2277
70b. Beswick JA, Jortner J. 1981. *Adv. Chem. Phys.* 47: 363
70c. Ewing GE. 1978. *Chem. Phys.* 29: 253
70d. Ewing GE. 1982. *Faraday Discuss. Chem. Soc.* 73: 325
70e. Pine AS, Lafferty WJ. 1983. *J. Chem. Phys.* 78: 2154
71. Klemperer W. 1974. *Ber. Bunsenges. Ges.* 78: 128
71a. Dayton DC, Jucks KW, Miller RE. 1989. *J. Chem. Phys.* 90: 2631
72. Marshall MD, Charo A, Leung HO, Klemperer W. 1985. *J. Chem. Phys.* 83: 4924–33

72a. Evenson KM, Broida HP, Wells JS, Mahler RJ, Mizushima M. 1968. *Phys. Rev. Lett.* 21: 1038

73a. Cohen RC, Saykally RJ. 1991. *Annu. Rev. Phys. Chem.* 42: 369–92

73b. Cohen RC, Saykally RJ. 1992. *J. Phys. Chem.* 96: 1024–40

73c. Fraser GT, Leopold KR, Klemperer W. 1984. *J. Chem. Phys.* 80: 1423

73d. Nelson DD Jr, Fraser GT, Klemperer W. 1987. *Science* 238: 1670

74a. Olthof EHT, van der Avoird A, Wormer PES. 1985. *J. Chem. Phys.* 101: 8430

74b. Olthof EHT, van der Avoird A, Wormer PES, Loesser JG, Saykally RJ. 1985. *J. Chem. Phys.* 101: 8443

75a. Fraser GT, Nelson DD, Peterson KI, Klemperer W. 1986. *J. Chem. Phys.* 84: 2472

75b. Fraser GT, Nelson DD, Peterson KI, Klemperer W. 1987. *Science* 238: 1670

76. Held A, Pratt DW. 1993. *J. Am. Chem. Soc.* 115: 9718

77. Deleted in proof

78a. 1988. *Chem. Rev.* 88(6)

78b. 1994. *Chem. Rev.* 94(7)

79. Deleted in proof

80a. Lehmann KK, Scherer GJ, Klemperer W. 1982. *J. Chem. Phys.* 77: 2853–61

80b. Lehmann KK, Scherer G, Klemperer W. 1984. *J. Chem. Phys.* 81: 5319

81. Nesbitt DJ. 1988. *Chem. Rev.* 88: 843–70

82. Miller RE. 1986. *J. Phys. Chem.* 90: 3301–13

83. Bohac EJ, Miller RE. 1993. *J. Chem. Phys.* 99: 1537–44

84a. Zhang DH, Zhang JZH. 1993. *J. Chem. Phys.* 98: 5978–81

84b. Zhang DH, Zhang JZH. 1993. *J. Chem. Phys.* 99: 6624–33

85a. Chang HC, Klemperer W. 1993. *J. Chem. Phys.* 98: 9266–78

85b. Chang HC, Klemperer W. 1994. *J. Chem. Phys.* 100: 1