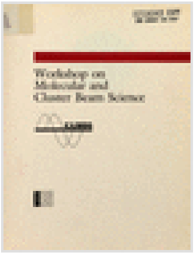

Workshop on Molecular and Cluster Beam Science (1988)

Pages
98

Size
8.5 x 10

ISBN
0309319854

Committee on Atomic, Molecular, and Optical Sciences; Board on Physics and Astronomy; Commission on Physical Sciences, Mathematics, and Resources; National Research Council

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Workshop on Molecular and Cluster Beam Science

The National Academy of Sciences
April 24, 1987

CAMOS

Committee on Atomic, Molecular, and Optical Sciences (CAMOS)
Board on Physics and Astronomy
Commission on Physical Sciences, Mathematics, and Resources
National Research Council

NATIONAL ACADEMY PRESS
Washington, D.C. 1988

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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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This report was supported by the National Science Foundation under Grant No. PHY-851040, the U.S. Department of Energy Division of Chemical Sciences under Grant No. DE-FG05-85ER13326, and the Office of Naval Research under Grant No. N00014-86-G-0098.

Available from

Board on Physics and Astronomy
2101 Constitution Avenue, N.W.
Washington, D.C. 20418

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PREFACE

Molecular beam science was recently highlighted by the awarding of the 1986 Nobel Prize in Chemistry. When coupled with the exciting developments in the area of cluster beam research, it is clear that there are new scientific opportunities in the molecular and cluster beam research arena. Thus, the Committee on Atomic, Molecular, and Optical Sciences (CAMOS) of the National Research Council held a workshop on this topic at the National Academy of Sciences on April 24, 1987. This workshop was aimed at highlighting an area of research that will have broad impact on neighboring sciences, and where related technological advances will affect federal and industrial programs.

This report, comprising presentations from the workshop, constitutes a statement that our scientific community, in its collective wisdom, finds molecular and cluster beam science to be an exciting and important area of research.

We thank all of the speakers for their contributions to this workshop, including their oral presentations and the preparation of these papers.

James J. Wynne
Workshop organizer
Member, CAMOS

1

MOLECULAR AND CLUSTER BEAM SCIENCE: A HISTORICAL PERSPECTIVE

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When I was asked to undertake the task of presenting a historical background to the enormously productive and highly complex and varied field of molecular and cluster beam science, I said, "sure, why not?" Very often when one says "sure, why not?" one finds out why not. In trying to figure out a tractable approach to this task, I've decided to mix some personal and some anecdotal information in with a modicum of dry history.

Molecular beams have been around since the time of Dunoyer who in 1911 showed that atoms move in straight lines when they are allowed to travel in vacuum in collision-free space.[1] A lot of work was done by physicists with molecular beams over a number of years. The principal early practitioners were Otto Stern and his coworkers at Hamburg who, during the late 1920s and early 1930s, proved many of the fundamental principals of quantum mechanics using molecular beams. Perhaps the most memorable of these was the Stern-Gerlach experiment, which demonstrated space quantization. It was at Rabi's school at Columbia, starting in the mid-1930s, that these methods were highly developed using magnetic resonance and electric (Ramsey) resonance techniques to measure nuclear spins and moments. Rabi also did some less well known, but important, atom-atom scattering experiments. Rosin and Rabi[2] gave experimental proof of the quantum mechanical limit on the range of potentials falling off faster than 1/r by showing that, as we defined the scattering angles smaller and smaller, the cross section did not go to infinity. In general, physicists learned early on that to obtain detailed dynamic information, one must measure angular and velocity distributions and that knowledge gained from dynamical processes can also lead to important findings on structure (e.g., Rutherford scattering).

On the occasion of Otto Stern's seventieth birthday, which was in 1959, there was a symposium held at Heidelberg in his honor. At that time, I was invited to talk about our molecular beam work in chemistry and to contribute a review on molecular beams in chemistry to a Festschrift in his honor.[3] This task sends one to search the literature and to discover things one had never dreamed ever existed! It turns out that there was quite a bit of molecular beam work that had been done in chemistry (120 references). Much of it was in effusion and surface condensation, but there were also attempts at studying chemical reactions. Of these efforts, some were successful, most were not. I would like to point to one or two of these references.

In 1928, F. O. Rice, Harold C. Urey, and R. N. Washburn published a paper entitled "The Mechanism of Homogeneous Gas Reactions. The Effect of Black Body Radiation on a Molecular Beam of Nitrogen Pentoxide."[4] They tried to test the then current "radiation hypothesis," which proposed that unimolecular reactions did not occur because of collisional pumping, but were induced by the absorption of infrared photons from the thermal background. It was a short-lived hypothesis, and this experiment, carried out in 1927 by the redoubtable team of G. N. Lewis and J. E. Mayer,[5] who showed no effect of passing a beam through a hot tube on the internal racemization of pinene, was the deathknell for this theory.

The glass molecular beam apparatus that was used by Rice et al. is shown in Figure 1-1. The nitrogen pentoxide comes in through I, and effuses through little holes in the upward and downward direction. The upward directed beam was illuminated by a heated section, D, and the molecules were condensed at surface F. They measured whether anything had actually happened to these molecules as a result of passing through this radiation field. In fact, nothing had happened to them. Now I remind you that some of the experiments that we have these days (e.g., multiphoton ionization) look very much like this in concept, except, of course, the intensity of the radiation is a bit higher.

In any case, we go back now to Harold Urey, who was an early boss of mine when I was a teenager working at the SAM Labs (Manhattan project) at Columbia. When he later visited us during my post-teenage life at Oak Ridge, while we were working on molecular beam chemistry and trying to get the experiment to work, he made the now historical remark, "What in the hell are you doing that for?" It was clear that there was not much point in doing "that" anymore, either because it had already been done and had proved nothing, or it was too hard to do (a comment by Henry Eyring made at about the same time).

Let's now talk about molecular beam chemistry. How has this come to pass? Well, it has come because of the yen of the chemist to escape the chaos of the test tube and his consuming desire to test his theory of reaction kinetics, which is collisionally based on a direct molecular basis.

I am going to concentrate in this brief talk on reactive scattering where one is looking at product angular distributions. Otherwise, the thing gets so enormous that one is not even able to mention the titles. If you are just going to have one shot at the possibly reactive collision, rather than $\sim10^{10}$/sec, as in gas at atmospheric pressure, you had better pick a reaction with high probability. That is an obvious statement, but if you read our 1959 review article about early attempts at molecular beam chemistry, you will find that it was not so obvious as you might think. Michael Polanyi, the eminent father of the eminent son John C., in the late 1920s and early 1930s used the method of highly dilute and diffusion flames to measure the reactions of alkali atoms with halogen-containing molecules,[6] and, in many cases, the reaction rates were faster than predicted by gas kinetic cross sections. This was astounding! How could they react before they "collide"? In 1940, in the *Journal of Chemical Physics*, John McGee of Notre Dame explained Polanyi's results as being due to the crossing of ionic and Van der Waals potentials at large distances.[7] This mechanism later came to be known as harpooning, i.e., the electron was "shot" over at large distances and the reactants were pulled together by the "rope" of the Coulomb force.

So here are ready made reactions with large cross sections and, moreover, how fortunate we are that we had available to us the very sensitive surface ionization method to detect alkalies and alkali halides, which had been developed in 1933 by J. B. Taylor and I. Langmuir,[8] and which had been applied to molecular beam studies by the Stern group.

This sensitive method was absolutely necessary to start with. Molecular beams are tenuous and not much more than a monolayer per year of reaction product would be expected. The choice was obvious: study alkali reactions. The question was which ones? There is a wide choice, but the initial one that we chose[9] was the reaction of $K + HBr \rightarrow KBr + H$.

This particular reaction was chosen as the first candidate for several reasons. First, because when the products fly apart, you want the deflected product to be concentrated in one place to maximize the signal. Therefore, you want to choose a light recoiling atom like hydrogen, which cannot kick the alkali halide around very much. The reason for the choice of the Br atom was that one could use sensitive neutron activation analysis to detect it. This addresses the crux of the problem. How are you going to tell the product alkali halide from the elastically scattered alkali? The Langmuir-Taylor ionization gauge detected both with equal efficiency. How then do you tell the product alkali halide from the reactant alkali? For that, we initially used probably the world's largest molecular beam detector, i.e., the old graphite reactor at ORNL. The idea was to collect KBr onto little strips placed around the scattering center and then very carefully shoot the samples into the Oak Ridge Graphite Reactor and activate them with neutrons. Measuring the radioactivity from the Br would then give the KBr distribution. After spending a year and a half learning about radio-bromine, I tried to find a better way to do it. The result was the famous, two filament, differential surface ionization gauge.[10] One filament, the traditional tungsten one, detected both alkalis and alkali compounds. The second, a platinum one, detected only free alkali atoms. The device worked, but not for the reasons I thought. (Actually in case anyone cares, I can tell you the real reasons, which were confirmed during a 1978 investigation of ours[11] on the negative surface ionization of UF_6. I know it seems obscure, but there is a connection).

I was looking through the files the other day and spotted this photograph of our Mark 1 apparatus (Figure 1-2) taken in, ca. 1954. At that time "O-rings" were not really trusted for anything but round flanges, hence the black wax and hence the leak detector at the left. The innards of this machine are shown in Figure 1-3. We used a two-chamber alkali oven (ABCD) so that we could establish a vapor pressure in part A and raise the beam temperature in chamber C. The crossed beam of HBr entered from oven I at right angles (but rotatable) to the alkali beam and the two filament differential surface ionization gauge (N) is rotated about the scattering center. The signals from each of the filaments, as a function of angle, is shown in Figure 1-4, and when one subtracts one from the other, one obtains a signal attributable to the alkali halide product KBr.

In Figure 1-5, we show a picture of the famous Bertha apparatus taken from the 1961 paper by Herschbach, Kwei, and Norris.[12] There is a two-chamber oven, a crossed beam, and a two-filament differential surface-ionization gauge. In "Bertha," the lid rotates, and the two-filament gauge stays in one place. The reaction studied here was the famous $K + CH_3I \rightarrow KI + CH_3$ and Figure 1-6 shows the two-filament signals and the KI difference signal. The very important point here is that if you make KI, the recoiling CH_3 can give a larger kick than a hydrogen atom, and the result was the observation of rebound reactions, i.e., there is mainly a backward kick to the KI product, presumably because you have to hit the molecule in the right place at small impact parameters and you get backward scattering in the center-of-mass frame of reference.

In 1966, Dudley Herschbach wrote a review on the subject in the *Advances in Chemical Physics* in which he listed 25 reactions that had been studied.[13] All of these were alkali reactions, and they had been reported in 16 experimental papers. Among the early contributors to this field were the Brown University group, Dieter Beck, Ned Green, and John Ross.[14] They introduced velocity selection. They also looked at rainbow scattering--rainbow scattering, if you recall, is, in this manifestation, a consequence of elastic scattering from a potential with both attractive and repulsive components. For a given collision energy, there is a scattering angle at which the attractive and repulsive forces balance and $dq/db = 0$. For angles larger than the rainbow angle, the corresponding impact parameter is single valued. Knowing the van der Waals potential and using an optical model (i.e., looking where the large angle elastic scattering ought to be), one can adduce reactive scattering from a lack of elastic scattering. An extreme example of optical opacity occurred when we observed "spectator stripping" in the reaction of $Cs + Br_2$. The rainbow peak did not appear at all because the reactive collision radius was so large that the impact parameter, which led to rainbow scattering, was already in the reactive channel.[15]

At Wisconsin, Bernstein and coworkers introduced product velocity analysis. Bernstein's group also introduced spacial orientation of the reactant molecule[16]--an extremely subtle and very interesting modification to this business, which is still under intensive investigation. At Berkeley and Harvard, depending upon the time, Herschbach and his coworkers looked at rebound reactions and introduced electric deflection to differentiate between alkali and alkali halides which confirmed the results of the differential surface ionization gauge measurements. In 1974, Farrar and Lee wrote a review for the *Annual Reviews of Physical Chemistry*.[17] Between the 1966 review and the 1974 review, some very important changes had taken place. The most important was the development of the "universal detector" (i.e., mass spectrometric detection) by Lee and coworkers.[18] This development required highly sensitive ionizers, advanced vacuum techniques, and a qualitative increase in the scale of the apparatus as shown in Figure 1-7. (Actually there had been some earlier attempts,[19] but the results were a bit dicey because of backgrounds due to insufficient differential pumping). The existence of these machines unleashed molecular beam chemistry from its alkali fetters. In particular, reactions involving halogen atoms and molecules and hydrogen and oxygen atoms came under study. In contrast to the 1966 review, the 1974 review listed 51 papers that had been published in just the preceding two years; 23 of these were on non-alkali reactions.

Not only was the scope of reactions studied enlarging, but also the degree of sophistication. True state-to-state analysis was greatly enhanced by utilization of lasers for, on the one hand, reactant state preparation and, on the other, as a probe for product ro-vibrational analysis. The growth of the field was annunciated in Volume 55 of the *Transactions of the Faraday Society* (410 pages), which was devoted to molecular beam scattering. Reactive scattering took up 177 of these pages. An illustration of this growth is shown in Figure 1-8, which is taken from Herschbach's paper[20] in that volume. This illustrates the range of chemical reactions studied, the subtlety of analysis of the product states, and the modes of state preparation for the reactants (to which I must modestly add the role of electronic excitation to reaction).[21] The continued growth of laser technology and the clever ways it has been applied have continued to increase the subtlety not only of reactive studies but, as you will hear today, also in the use of molecular beams to determine molecular structures.

Much of this symposium is concerned with cluster beams; aggregates of atoms and molecules that exist in the gas phase. "Clusters" by their present definition can range in size from simple dimers to aggregates large enough to approach, in many respects, a condensed phase. Clusters were at first accidental curiosities, which were observed as polymeric ions in sputtering of solids by ion beams and as an "unfortunate" side effect which accompanied the development of high pressure nozzle beams for isotope separation. This fact just illustrates again the old saw that "one man's poison is another man's meat" and as a coda to this introduction, I will come around full circle to mention two anecdotal events. First, the "dilute flame" work of M. Polanyi's institute[6] was based upon following alkali reactions by the light emitted at the reaction interface where two gases met, e.g., the Na-D line in the reaction of Na + Cl_2. The only problem is that this reaction is not sufficiently exothermic to excite the Na-D line. The light actually came from the reaction of Na_2 molecules (clusters?) with Cl_2. The second relates to some strange observations made in the course of experiments at Columbia on molecular beam spectroscopy using alkali-halide beams where it appeared that some hyperfine properties were temperature dependent.

It had been assumed that alkali-halide beams were monomeric; however, Miller and Kusch,[22] using molecular beam velocity analysis, showed quite the contrary. Dimers and trimers were present and in some cases (e.g., LiBr) were even dominant. This observation caused a fair amount of furor in the physical chemistry community, but that's another story.

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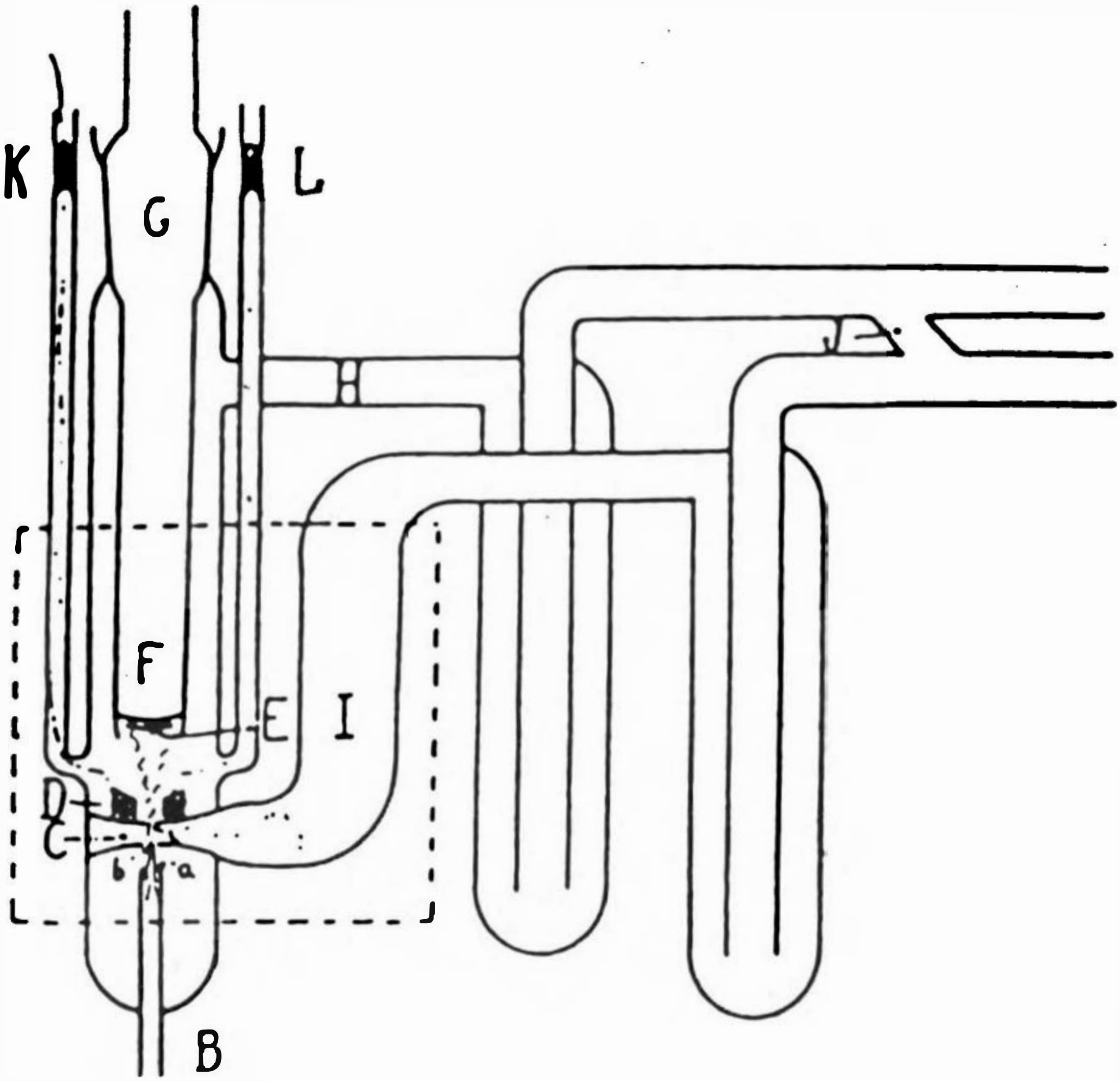

FIGURE 1-1 Diagram of apparatus used by Rice, Urey and Washburn in 1928 (see ref. 4).

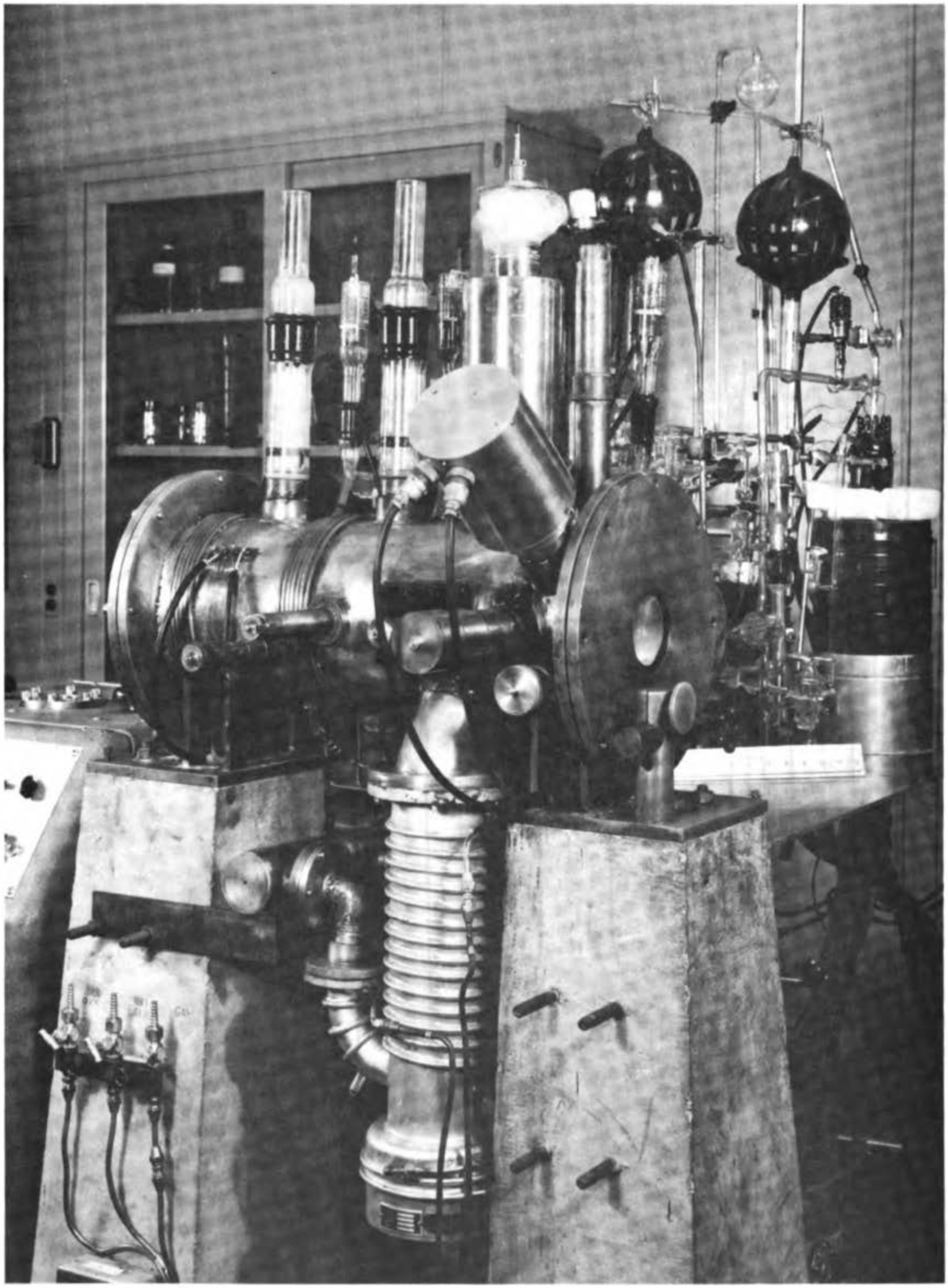

FIGURE 1-2 Photograph of our first molecular beam apparatus, Mark I, circa 1954.

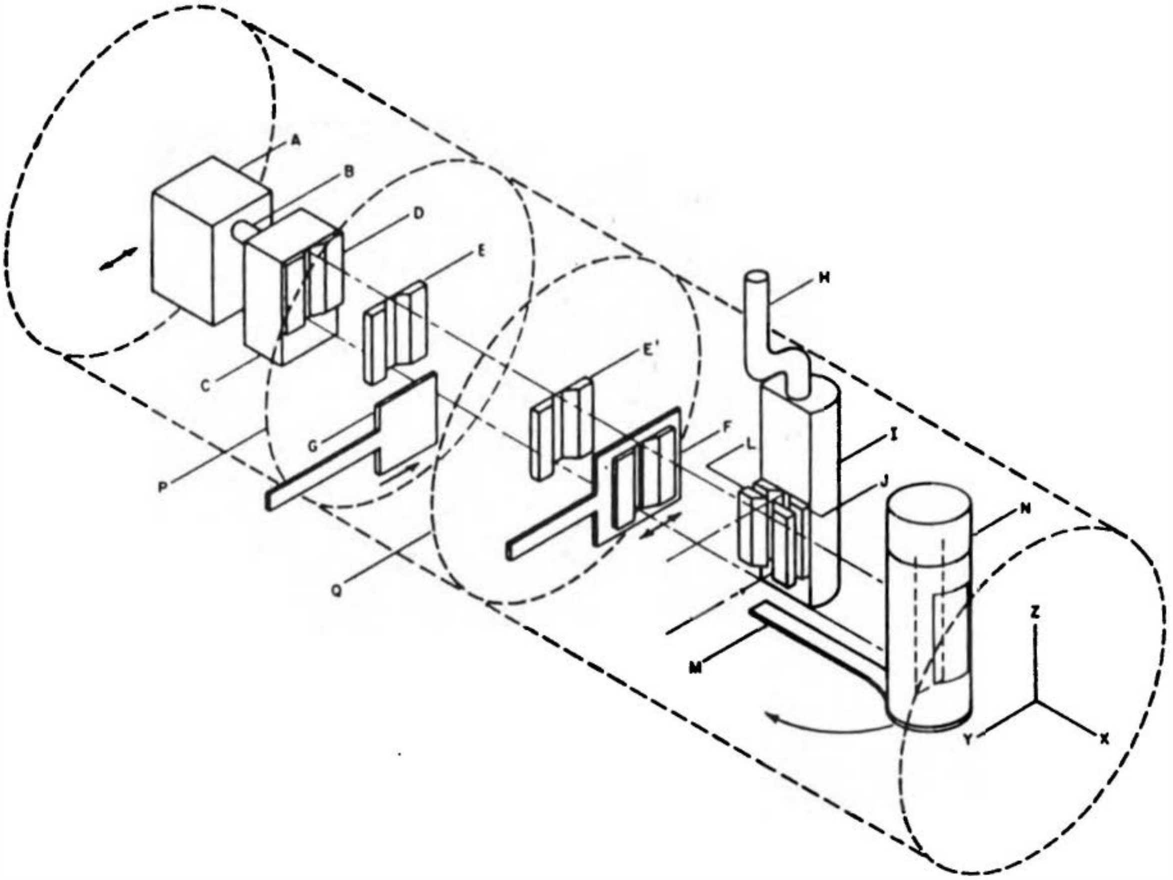

FIGURE 1-3 Schematic of the insides of Mark I.

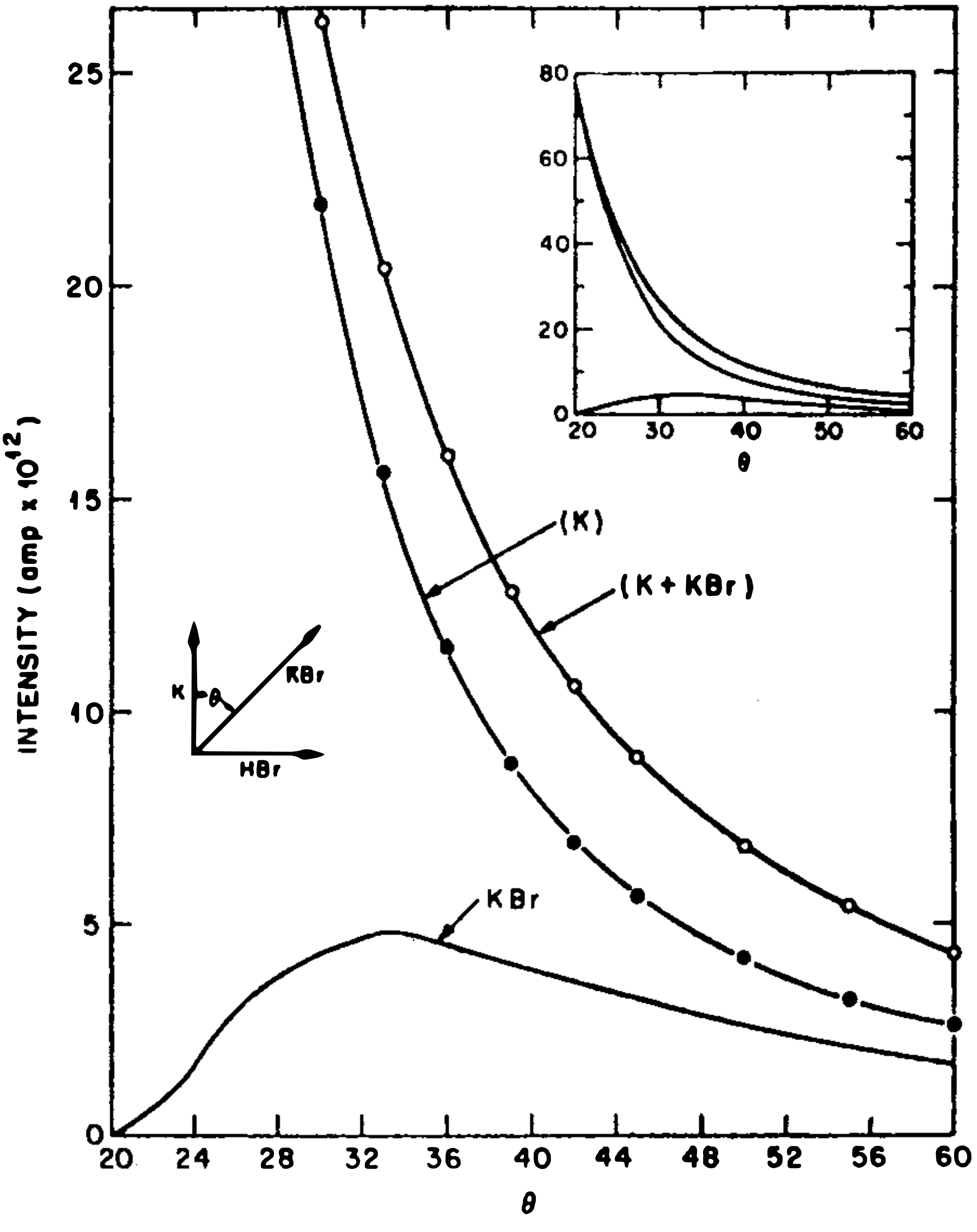

FIGURE 1-4 Typical experiment. The K + KBr signal measured directly on W detector. The K signal obtained from measurement on Pt and KBr signal by difference.

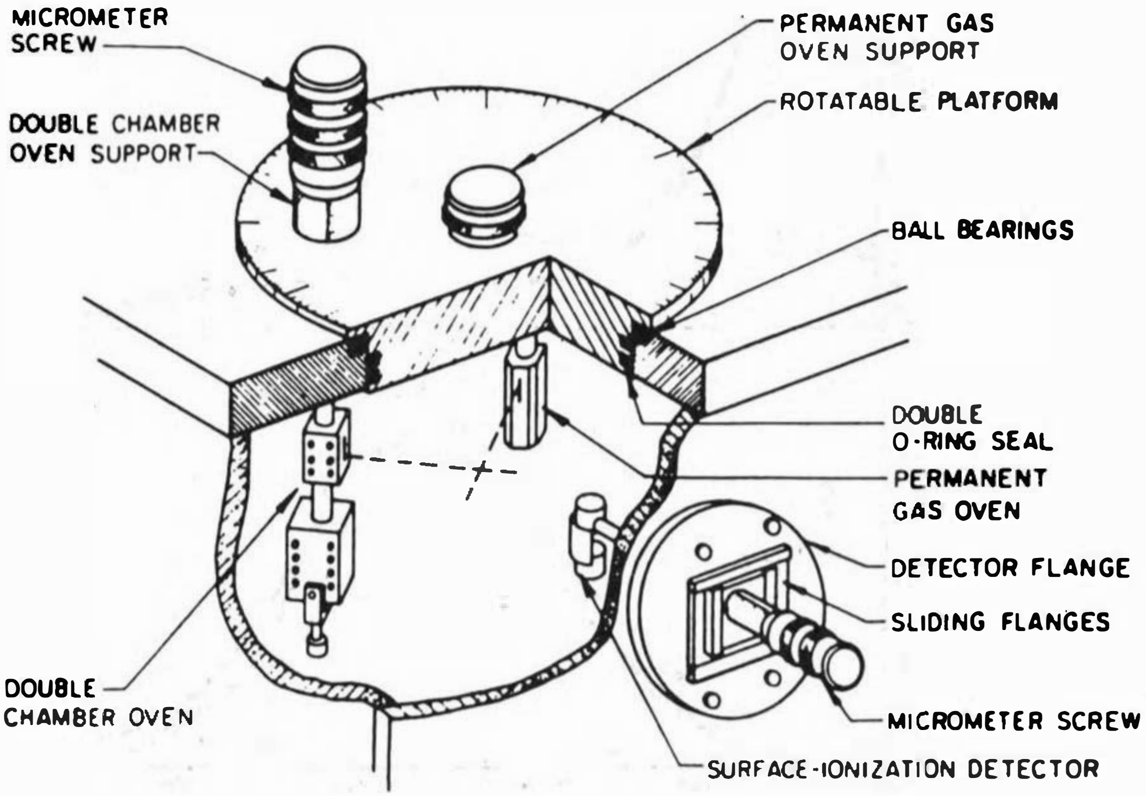

FIGURE 1-5 Schematic of the Bertha molecular beam apparatus, circa 1961.

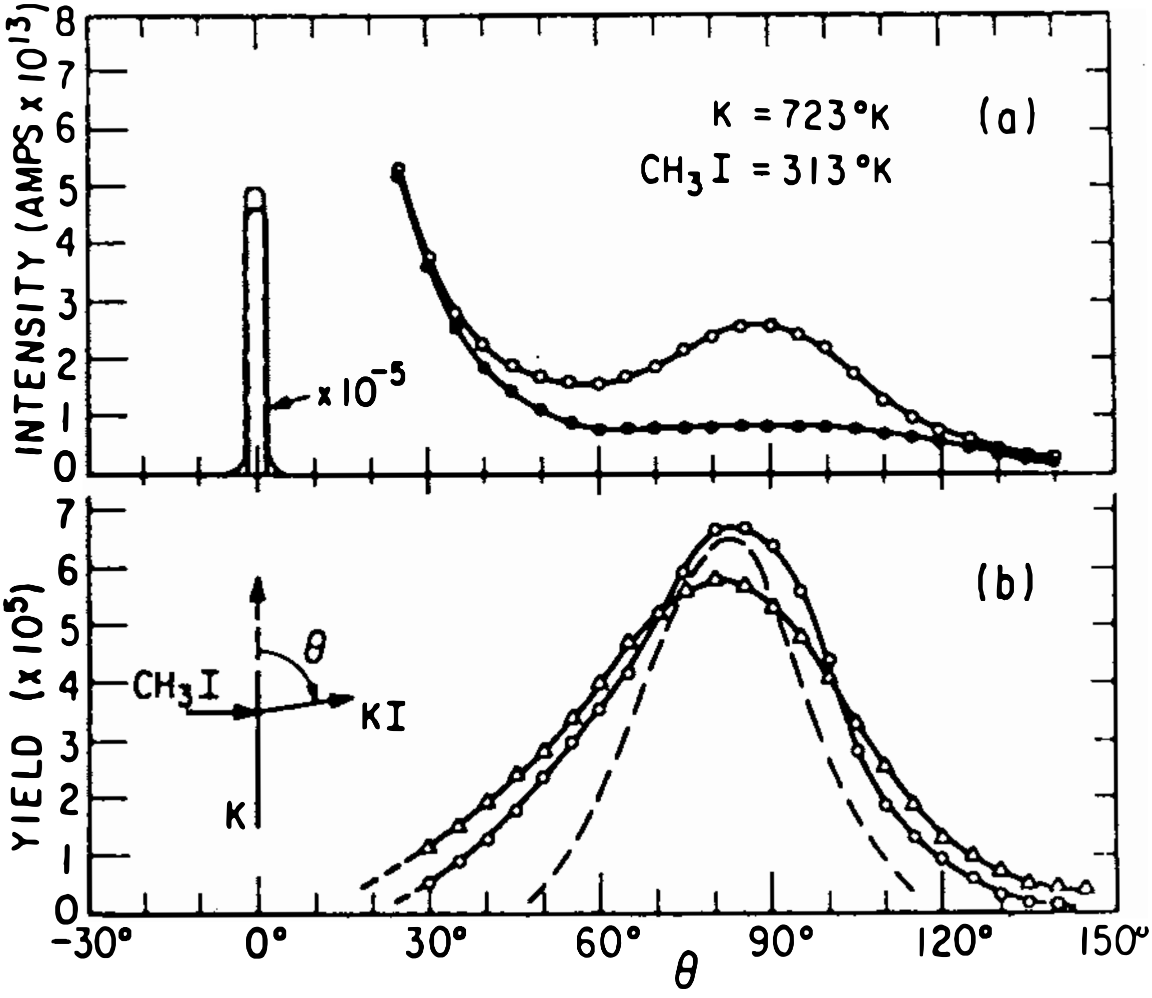

FIGURE 1-6 Result from Bertha: (a) open circles are from W detector, closed circles are from Pt detector; (b) some KI distributions.

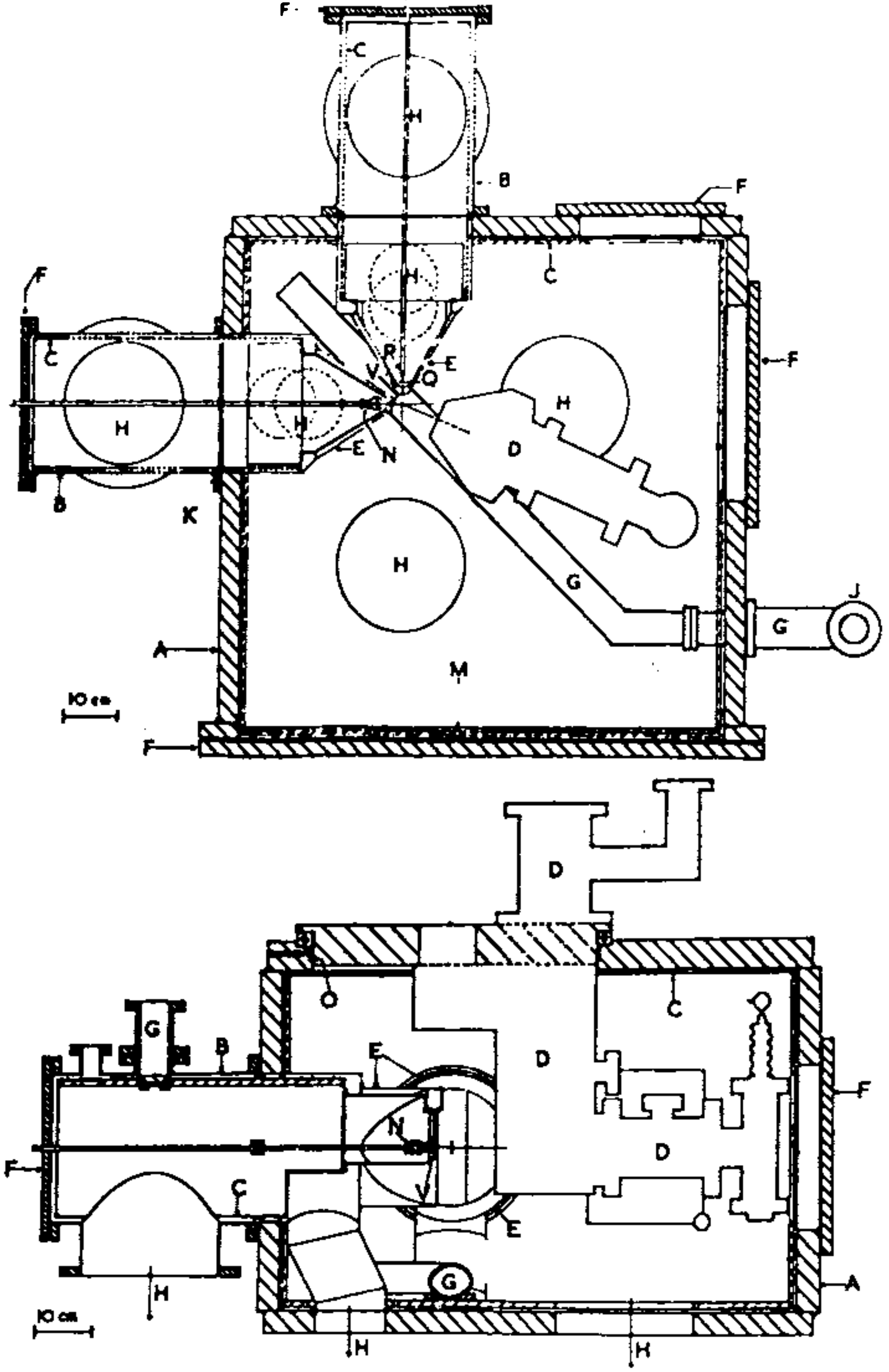

FIGURE 1-7 Universal molecular beam apparatus developed by Lee and coworkers circa 1969 (see ref. 18). Note particularly the scale of this equipment. (Some parts are D, detector UHV chamber; N, free radical source; P, nozzle source; Q, skimmer; V, beam chopper.)

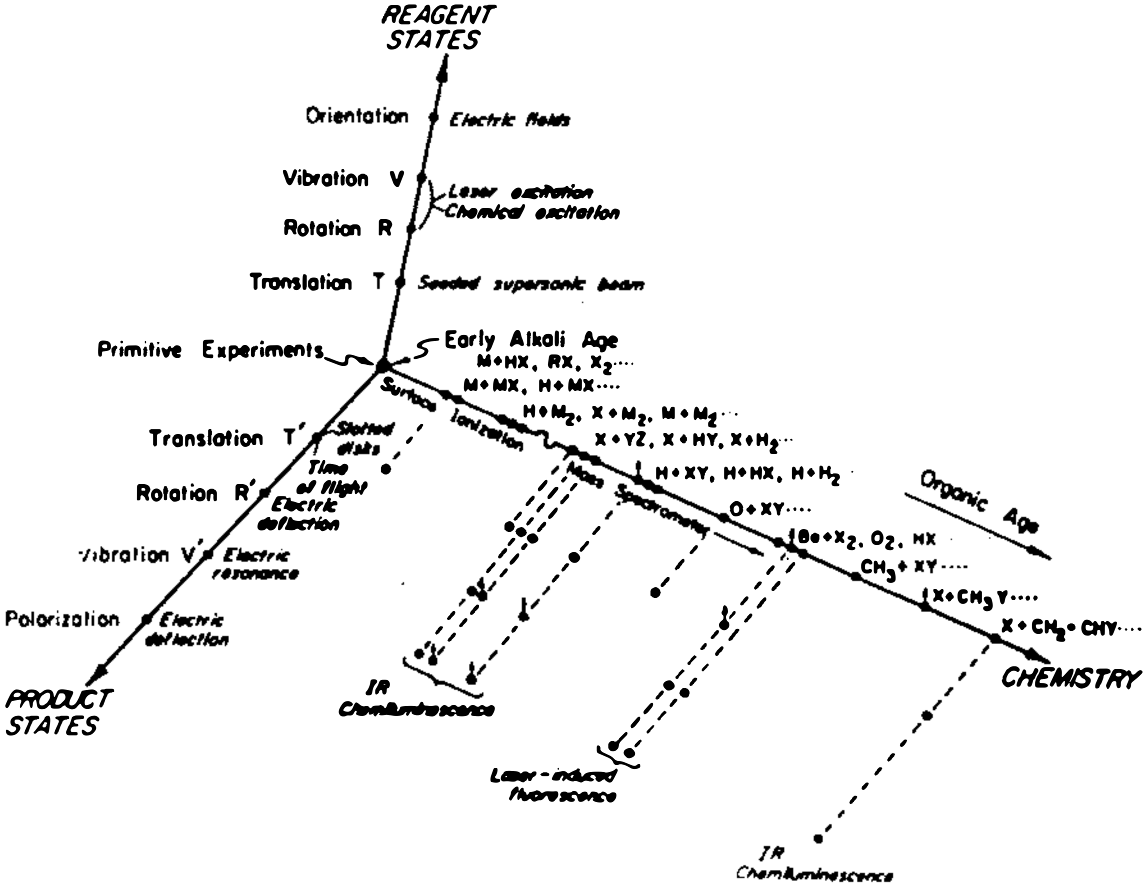

FIGURE 1-8 Domains accessible to molecular beam chemistry, circa 1973 (from ref. 2)).

2

DYNAMICS OF FEEBLE BONDS IN MOLECULAR COMPLEXES AND CLUSTERS

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Our workshop owes to Ellison Taylor and Sheldon Datz a fervent vote of thanks for their 1955 paper. As an impressionable graduate student, elated by that paper and convinced that a large class of alkali reactions could indeed be studied in crossed molecular beams, I was puzzled to find senior professors still dubious about the prospect. In retrospect, I realize that new approaches usually encounter attitudinal barriers. A myopic preoccupation with quick results is even more prevalent in research today. Let us hope that this workshop will encourage some youthful scientists (as well as funding agencies) to take a longer-range view of quixotic projects in pursuit of fundamental questions.

This paper fosters such a longer perspective by revisiting several studies that exemplify chief themes in the early development of cluster beam chemistry and now offer opportunities for much more incisive research. After praising virtues of supersonic beam and matrix isolation techniques, we consider two central questions: (1) How can weak van der Waals or hydrogen bonds facilitate or enhance control of the transformation of strong chemical bonds? (2) How are weak bonds broken or made when the chemical bonds in the linked molecules remain intact?

The Supersonic Boon: A New State of Matter

The key tool for cluster beam experiments is the supersonic nozzle. Its modern history began with a theoretical study by Kantrowitz and Grey in 1951, which focused on the intensity enhancement and velocity narrowing. Experiments attempted by Kistiakowsky and Slichter[1] to test the predictions were inconclusive and a miserable struggle, because of inadequate pumping speed. Legend has it that afterwards Kisty destroyed the apparatus with an ax! However, thereafter many chemical engineers took up the study of fluid flow in nozzles. John Fenn and Jim Anderson were particularly ardent evangelists for the use of supersonic beams in collision experiments, but there was a cultural gap to be bridged. At a 1965 ecumenical meeting: "The engineers spoke only to one another and only about Reynolds numbers; the chemists likewise talked just to each other about harpooning electrons."

Nowadays, the variety and scope of experiments performed with supersonic beams has transcended mere technique; such beams are aptly viewed as "a new state of matter," with special properties quite different from the old trinity of gas, liquid, and solid. The collisions occurring in the high pressure region of a supersonic nozzle organize the beam molecules to a remarkable extent. The emerging crowd of molecules thus may have mean separations of only 50 diameters, yet have nearly the same velocity and direction, and hence suffer almost no collisions. Likewise, the temperatures associated with relative translation and rotation of molecules within the beam are typically very low (of the order of 1 K or less), whereas the vibrational temperature can be kept high or made low by choice of conditions. Collisions during the expansion can also provide high or low translational energy if the gas of interest is "seeded" in a large excess of lighter or heavier diluent gas. Chemical reactions within the expanding jet are, in effect, freed from the second law, since in $\Delta H - T\Delta S$ the entropy factor is suppressed by virtue of the extremely low translational temperature for relative motion. This permits large mole fractions of molecular clusters to be readily generated.

Figure 2-1 offers a whimsical perspective on the vast realm of chemistry accessible with cluster beams. The ordinate scans dissociation energy, from chemical to van der Waals bonds. The abscissa gives the number of pairwise bonds that can be formed among N moieties. For ordinary chemistry, with $N \sim 100$, this number is only ~5000; for van der Waals chemistry, with $N \sim 5$ million, the number of pairwise bonds is roughly a billionfold larger. The amplification is vastly greater for clusters involving more than pairs of moieties. Of course, not all of these feebly-bonded complexes or clusters would be volatile enough, but, for a sizable fraction, beams can be made, since in fact rather low vapor pressure is sufficient. This exemplifies the theme (spoofing a movie title) of a celebrated talk by Richard Feynman: "There's lots of room at the bottom."

Several useful variants of seeded supersonic jets can now be obtained from nozzle designs suitable for solid or liquid substances,[2] for pulsed gas beams,[3] or for metals or other refractory materials sputtered by a pulsed laser.[4] In combination with laser or electron beam excitation or ionization, these versatile sources greatly enlarge the domain of cluster beam chemistry. The splinters from Kisty's ax have indeed sprouted into a bountiful garden.

Matrix Isolation: How to Freeze Harpooning Electrons

Before considering cluster beam experiments that exploit the special properties of supersonic beams, we discuss some work that merely uses beams to codeposit the requisite moieties in a low temperature rare-gas matrix. Much information about molecular complexes or fledgling clusters formed in this way has been obtained by vibrational or electronic spectroscopy. Here we note two prototypical studies that employed electron paramagnetic resonance spectroscopy to characterize the bonding of the odd, "harpooning" electron in triatomic reaction intermediates.

The first of these studies, carried out in the early 1970s by Derek Lindsay and Al Kwiram,[5] dealt with sodium trimers. At that time, it was still not clear whether such metal trimers or larger clusters were held together by chemical bonds or were merely van der Waals adducts. In 1967 Leckenby and Robbins had produced sodium clusters by a nozzle expansion and shown that, as the size of the cluster grows, the ionization potential decreases in an undulatory fashion towards the work function of the bulk metal. However, Milne and Greene had likewise generated argon clusters, which also exhibit a marked decrease in ionization potential, because removing an electron creates an open shell structure. Thus the nature of bonding in the neutral clusters could not be inferred because the ionization potential depends strongly on the stability of the ionized clusters.

The ESR spectrum revealed that the sodium trimer is chemically bonded. The spin density of the odd electron indicates that the molecule is bent and has isosceles symmetry. Lindsay and his students have recently completed similar ESR studies of several other alkali clusters.[6] The lithium trimer is found to be fluxional, as evidenced by pseudorotation, whereas the Li_7, Na_7, and K_7 clusters all have pentagonal bipyramidal geometry. In the same way, Weltner and coworkers[7] have now found the same structure for the Ag_7 cluster. These ESR studies have given us the only experimental information we have at present about the geometrical structures of metal clusters.

The second prototypical ESR experiment, also by Lindsay and Kwiram,[8] deals with the nature of the molecular orbital occupied by the odd electron in the K + HCl reaction complex. The link to Taylor and Datz is not coincidental. In the 1955 paper, they concluded that ". . . collisions with the H end of the HBr are more often fruitful than other configurations." At the time, such a conclusion seemed downright perverse; Kistiakowsky cited it as a reason to doubt the experiment.[9] Yet, about 15 years later, studies of many other reactions had led to a principle of *orbital asymmetry*, which predicts that, frequently, reactant atoms or radicals will attack the "wrong end" of a target molecule.[10] For the K + HCl case, the harpooning electron from the alkali enters a strongly antibonding sigma orbital of hydrogen chloride. As indicated in Figure 2-2, this orbital is mostly made up of the H atom 1s orbital, because the conjugate bonding sigma orbital is mostly comprised of the Cl atom 3s and $3p_z$ orbitals as a consequence of the much higher electronegativity of the halogen. Indeed, the ESR spectrum of the matrix isolated K + HCl complex shows that the unpaired spin resides in an antibonding sigma orbital, which has about 85% of its density located on the hydrogen atom. The absence of hyperfine splitting due to the alkali cation suggests that the likely geometry corresponds to a collinear K^+Cl^-H complex. Although the harpooning electron lands in an orbital mainly located on the wrong end, the H atom can readily pirouette to reach the "right" alignment.

Such ESR studies exploiting matrix isolation are feasible for a host of other clusters and intermediate reaction complexes that have unpaired electrons. The information about electronic and geometrical structures thus obtained would permit more comprehensive interpretation of the extensive results from supersonic beam experiments on metal clusters. That work, as conducted by Schumacher, Knight, Kaldor, Smalley, and many others, has provided a cornucopia of data concerning ionization potentials and reactivity variations among clusters, but correlations with structure are essential in order to reap a corresponding harvest of chemical understanding.

Extrinsic Dynamics of Strong Bonds Fostered by Weak Bonds

Next we review four experiments, all employing supersonic beams, that exemplify some major aspects of cluster chemistry. These display the role of van der Waals bonds as catalysts for facile chemical bond exchange reactions, chaperons for atom recombinations, promoters of solvation-induced reactions, and precursors limiting geometrical alignment in photochemical processes.

Unconventional Catalysis. Figure 2-3 illustrates the celebrated Woodward-Hoffmann orbital correlation diagrams for exchange of two or three electron-pair bonds between atoms of comparable electronegativity. For a four-electron, bimolecular reaction between two diatomic molecules, one of the doubly-occupied orbitals that is bonding for the reactants becomes antibonding for the products. Since this implies that the activation energy exceeds the product bond strength, the orbital anticorrelation predicts such four-center exchange reactions are "forbidden." In contrast, for a six-center, termolecular reaction among three diatomic molecules, the bonding orbitals for the reactants all remain bonding for the products; that implies a relatively low activation energy, so such six-center exchange reactions are "allowed." More generally, bond swapping reactions involving 4, 8, 12, . . . electrons are forbidden while those involving 6, 10, 14, . . . are allowed. As indicated in Figure 2-3, this topological consequence of orbital phase relations is actually isomorphous with the rule for seating guests at formal dinner parties. Whereas Woodward-Hoffmann deal with the disposition of electron-pairs, the analogous "Post-Vanderbilt" rule pertains to spouse-pairs and specifies that genders should alternate around the table.

This view of molecular etiquette led to a search for van der Waals catalysis. For fifty years or more, mixing bromine and chlorine in a bulb has been observed to readily form BrCl, although the mechanism has remained suspect because of "possible catalysis by moisture or surfaces," a traditional lament in kinetic studies. After finding that in a crossed beam experiment $Br_2 + Cl_2 \rightarrow 2BrCl$ did not go, even at high collision energies, we decided to look for $Br_2 + Cl_2 \cdots Cl_2 \rightarrow 2BrCl + Cl_2$. To overcome the hopeless entropic handicap of three crossed beams, we used van der Waals dimers generated by a supersonic expansion. Yet we expected there might still be a sizable activation barrier, perhaps even requiring vibrational excitation. Thus, we were startled to find that the dimer reaction apparently goes readily at thermal collision energies.[11] Velocity analysis data for this system and the analogous HI reaction with chlorine dimers provided several kinematic consistency tests, which also indicated that three sequential bond scissions can be resolved in the termolecular exchange process. A kindred example was soon found in an infrared chemiluminescence study,[12] in which F_2 + HI gave no HF emission, whereas $F_2 + (HI)_2$ gave intense emission. Whether or not these examples actually involve six-center transition states, the weak van der Waals bond is remarkably effective in promoting a reaction that otherwise does not go.

A large number of reactions are known that nominally involve bond exchanges among molecules (without obvious intervention of atoms or radicals). Often, like bromine + chlorine, these exhibit marked sensitivity to "wall effects." It is tempting to speculate that many such reactions may actually go by low activation energy pathways involving van der Waals dimers; when the gas-phase concentration of dimers is depleted, the reaction has to shift to the walls in search of more dimers.

Uncaging Chaperons. In solution kinetics, much attention has been devoted to photodissociation and recombination processes. These are usually interpreted in terms of the "cage effect," in which the solvent inhibits diffusive separation of the photofragments. The prototype example is photolysis of I_2 and geminate recombination of the I atoms. A different perspective has emerged from beam experiments.[13] Complexes of I_2 with various solvent species, such as Ar, N_2, benzene, etc., were formed by supersonic expansion and excited with a laser in a spectral region above the dissociation threshold for the bare I_2 molecule. This produced intense fluorescence, showing that, instead of dissociating, much of the I_2 relaxes into bound vibrational levels of the electronically excited state. Energy balance is maintained by breaking the van der Waals bond(s) of the original solvent complex and releasing some repulsion into relative translation of the product fragments. In solution, photodissociation must likewise be mollified by energy transfer to the solvent, and the surviving excited iodine molecules may account for features previously attributed to recombination of caged atoms.

The term *chaperon* may be unfamiliar in this context. I adopted this term in 1962, after hearing George Porter describe his classic study of gas-phase iodine atom recombination at a Faraday Discussion in Cambridge. Fred Kaufman objected: "A chaperon is someone who keeps labile species apart!" George gleefully responded: "On this side of the water, a chaperon promotes a stable union!" Indeed, that seems likely to be a typical role of van der Waals bonds.

This theme is strikingly illustrated in recent work by Ron Naaman and his students[14] on the "carbon monoxide flame," one of the historic systems of chemical kinetics. The key step involves chaperon-assisted union of an $O(^3P)$ atom with CO to produce an electronically excited CO_2 molecule. Naaman used a supersonic expansion to supply the CO with up to six or seven chaperons. With only one chaperon, he found the best choice to be another CO molecule. But when more than one chaperon is present, the rare gases prove better than more CO or polyatomic molecules. Too many chaperons inhibit the reaction. Both the physical and chemical mechanisms governing these variations remain to be elucidated, and many other important kinetic systems invite such exploratory studies.

Driving Reactions by Solvation. A related and typical category of cluster-promoted reactions is exemplified by ammonia + hydrogen halides. In the bulk, these reactions go readily. However, for unclustered ammonia, in gas-phase single collisions these reactions are endoergic at thermal kinetic energies. Proton transfer to form the ionic salt, $NH_4^+X^-$ is thermochemically unfavorable, increasingly so for $X = I \rightarrow Br \rightarrow Cl$. In crossed-beam scattering with clustered ammonia,[15] new mass peaks appear that correspond to $(NH_3)_nHX$ adducts with n as large as 15 or more. Fragmentation of these peaks appears to decrease markedly on completion of the first solvation shell. For sufficiently large clusters the adduct formation probably involves proton transfer and is driven by solvation of the resulting $NH_4^+X^-$ ion-pair by the "extra" ammonia molecules in the reactant cluster. Many reactions driven by solvation might be elucidated in this way.

Such reactions typically involve solvated ions, but in condensed phases the individual molecular species and processes often cannot be resolved or characterized. For instance, the elusive hydrated electron, invoked in a host of solution reactions, has long seemed enigmatic. In the gas phase, interaction of an electron with a single water molecule gives only simple scattering or dissociative attachment. Now the hydrated electron has been produced in beams of unfragmented water clusters.[16] Beam studies of molecular cluster ions thus are becoming another subject of major importance for chemistry.

Precursor Limited Reactant Geometry. An elegant and versatile new photochemical technique for studies of reaction dynamics exploits the mutual orientation of molecules in a van der Waals complex. Figure 2-4 portrays the case used by Buelow, Radhakrishnan, and Wittig[17] to introduce this technique. The BrH···OCO complex was formed in a supersonic expansion, and the hydrogen halide portion photolyzed to impel the H atom to attack the adjacent carbon dioxide molecule. The precursor complex is one of many whose structures have been determined by Klemperer and his students using electric resonance spectroscopy.[18] As indicated, the complex is hydrogen-bonded, and its equilibrium geometry is collinear. The floppy bond permits large-amplitude bending vibrations, however, so in the photolysis-induced "hot atom" reaction the incident H has a correspondingly broad range in impact parameter and initial angle of attack. The experimental results thus require deconvolution, but offer a new source of information about the dependence of reaction probability and product energy distributions on reactant orientation.

Several variants of this POP technique (photolysis of precursors) are being developed. By varying the photodissociation wavelength, the initial kinetic energy of the attacking atom can be scanned. By employing two wavelengths, one photon can inject the hot atom while the other excites the target molecule. By using wavelengths capable of electronic excitation but not photolysis, the orbital alignment of a reactant moiety relative to the target molecule axis can be varied. This option has been nicely demonstrated by Soep and his coworkers at Orsay,[19] by forming $Hg \cdots H_2$ complexes and exciting the Hg atom with a polarized laser. The product HgH shows marked changes in its rotational distribution as the alignment of the Hg atom p orbital is switched from end-on to the H_2 bond (σ-attack) to broadside (π-attack).

Augmenting POP with picosecond pulse techniques enables the time development of stereodynamical features to be explored, as recently shown by Bernstein, Zewail, and coworkers.[20] Using a picosecond laser to photodissociate the hydrogen iodide moiety in IH···OCO complexes and a second, delayed picosecond laser pulse to probe the OH product, they were able to clock the formation and decay of the reaction complex for $H + CO_2 \rightarrow HOCO \rightarrow OH + CO$. Since the first pulse establishes the zero of time for the bimolecular reaction, the real-time evolution of the asymptotic distributions in energy and orientation of product states can be observed. This has great portent for reaction dynamics.

Intrinsic Chemical Dynamics of Weak Bonds

Now, we consider two topics that involve breaking or making van der Waals bonds without disruption of the chemical bonds in the linked molecules. One topic emphasizes how durable a weak bond can be, even when vibrational excitation of an adjacent chemical bond renders the complex metastable. In contrast, the other topic deals with the impulsive, "billiard-ball" dynamics of the collisional exchange of van der Waals bonds.

Vibrational Predissociation of Complexes. The possibility that vibrationally excited van der Waals complexes might have extremely long lifetimes for predissociation was raised about a decade ago in theoretical studies, chiefly by Child, Jortner, and Ewing. An exploratory experiment[21] on inelastic energy transfer to chlorine dimers in collisions with Xe and other molecules indicated that vibrationally excited metastable dimers indeed survive long enough to travel to the detector, which implies a lifetime longer than about 10^{-4} sec. Without attempting to summarize many subsequent experiments and calculations, we note here recent lifetime results obtained by Roger Miller[22] from infrared linewidths of HF complexed in supersonic expansions with eight different partners. For the complexes with Ar and Kr, he got a lower bound of 3×10^{-4} sec by using a bolometer detector to confirm that vibrationally excited complexes reached the detector. For other complexes, he found values ranging from about 2×10^{-9} sec (HF with CO or acetylene or ethylene) to about 5×10^{-8} sec (HF with N_2 or H_2). For the HF···HF dimer, he found two quite distinct lifetimes; that for excitation of the moiety containing the hydrogen-bonded H is short, about 1×10^{-9} sec; that for excitation of the other HF moiety is about 25 times longer.

Figure 2-5 shows a simple model[23] for predissociation lifetimes of vibrationally excited complexes. Much more sophisticated treatments are available, but this simple model serves to emphasize heuristic aspects. The Ar···HCl complex is the archetype for theory, because it was Klemperer's choice for his first structural studies. In effect, the Ar is nearly free except when it collides with HCl at the inner turning point of each oscillation in the shallow van der Waals well. This suggests that the predissociation lifetime t might be at least qualitatively related to the transition probabilities for vibrational-to-translational energy transfer from the HCl molecule. These probabilities are customarily specified by Z_{10}, the average number of gas-kinetic collisions required to deactivate a molecule from the first excited to the ground vibrational state. Accordingly, we take $\tau = Z_{10}\tau_0$, where $\tau_0 \simeq 10^{-12\pm1}$ sec represents the duration of a collision. This should give a lower limit for τ, since for a complex the inner turning point that produces the "collision" occurs at a lower and less repulsive region of the intermolecular potential than for collisions of free Ar with HCl. As seen in Figure 2-5, estimates obtained in this way from vibrational relaxation data indicate that an extremely wide variation in the magnitude and temperature dependence of predissociation lifetimes can be expected. It is gratifying that this simple model correctly predicts τ for Ar···HCl to be about a million-fold longer than for the HF dimer. For such processes, feeble bonds by no means behave alike!

Collisional Exchange of van der Waals Bonds. Since thermal kinetic energies are ordinarily several times larger than the dissociation energies of weak van der Waals bonds, for a typical system like Xe + Ar_2 the main outcome is simply collision-induced dissociation of the dimer bond. Nevertheless, crossed-beam reactive scattering experiments to characterize the smaller yield of exchange products XeAr + Ar are feasible. Figure 2-6 shows an angle-velocity contour map obtained by Worsnop and Buelow[24] for this reaction. Conservation of energy and momentum constrain the scattered diatom product to a narrow circular band centered on the center-of-mass velocity; only within that band can XeAr be formed with low enough internal (rotational + vibrational) excitation to hang together. However, several other features provide dynamical information. These include the pronounced "hole" in the reactive scattering in the forward direction, which is accompanied by strong peaking near 50°, and an even stronger backward scattering.

This pattern is remarkably similar to that found for some ion-molecule reactions, such as the $O^+ + HD \rightarrow OH^+ + D$ reaction, for which the collision energies and bond strengths are more than a hundredfold higher. As illustrated in Figure 2-6, several properties prove to be in nearly quantitative agreement with an impulsive model based on pairwise hard sphere interactions. Two distinct collision modes give the chief contributions. In the mode that accounts for the forward pitched scattering, A + BC interact via *sequential* hard sphere elastic collisions (A off B, then B off C); the exchange reaction occurs only when the final relative velocity of A and B corresponds to an energy less than the AB bond strength. For this mode, the angular distribution may be found from a geometric construction devised by Mahan for high energy ion-molecule reactions.[25] The other mode gives strong backward scattering by a process familiar in billiards; A *knocks out* B and thereby comes nearly to rest with respect to the C atom, so the resulting AC molecule moves briskly backward with respect to the center-of-mass. This study of the exchange of feeble bonds thus helped develop a more comprehensive asymptotic model applicable to any atom transfer reaction when the ratio of collision energy to bond strength becomes large. Looking at "the bottom" can give new insight about "the top" of chemical dynamics.

Impulsive dynamics does not account for all features of these exchange reactions, however. Comparing the velocity distribution of the product XeAr with that for elastic scattering reveals an appreciable yield of dimers with rotational + vibrational excitation that exceeds the bond strength. These are attributed to metastable complexes, in which dissociation is inhibited by centrifugal barriers. This can account for metastable lifetimes exceeding the flight time, because tunnelling through these barriers is exceedingly slow. Again, a weak bond can be surprisingly persistent.

As evidenced in the papers to follow at this workshop, and in other such clusters emerging from several recent conferences,[26] feeble bonds now form a multifaceted and extremely lively frontier of chemical physics.

Acknowledgements

With pleasure I thank colleagues near and far who performed the experiments reviewed here and gratefully acknowledge support of our current Harvard work by the National Science Foundation.

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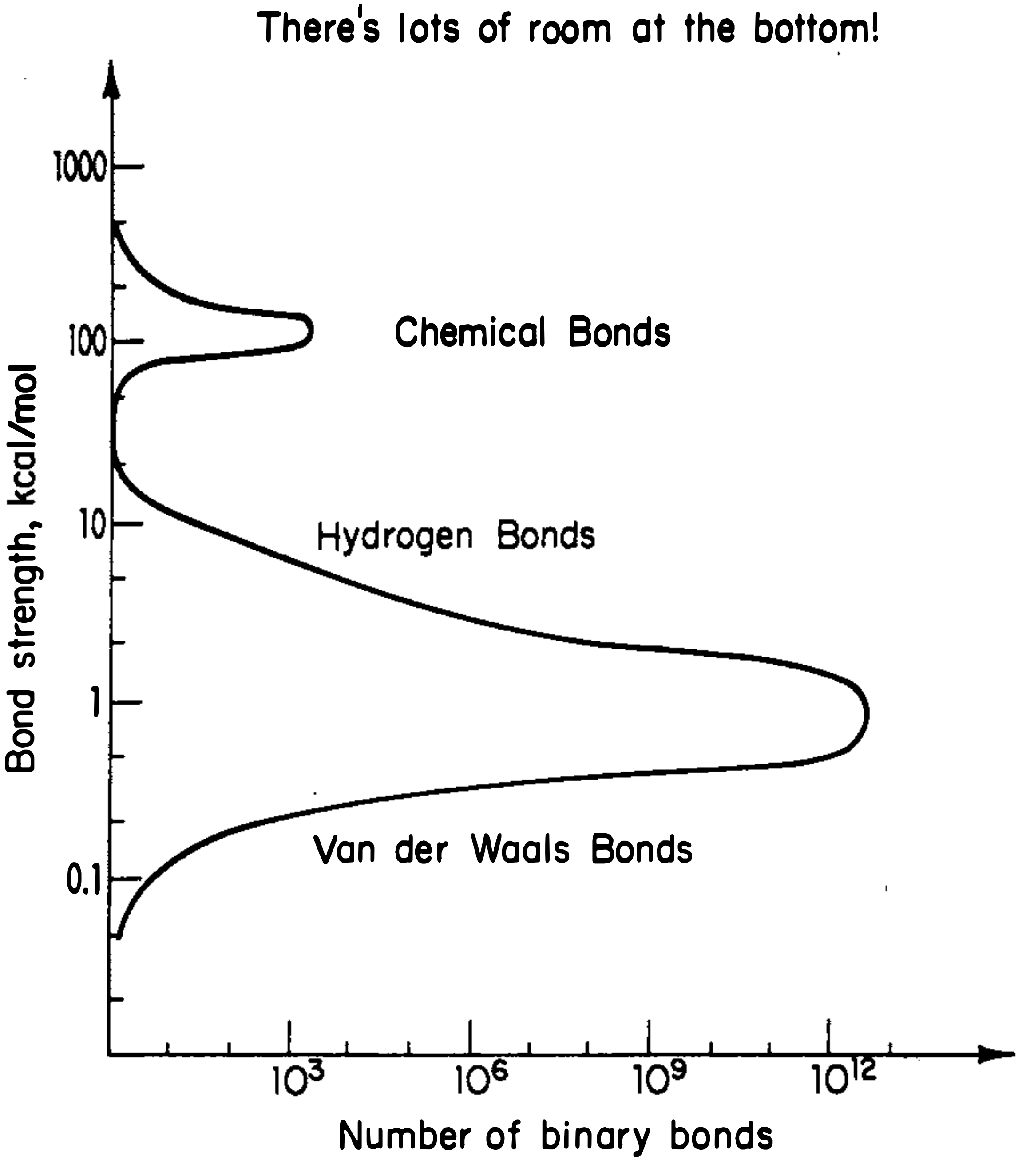

FIGURE 2-1 Distribution of pairwise bonds in strong (chemical) and weak (van der Waals or hydrogen bond) domains. For N moieties, the number of pairwise bonds is given by N(N-1)/2.

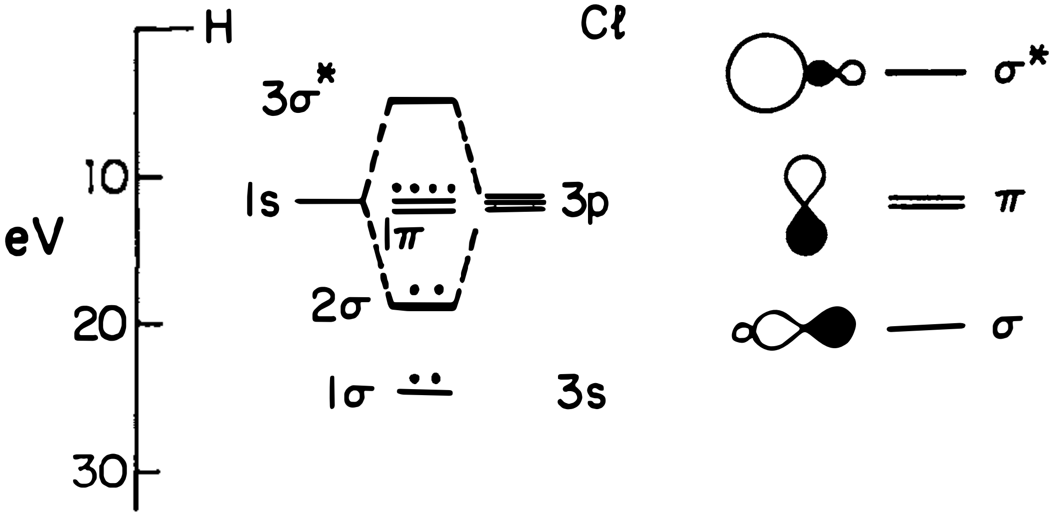

FIGURE 2-2 Qualitative molecular orbital diagram for HCl, indicating asymmetric composition of valence orbitals. Chlorine atom is dominant in the bonding sigma (1σ and 2σ) and nonbonding pi (1π) orbitals and hydrogen atom in the strongly antibonding sigma orbital (3σ).

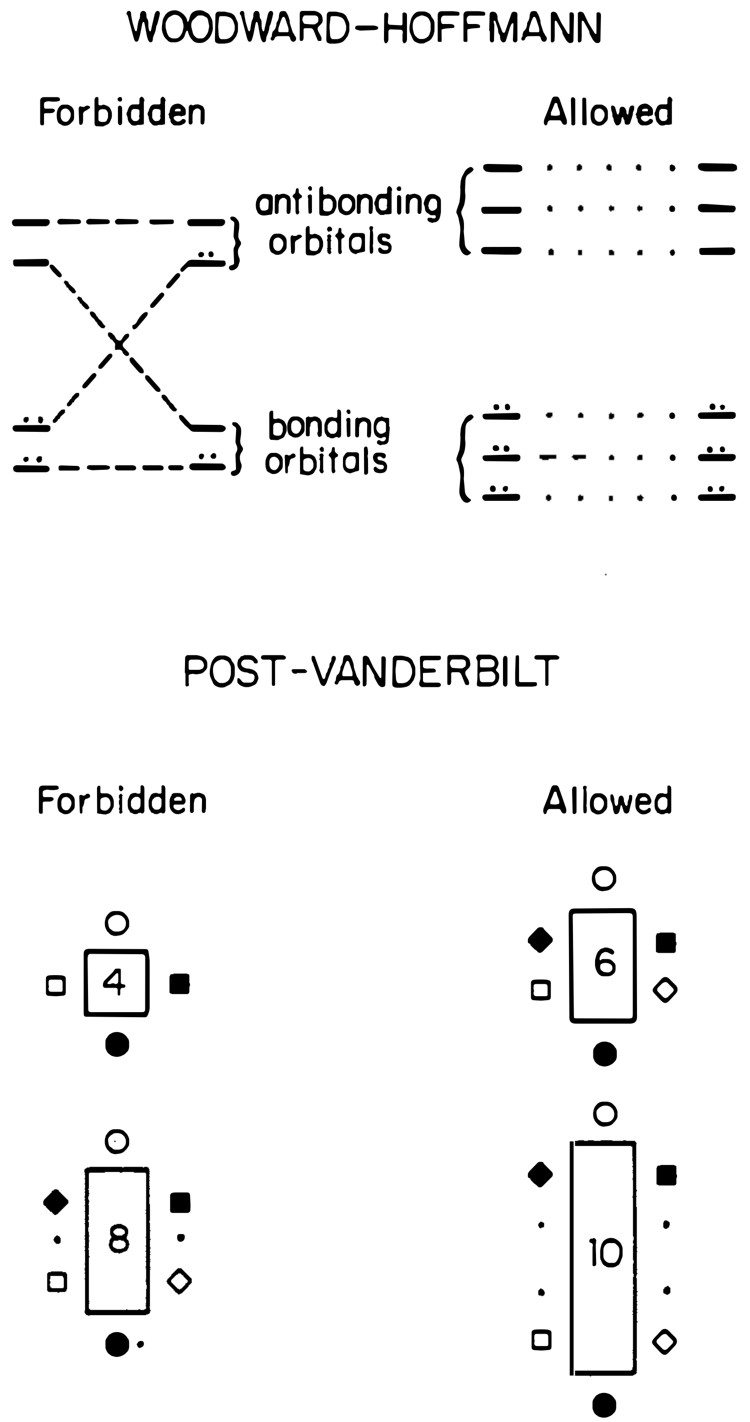

FIGURE 2-3 Schematic Woodward-Hoffmann molecular orbital correlation diagrams for archetypal *forbidden* (four-center) and *allowed* (six-center) electron-pair bond exchange reactions (upper panel) and Post-Vanderbilt seating diagrams for spouse-pairs at formal dinner parties (lower panel).

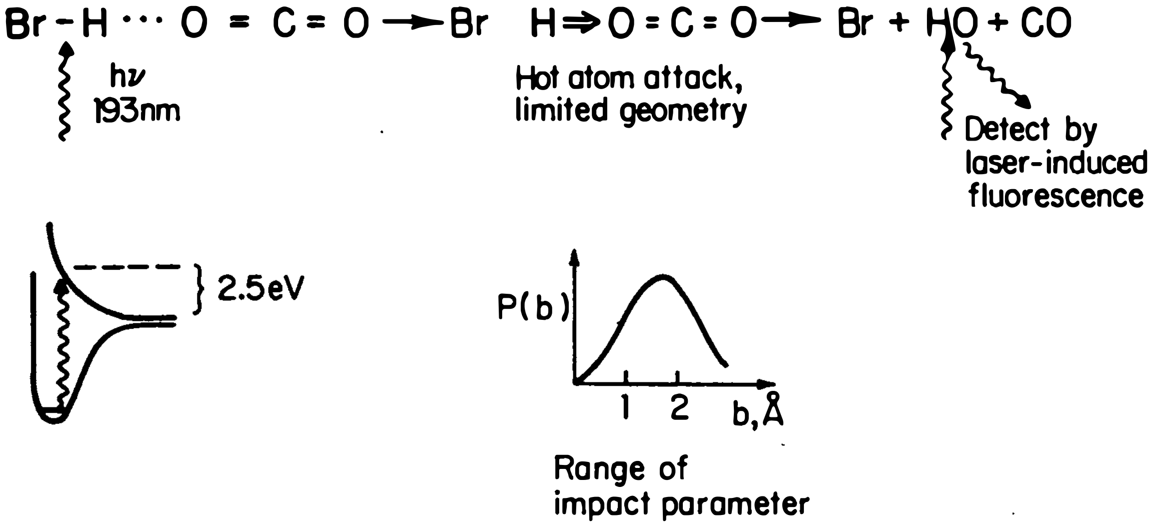

FIGURE 2-4 Experimental design for POP technique employing photolysis of precursor complex to study stereochemical dynamics of H + OCO reaction.

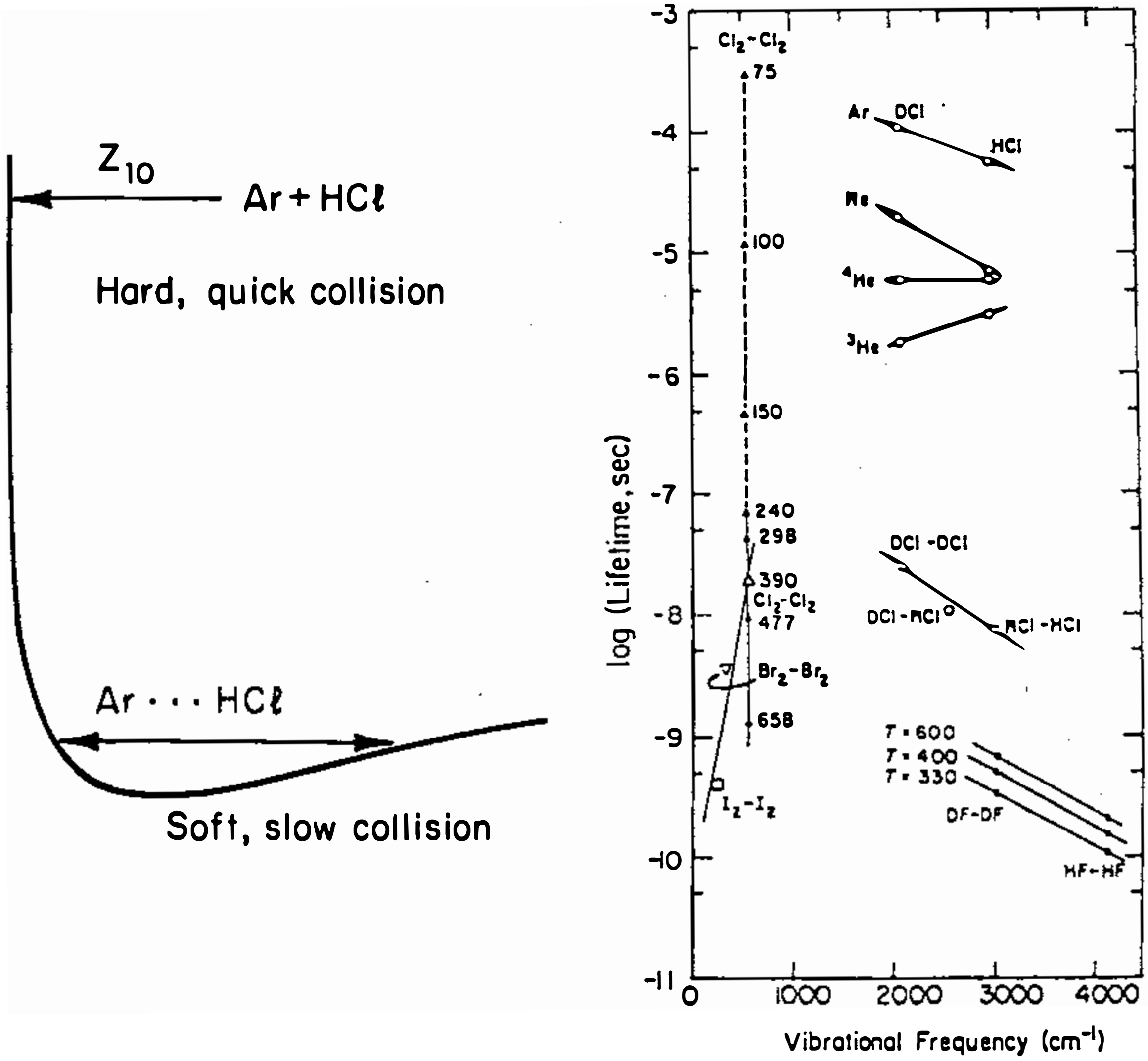

FIGURE 2-5 Model for vibrational energy transfer between free Ar + HCl or complexed Ar···HCl (at left). Estimates of vibrational predissociation lifetimes derived from model (with $\tau_0 = 10^{-12}$ sec, see text) versus vibrational frequency of the diatomic moiety (at left, from Ref. 23).

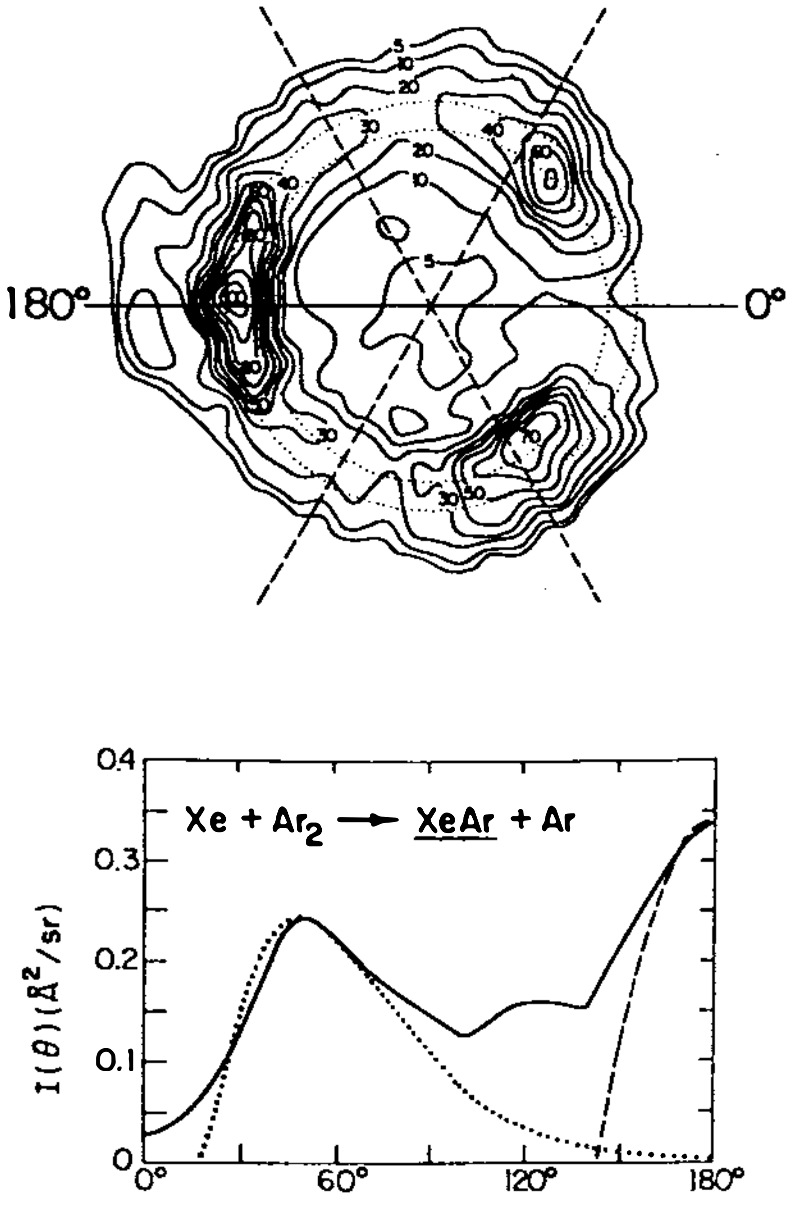

FIGURE 2-6 Angle-velocity contour map for XeAr from Xe + Ar_2 reaction at collision energy of 1.3 kcal/mol. The dotted circular band shows the kinematically allowed scattering region for nominal parent beam velocities. At right angular distribution derived from experimental map (solid curve) is compared with predictions from the hard-sphere model, including *knock-out* (dashed curve) and *sequential impulse* (dotted curve) contributions.

3

PROBING THE DYNAMICS OF GAS-SURFACE INTERACTIONS

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Introduction

With the development over the last two decades of techniques for reproducibly preparing and determining static properties of surfaces in ultrahigh vacuum, it has become possible to apply many of the techniques of gas-phase chemical dynamics to study the dynamics of gas-surface interactions.[1] Molecular beam and laser techniques have enjoyed a spectacular success in elucidating the important features of the dynamics of atomic and molecular interactions in the gas phase. Perhaps nothing better symbolizes this success than the award of the 1986 Nobel prize in chemistry to three of the leaders in this field, Dudley Herschbach, Yuan Lee, and John Polanyi. It is thus a particular pleasure to present a review of some of the recent developments in analogous gas-surface interactions studies in this workshop in which Dudley Herschbach and Yuan Lee are also presenting papers.

There are strong motivations for applying these techniques, which have been so successful in gas-phase studies to the study of gas-surface interactions. Many of the issues we face in gas-surface interactions have close analogs in the gas phase. We are interested in understanding the energy requirements of chemical processes on surfaces; questions such as what is the nature of activation barriers and how can various forms of energy be utilized in overcoming them. Likewise we are interested in questions of energy transfer and energy disposal in elementary processes on surfaces. What are the important energy transfer channels? How is the energy of chemical processes partitioned among the available channels such as rotational, vibrational or electronic excitation of the molecules involved and phonons and electronic excitation of the substrate. Since molecular beam and laser techniques provide means for controlling the initial state and probing the final state of many important dynamical variables, they have great potential to provide insight into these questions.

Having stressed the similarities of the issues of gas-phase chemical dynamics to those of gas-surface chemical dynamics, it is also important to mention a crucial difference that has important implications for the kinds of experimental studies that are necessary to understand the surface case. The target in a gas-surface scattering experiment is a many particle system. In general the only knowledge we have of the state of this system is its structure and temperature. Thus in gas-surface interactions we are potentially dealing with a complicated sequence of processes. An important goal of research in this area is thus to distinguish experimentally the various processes involved so they may be isolated and studied individually. As we will see, beam methods are providing powerful new insights into these questions.

In addition to the purely scientific motivations, studies of gas-surface interactions are strongly motivated by important applications. In the microelectronics industry, many important materials and processing issues rest on a knowledge of gas-surface interactions. These include etching of semiconductor devices, deposition of materials for semiconductor devices, as well as issues of etching and deposition for packaging applications. The miniaturization of integrated circuits, which has been so crucial to the reduction of costs, improvement of function, and wide ranging applicability of micro-computers literally would not have been possible without these advanced processing techniques. The understanding of gas-surface interactions are of importance in applications ranging from catalysis to corrosion, and from aerodynamic drag to flying heads in disk files.

A wide variety of measurements are used to gain information on the dynamics of gas-surface interactions. As the experimental art has advanced, measurements have been developed to separate and study the various channels that are involved. It is useful to classify these methods in a hierarchy based on how many dynamical variables they determine and to understand the ambiguities of interpretation, which are removed as we move up this hierarchy. We begin with a brief discussion of experimental methods. Next, we turn to the study of energy transfer at surfaces, discussing in turn differential cross sections (angular distributions), double differential cross sections (velocity distributions or internal state distributions at a given angle), and triple differential cross sections (velocity distributions for a given angle and internal state). An understanding of energy transfer is a prerequisite to understanding sticking and reactive events on surfaces. In the last section, we turn to a brief discussion of beam studies of the simplest surface reactions--dissociative chemisorption.

Experimental Methods

The basic concepts of the application of molecular beam techniques to the study of the dynamics of gas-surface interactions are very simple. A beam of atoms or molecules in a well-defined initial state is incident on a well-defined surface, and the residence time, angle, velocity, and internal state distributions of the particles leaving the surface are measured. The elements of an experiment thus include beam preparation, beam modulation, sample temperature and incidence angle control, and product detection. An example molecular beam instrument designed for such experiments is shown in Figure 3-1. The beam source (BS) is of the supersonic type, which yields a beam of high flux and narrow velocity distribution. The beam is collimated by a series of skimmers and apertures and pumped by four stages of differential pumping (via pumps Pl . . . P4) to reduce background loading on the scattering chamber to negligible values. A chopper (C) allows for the generation of narrow pulses, and flags (Fl and F2) allow the beam dose to be accurately controlled. By variation of source temperature and gas mixture (seeded beam technique), the energy of the incident beam can be controlled over a wide range. For molecules, some separate control over vibrational and translational energy of the beam is possible by manipulation of source conditions.

The two key angles in a scattering experiment are the initial and final polar scattering angles. These angles are controlled independently by mounting the target and detector on separate rotating platforms sealed with spring loaded teflon seals.[2] The application of teflon seals to provide rotating flanges for UHV operation is an important innovation in surface scattering instruments. It allows for the introduction of differentially pumped detectors and simplifies cryogenic cooling, heating of targets, and the accurate control of sample and detector angles.

The detector shown in Figure 3-1 is a quadrupole mass spectrometer (QMS) with two stages of differential pumping to reduce background. By measurement of the arrival time distribution relative to opening time of the chopper (C), velocity or residence time distributions can be measured. For state-specific detection experiments, the QMS detector is replaced by a detection scheme based on laser spectroscopy. This can be laser-induced fluorescence (LIF) or multi-photon ionization (MPI).

In addition to control of incidence conditions and measurements of scattered particle distributions, control, cleaning, and characterization of the surface are very important in these experiments. As shown in Figure 3-1, some common surface science techniques are available in the molecular beam scattering instrument. The base pressure in the scattering chamber is ~ 2 x 10^{-11} Torr.

Angular Distributions

Angular distributions are the simplest measurements of those discussed here. Since particles of all velocities and all internal states are measured, the signal to noise ratio is larger for angular distribution measurements than for measurements that determine other dynamical variables as well; thus historically angular distributions were the first kinds of measurements to be used for the study of surface scattering.

Figure 3-2 illustrates the in-plane angular distribution of Ar scattering from Pt(111)[3] at a variety of surface temperatures. Ar is seen to scatter in a broad lobe centered near the specular direction. As the surface temperature is increased, the angular distribution broadens. By careful systematic variation of surface temperature and beam energy, it was shown that these distributions result from direct inelastic scattering of the Ar from the Pt surface; they are quite typical of scattering from low index planes of metal surfaces. At higher surface temperatures, the broader angular distributions result from increased surface-atom thermal motion.

Although angular distributions provide a quick way to gain information about the inelasticity involved in a given molecule-surface interaction, there are severe problems in quantitative interpretation because the angular distribution has important contributions from several sources: (1) momentum transfer perpendicular to the surface, (2) momentum transfer parallel to the surface, (3) static corrugation of the gas-surface interaction potential, (4) dynamic corrugation resulting from motion of surface atoms, and (5) the degree of surface regularity, and freedom from contamination and defects. Only if we assume a flat surface and parallel momentum conservation is there a one-to-one relationship between scattering angle and final energy. This assumption is not rigorously valid in any case, but in favorable cases (e.g., rare gas scattering from metal surfaces) the transfer of perpendicular momentum may dominate, and hence the angular distribution will yield information on energy transfer.

Velocity Distributions

Measurements of velocity distributions are required to resolve the ambiguities inherent in the interpretation of angular distributions. At a given angle, velocity distributions are determined and thus distributions of perpendicular and parallel momentum are directly measured. The effect of corrugation can be studied by systematic variation of beam energy and surface temperature.

Velocity distributions can also be used[4] to separate the scattering into two important channels: direct inelastic scattering and trapping followed by desorption, as illustrated in Figure 3-3. Shown are time-of-flight spectra for Xe scattering from Pt(111) at various scattering angles. Curve (b), measured in a direction normal to the surface, is a Boltzmann distribution at the surface temperature. Its peak position did not change when the incidence velocity was changed, demonstrating directly that it arises from trapping and consequent loss of memory of the initial conditions. Curve (c), measured at an angle of 45° from the normal to the surface, shows two peaks, one of which is the Boltzmann distribution and the other arising from direct inelastic scattering. Curve (d), measured at the specular angle, shows a much stronger direct inelastic peak (because this channel peaks near specular) and a weak trapping desorption peak. For the case shown here, the separation of direct inelastic and trapping desorption scattering is very clear. However under different conditions it is possible for the velocity distributions from these two channels to overlap making a clear separation difficult. Nonetheless it has been possible to use the velocity distributions to learn about trapping even in these cases.[5]

The separation of scattering into two distinct channels allows the direct inelastic scattering to be characterized. A good example is found[3] in the work of Hurst et al., who report a detailed study of the direct inelastic scattering of Ar from Pt(111) over a wide range of surface temperatures and incident beam energies and angles; the normal kinetic energy range extended from 1.7 meV to 1.7 eV, and the surface temperature from 90 to 900 K. A novel analysis of the angular and velocity distributions allows the scattering process to be experimentally resolved into the three natural physical directions of the problem: normal to the surface (z), parallel to the surface and in the scattering plane(y), and parallel to the surface and perpendicular to the scattering plane(x). This is done by using the angular and velocity distribution measurements to construct isoflux contour maps in cartesian velocity space. A typical result is shown in Figure 3-4 for 0.094 eV and 0.34 eV Ar incident at an angle of incidence of 45° on Pt(111) at 500 K. From such isoflux contour maps we see that there is a much larger variance in the component of the velocity of the scattered particles normal to the surface than along the parallel directions. The energy accommodation is found to be much larger in the z (normal) direction than in the y direction.

Molecular Scattering--State Resolved Measurements

The study of energy transfer for molecules scattering from surfaces presents new difficulties, since the internal energy states of the molecule must also be considered. The result is that new ambiguities are introduced, and angular and velocity distributions no longer suffice to fully define the problem. For example, Asada[6] reported the scattering of N_2, O_2, NO, CO, CO_2 and CH_4 molecules from Ag(111). Broad lobular angular scattering patterns were observed with no hint of state resolved features. From such curves alone, it is hard to say anything in detail about the excitation of internal energy. While velocity distributions provide more information they do not remove all the ambiguities of interpretation if internal states play an important role. Velocity distributions let us measure unambiguously the final kinetic energy. We can then write an energy conservation equation:

$$E_i^{kin} + E_i^{rot} + E_i^{vib} + E_i^{el} = E_f^{kin} + E_f^{rot} + E_f^{vib} + E_f^{el} + \Delta E^{phonons} \qquad (1)$$

where the subscripts i and f refer to initial and final conditions and E^{kin} is the kinetic energy, E^{rot} the rotational energy, E^{vib} the vibrational energy and E^{el} the electronic energy. For atoms, rotational and vibrational states do not exist and the electronic states are often not accessible. Thus for atoms we can use the energy balance equation (1) to determine the energy transfer to phonons. For molecules, on the other hand, even velocity distributions do not provide sufficient information.

To fully study the partitioning of energy and momentum into all the channels expressed in equation (1), complete preparation of the initial state and measurement of the final state is required. Such state-to-state measurements have been done for vibrationally excited molecules.[7] A reasonable approximation is realized by using a supersonic beam for initial state preparation and laser spectroscopic methods with time-of-flight analysis for final state detection. The initial state is then approximately the ground state, and the final state and velocity distributions are measured. Such state resolved scattering at surfaces has been studied for relatively few systems, of which, one of the most thoroughly studied is NO scattering from Ag(111).[8-17]

Figure 3-5 shows the rotational state distributions for NO scattering specularly from Ag(111) at incident normal energies of $E_n = 0.19$ eV to 0.93 eV with $T_g = 650$ K.[9] The figure shows a plot of $\ln(N_J/(2J + 1))$ versus internal energy; on such a plot a distribution of Boltzmann form would appear as a straight line with slope inversely proportional to the apparent rotational temperature T_R. Clearly sharp departures from a Boltzmann distribution are observed for large J; at higher values of E_n, a broad maximum appears that is attributed to the rotational rainbow effect. Such rainbows are well-described in gas-phase systems,[18] and the high-energy rainbow here arises because the degree of rotational excitation passes through a maximum as the orientation angle, γ, of the molecule with respect to the surface varies from 0 to 90°, both of which lead to zero excitation. In general, rotational rainbows occur when the Jacobian $(dJ/d\gamma)^{-1}$ blows up at extrema in $J(\gamma)$, leading to classical singularities in the differential cross section.

In addition to measuring the populations of various rotational states, LIF detection allows one to measure some properties of the alignment distribution of the angular momentum vector **J**. This is done by varying the polarization of the incident laser, detecting the polarization of the fluorescence, or both. Measurements of the variation of LIF intensity[12] with the angle θ_0 of the laser polarization to the surface normal are shown in Figure 3-6. Careful analysis of corrections for molecular effects indicates the polarization is indeed almost perfect[14].

Simultaneous measurements of velocity and state distribution are possible. This is accomplished using MPI detection either by measuring the time of flight of the ions created in a field free region[20] or by varying the time delay between the chopper open time and laser firing time to determine the time-of-flight of neutrals.[17] For NO scattering from Ag(111), a very strong anticorrelation is observed between the amount of energy going into phonons and that going into rotational excitation.[17] This anticorrelation is expected to be quite a general feature of energy transfer involving phonons and internal modes of molecules and thus has important implications to the understanding of trapping and sticking probabilities.

Dissociative Chemisorption

Dissociative chemisorption is the starting point for most surface chemistry. For a diatomic molecule, this elementary step involves breaking only one internuclear bond and forming two new ones to the substrate. However, the molecular dynamics of even this simplest example of surface chemistry are currently only poorly understood. This reflects both the complex nature of condensed phase chemistry and the fact that there have been only relatively few dynamical studies of such reactions. Many gas-surface systems have such a barrier, with the result that dissociation is often the rate-determining step in important reactions. Variation of the incidence translational energy permits this activation barrier to be probed rather directly and can provide insight into the dynamics of the activation process. For example, such studies have revealed that this barrier is often approximately one-dimensional, but not always so.[21]

Figure 3-7 displays the variation of the dissociative chemisorption probability with incidence energy for N_2, O_2 and CH_4 on a clean W<110> surface at normal incidence and a surface temperature of 800 K. It is clear that translational energy can be highly efficient in promoting chemisorption.[22-28] The dissociative chemisorption probabilities are seen to approach unity with increasing translational energy. While great differences are observed in the sticking probabilities for energies of ~0.1 eV, the behavior above ~1.0 eV is much more uniform. This behavior may be quantitatively different for other surfaces and gases, but it is likely that similar trends will apply to most systems which are unreactive at low energies. It is worth noting at this point that although the data are generally found to scale with the "normal kinetic energy," $E_n = E_i \cos^2\theta_i$, this is not the case for the HD and N_2 curves. In particular the N_2/W<110> system is found to scale quite accurately with the total kinetic energy, E_i. This is a good illustration of the complexities that may be encountered in reactive systems and should serve as a warning against over-simplistic interpretation.

Translational energy studies can also be of value in helping to elucidate the detailed mechanism of the chemisorption process. Most previous work has been discussed in terms of two mechanisms. In a number of cases there appears to be good evidence that dissociative chemisorption proceeds by way of a mobile-precursor mechanism,[29-33] while in other systems a direct mechanism seems more appropriate.[27,34] In the precursor model, the molecule loses sufficient incident translational energy upon collision to become trapped, or physisorbed, in a "precursor state," becoming accommodated to the surface temperature. The molecule remains in this state until it reorients into a favorable configuration or diffuses onto a favorable geometrical site for dissociation. Alternatively the molecule may desorb from the surface or remain in a molecular chemisorbed state. In the case of a direct mechanism, dissociation is pictured to occur upon essentially a single impact with the surface, provided the molecule possesses sufficient energy to surmount any activation barriers that may exist. The translational energy dependence of the chemisorption probability is reversed for these two mechanisms. Trapping into a weak molecularly bound state is expected to become increasingly inefficient as the collision energy is raised, so that reactions proceeding via a mobile precursor mechanism are expected to become less efficient with increasing translational energy, while direct processes would be expected to become increasingly more probable as this energy is raised. Thus Tang et al.[32] find that the probability of molecular CO chemisorbing on a Ni<111> surface decreases with increasing translational energy, which they take as evidence for a precursor-mediated process. This contrasts with the positive effect of kinetic energy observed in systems such as shown in Figure 3-7, which are believed to proceed via a substantially more direct mechanism. In the case of the O_2/W<110> system, careful analysis of the data for energies ~0.05 eV reveals a contribution to the dissociative chemisorption probability from a precursor mechanism, but this channel rapidly closes off at higher energies. The dashed curve for O_2 in Figure 3-7 shows our best estimate of the behavior of this channel.[26]

As another example, we have found that the translational energy dependence of the initial sticking probability of methane on W<110> is consistent with a model in which a hydrogen atom tunnels through the activation barrier.[23] This contention is based partly on the observed exponential increase of the sticking probability with increasing kinetic energy, but the strongest evidence for such a mechanism is that the dissociation probabilities for CH_4 and CD_4 differ greatly at low energies but converge as the incidence kinetic energy is increased. In fact the line drawn for CD_4 is based on a fit to the data for CH_4, and is found to give good agreement with the CD_4

results.[23] The dashed portion of the CD_4 curve in Figure 3-7 is an extrapolation of the model to energies below the last data point. The tunneling model can account for other reports[35,36] of strong isotope effects in methane chemisorption and our observations greatly strengthen the original proposal of Winters[35] that quantum tunneling may occur in methane chemisorption.

Summary and Conclusions

Molecular beam and laser techniques are providing powerful new insights into the dynamics of gas-surface interactions. For simple atoms and molecules the dominant energy transfer channels can be mapped out and include both excitation of phonons and rotational states. For selected systems, state selected measurements allow the observation of beautiful phenomena like rotational rainbows and rotational polarization with a detail comparable to that of gas-phase studies. Studies of dissociative chemisorption reveal the importance and nature of activation barriers. Translational energy is found to be quite efficient at overcoming such barriers for many systems. These studies provide a basis for constructing realistic theories of gas-surface collisions and should provide important insights into many processes which are crucial to applications in materials and processing technology and other areas.

Acknowledgements

It is a pleasure to thank the many co-workers who have assisted us at different stages of this research program. These include C.T. Rettner, A. Kleyn, A.C. Luntz, J.E. Schlaegel, J.A. Barker, R.J. Madix, J. Lee, H.E. Pfnür, L.A. DeLouise, J.P. Cowin, F. Fabre, J. Kimman, H. Morawitz and J.C. Tully. We also thank P. Alnot for valuable contributions to these experiments, and helpful discussions with H.F. Winters, M.T. Loy, H. Metiu, and W. Kohn are gratefully acknowledged.

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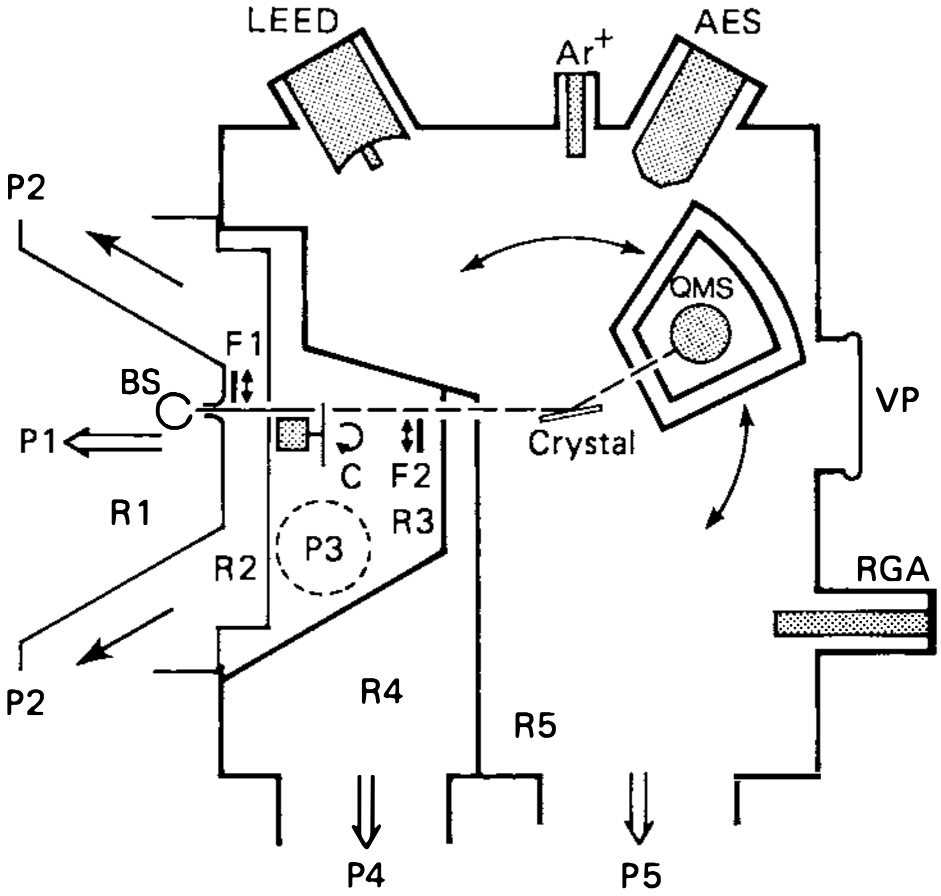

FIGURE 3-1 Molecular beam apparatus for determining inelastic scattering distributions. Key: R1-R5, vacuum regions; BS, pulsed beam source; C, high-speed chopper; F, beam flag; QMS, quadrupole mass-spectrometer detector; LEED, low energy electron diffraction screen; Ar+, argon ion sputtering gun; AES, Auger electron spectrometer; VP, 6 in. viewport; RGA, residual gas analyzer. The molecular beam system can detach at the R3 region and is non-bakable. The crystal is held on a manipulator, which provides for heating and cooling and rotates about the same axis as the QMS.

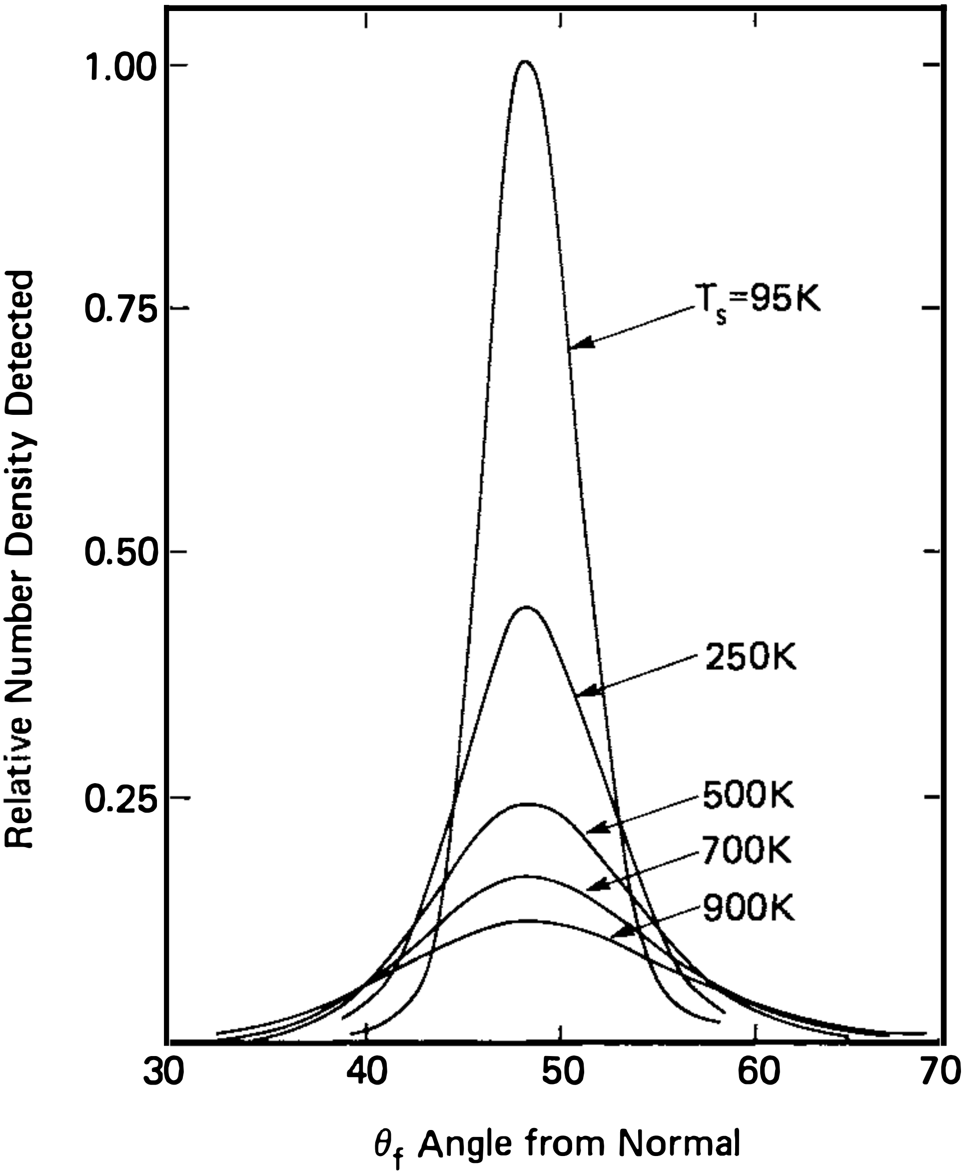

FIGURE 3-2 Number density distributions for Ar scattering from Pt(111). E_i = 0.9 eV, θ_i = 45° at various surfaces temperatures as indicated. (a) In-plane scattering distributions. (b) Out-of-plane scattering distributions (from ref. 3).

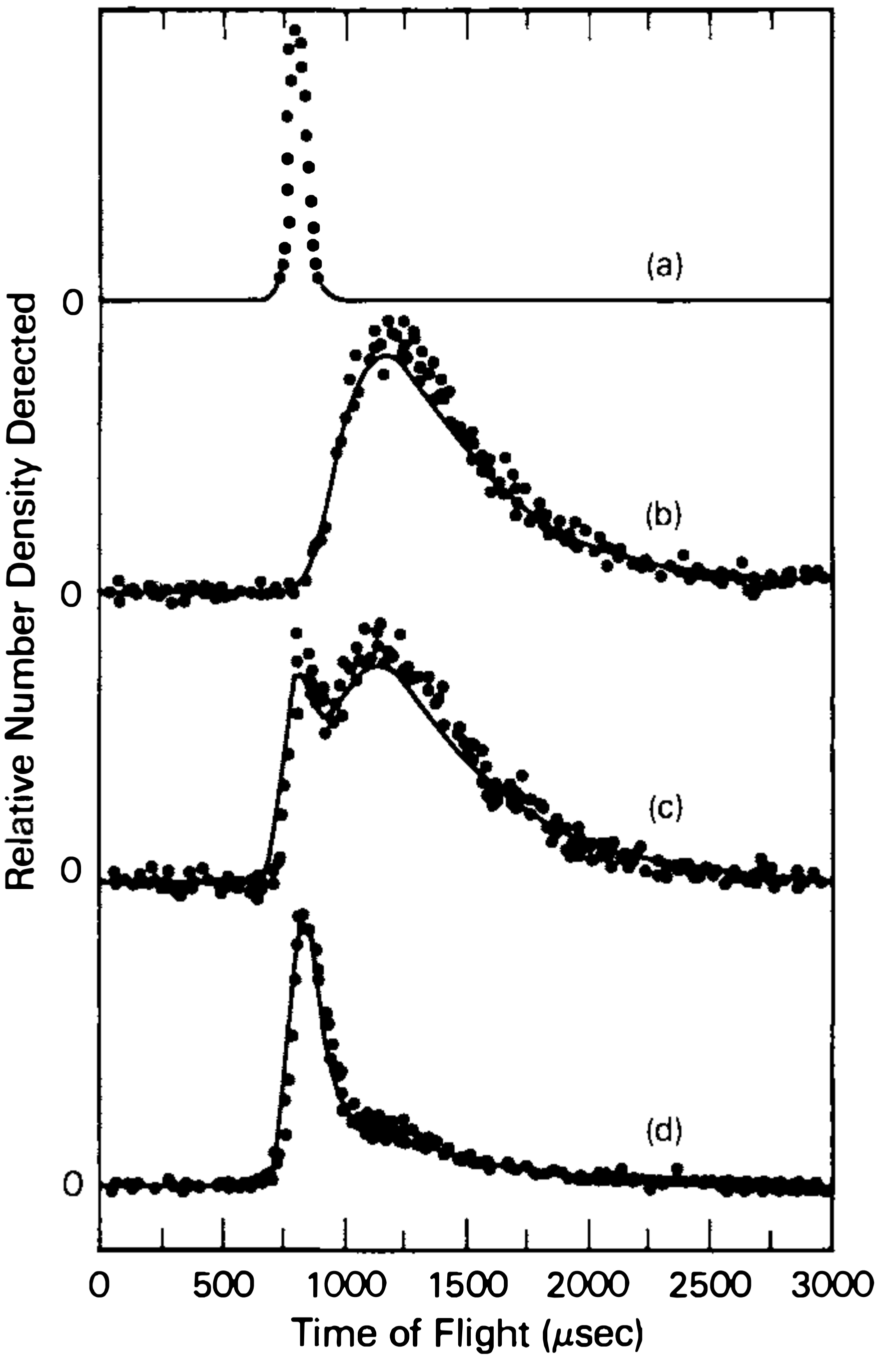

FIGURE 3-3 Time-of-flight spectra for Xe scattering from Pt(111) for $T_S = 185$ K, $\theta_i = 75°$, and $E_i = 0.14$ eV: (a) incident Xe beam; (b) $\theta_f = 0°$; (c) $\theta_f = 45°$; (d) $\theta_f = 75°$ (specular) (from ref. 4).

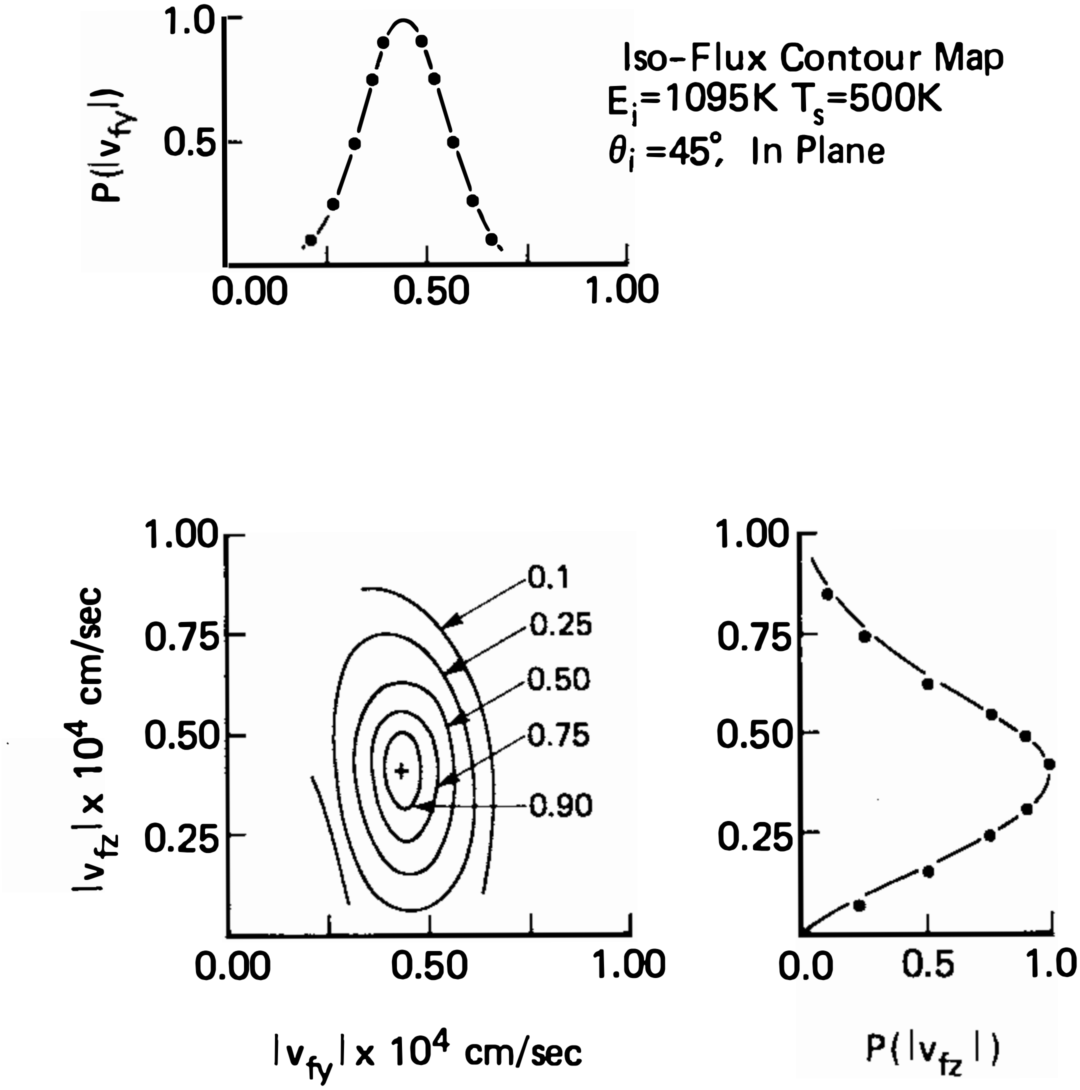

FIGURE 3-4 Typical isoflux contours for Ar/Pt(111): (a) E_i = 1095 K, T_s = 500 K, incident angle 45° in-plane scattering; (b) E_i = 3958 K, T_i = 500 K, incident angle 45° in-plane scattering (from ref. 3).

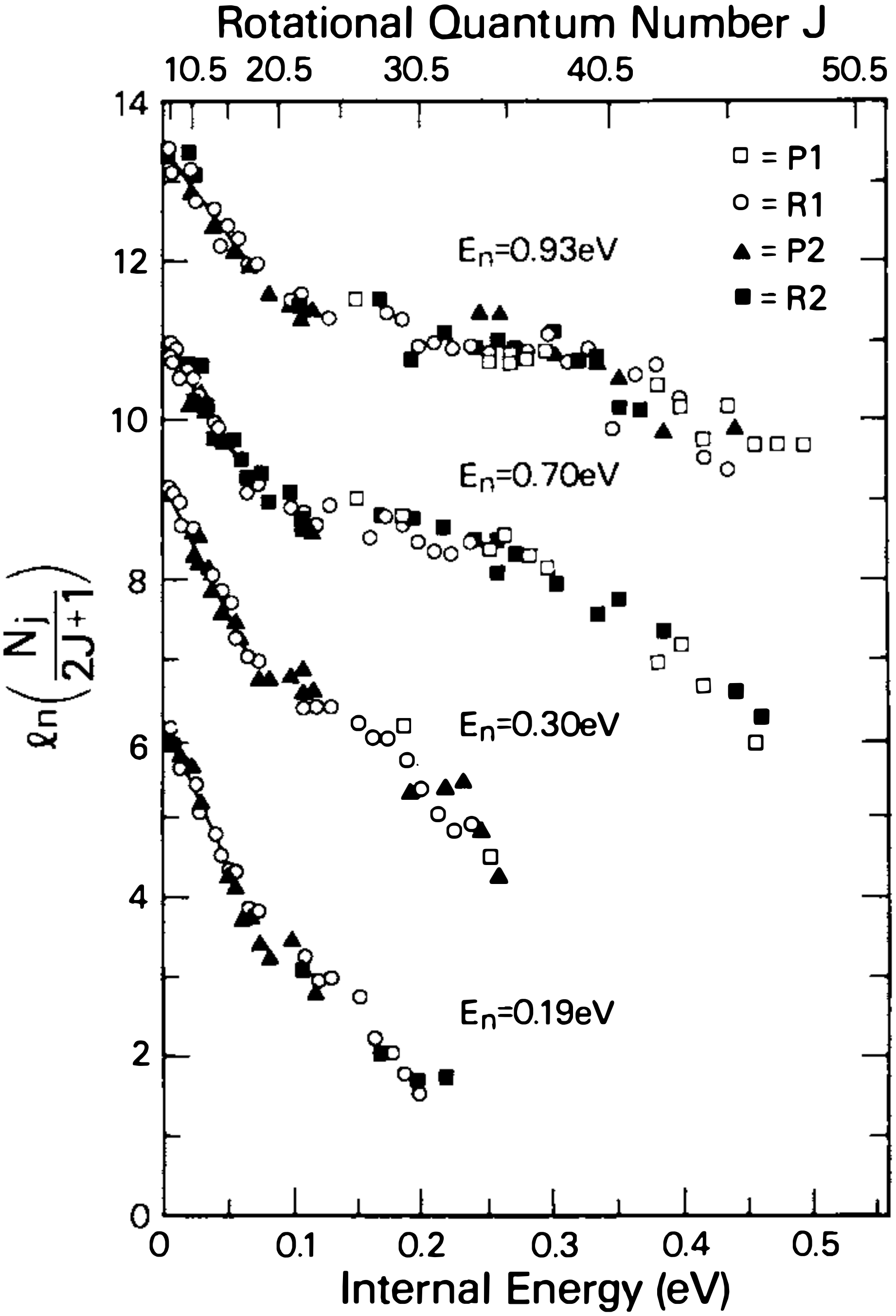

FIGURE 3-5 Rotational state distribution of NO scattering from Ag(111) as function of internal energy (bottom scale) or rotational quantum number J (top scale) (from ref. 9).

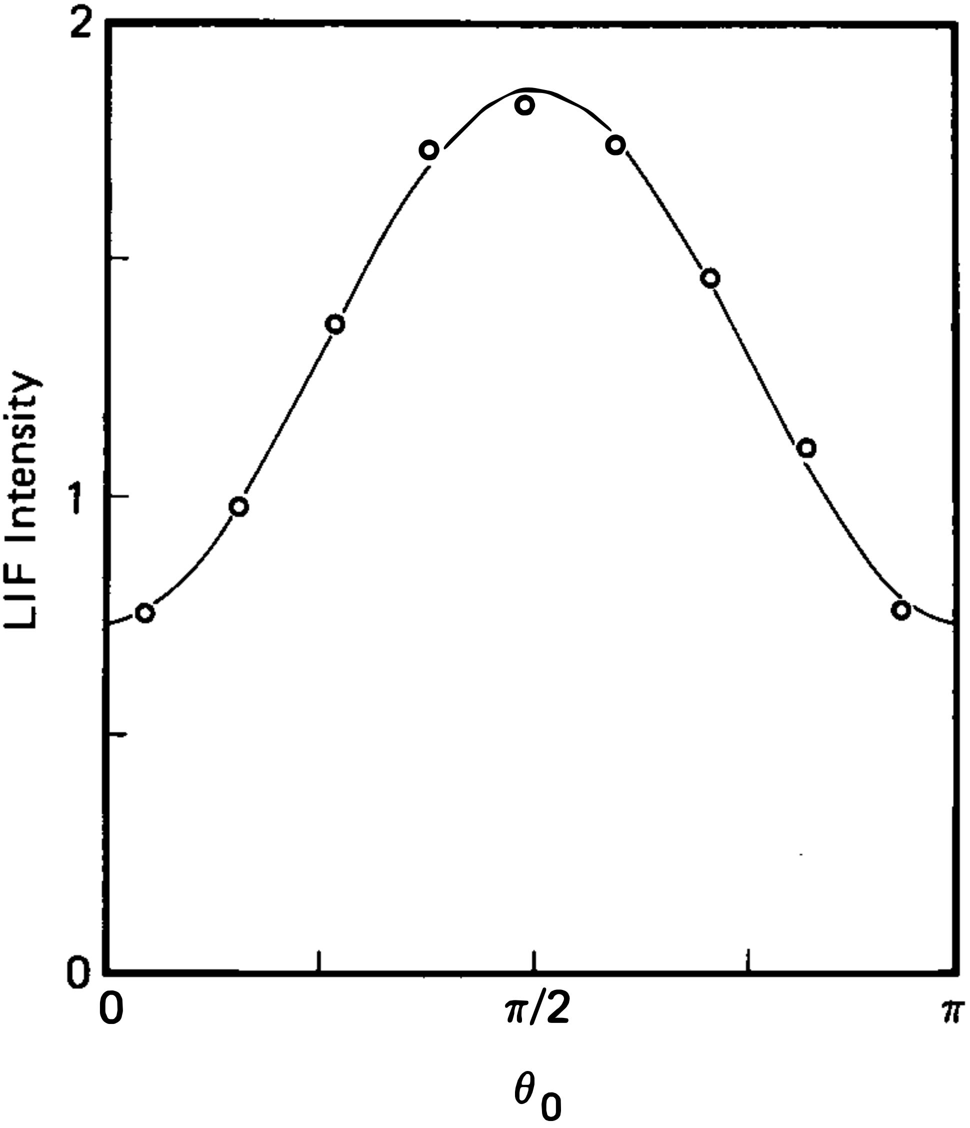

FIGURE 3-6 Rotational polarization-LIF intensity versus angle of laser polarization for a 0.75 eV beam of NO incident on Ag(111) at θ_i = 45° and T_S = 650 K (from ref. 11).

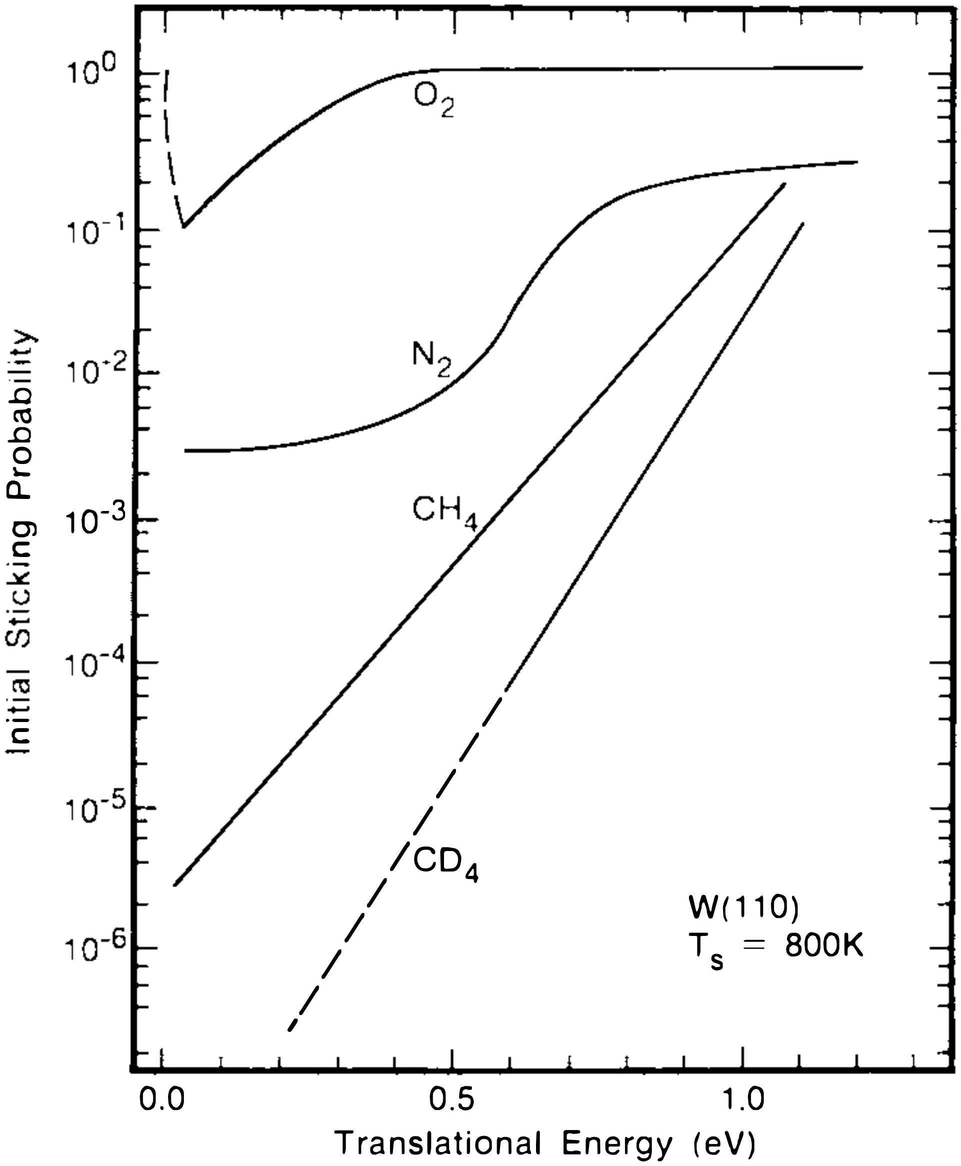

FIGURE 3-7 Effect of incidence energy on the dissociative chemisorption probability of O_2, N_2, CH_4, and CD_4 on a W<110> surface for a surface temperature of 800 K and at normal incidence. The dashed lines indicate theoretical curves (see text).

4

CHEMICAL DYNAMICS IN SYSTEMS OF FINITE SIZE

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Introduction

Surface chemistry and catalysis have, for a long time, dealt with systems of finite size such as clusters and monolayers. The same has been true for bio-related chemistry where reactions in membranes and micelles are as common as reactions in "infinite" size solutions.

However, progress in our fundamental understanding of molecular (and chemical) dynamics in finite-size systems has been hampered, so far, by the scarcity of data on "simple" finite systems, i.e., systems where the interatomic and intermolecular forces present are well known. Only for such systems is an unequivocal theoretical treatment possible and may conclusions of general validity be drawn.

Molecular beams and lasers have, in the last decade, been the source of enormous progress in our fundamental microscopic understanding of gas phase kinetic phenomena and in the clarification, sometimes in the smallest of the details, of atomic and molecular interactions. This area of chemical physics can be described as having reached a well-developed state of maturity.

Therefore, and only too naturally, presently, the power of these two magnificent scientific tools is being brought to bear on more complex systems such as clusters and large molecular complexes. As other speakers at this workshop will show, substantial progress has been made recently with metallic systems, while definitive progress with "simple" systems has been made difficult by the weakness of their bonding forces, by the strong perturbations introduced in using such probes as electron impactionization mass spectroscopy and by the difficulties introduced by the need of working at low temperatures.

However, nowadays, where there are problems, there are also solutions (it is only a matter of effort and economics), and, as we will try to prove here, the fundamental study of "simple" finite systems is off to a vigorous start.

Before examples of these new efforts are listed and speculations made on future trends, a further reason for the existence and the need for such studies should be mentioned. This reason is to be found in the accelerated trend towards the atomic level present in modern, existing or predicted, technology. Layered electronic materials possessing special properties, extremely small circuit lines prepared by laser induced chemical etching, very thin protective layers that provide unusual optical, mechanical or chemical properties to the surface of solids, are all examples of this trend towards smaller sizes in modern technology. These new devices provide the answer to many problems, but they also pose a lot of questions that may be fully answered only by studying the laws of behavior of molecules in finite size systems under well-defined interaction conditions.

The examples discussed below are drawn mostly from the activity in progress in the author's laboratory. However, the trend mentioned above (towards an increased importance of fundamental studies in finite size systems) is apparent from the spectrum of the activities in many other institutions.

Clusters as Microsolutions

The microscopic description of the relaxation behavior and chemical activity of molecules in solution represents one of the major unsolved problems of chemical physics.

While short-pulse laser spectroscopy, computer simulation and statistical mechanics are making inroads into the subject, a relatively recent line of work, made possible by the advent of molecular beam laser spectroscopy, studies the evolution of molecular behavior in a cluster environment as a function of the cluster size. In doing this one tries, in a quasi-continuous way, to bridge the gap between the free-molecular and the solvated behavior, gaining insight into the properties of the latter. Naturally, at the same time, the properties of the cluster itself come under inspection and, through their study, light is shed on this interesting but as yet largely unknown "state of matter."

Apart from the initial cluster studies, carried out largely with mass spectrometers and electron diffraction instruments, the bulk of the activity in this field has been spectroscopic in nature and has dealt mostly with rather small clusters. Large clusters have been the object of a relatively small number of studies [1]. This is especially true for studies on chemical reactions of *neutral* molecules *within* large clusters, since most papers in this category deal with *ionic* clusters and ion-molecule reactions [2]. If one studies reactions between neutral atoms and molecules *imbedded* in medium-large noble gas clusters (where the interactions are either known or can be calculated to a reasonable accuracy), the prior knowledge of the forces involved greatly facilitates the theoretical description of the dynamic behavior which often requires complex simulations and/or approximate statistical theories. The recent work carried out in several theoretical groups [3] shows that the analytical and numerical tools needed to tackle problems of this type are becoming available.

About ten years ago, Gough, Miller and Scoles showed that some of the problems of molecular beam spectroscopy in the infrared could be solved by means of tunable lasers and the *bolometric* detection of the power deposited by them into the molecules of the beam [4]. In recent years this technique has been used in many laboratories all over the world for (a) both high and low resolution spectroscopy of van der Waals molecules [5]; (b) spectroscopy of molecular overtones [6]; (c) state-selective gas-surface scattering [7]; (d) the monitoring of the preparation of highly vibrationally excited beams [8]; and (e) multiphoton spectroscopy [9], very high resolution molecular spectroscopy [10], and even visible spectroscopy [11].

One of the best applications of this optothermal technique became apparent just a few years after its introduction when it was realized that it could be easily applied to the spectroscopy of predissociating molecules [5a].

Since the temperature of large clusters appears to be determined by their evaporative cooling, the predissociation technique used so successfully on small clusters may be extended to clusters of much larger size, with the upper limit reached when the absorption of a photon, because of energy randomization, does not produce appreciable evaporation from the clusters before the latter reaches the detecting area of the apparatus.

More recently we have introduced a simple technique (see Figure 4-1) to deposit useful quantities of molecules on the surface of molecular clusters and obtain their IR spectra in this new environment [12]. We have further succeeded in monitoring the complex forming reaction between a molecule (CH_3F) imbedded in an argon cluster and another molecule deposited on its surface (HCl) (see Figure 4-2). The change in the reaction probability as a function of nozzle pressure (i.e., average cluster size) may help in obtaining experimental estimates of the diffusion of molecules in cold clusters.

Considering now the reaction of an atom (e.g., oxygen) with a molecule contained in the cluster, we can imagine that the products, *if the cluster is large enough*, will remain in the cluster without undergoing further reaction. This lack of suecessive reactions characteristic of a *finite* matrix is not typical of an extended solid or liquid matrix. Moreover, the determination of the size of the cluster that will contain the reaction products may provide interesting contributions to the study of the "cage effect" for molecular reactions in solutions. Another difference between extended and finite (cluster) matrices is that the cluster matrix, via the surface deposition technique, is more suitable for the production of relatively large quantities of reacted species. When reasonable quantities of reacted species have to be produced in a solid matrix, the reaction is made to occur in the gaseous flow just before condensation [13], making the interpretation of what happens substantially more difficult.

Cluster Surfaces: A Fast, but Clean, Act

Another problem, which has recently received a substantial amount of attention, is that of the vibrational relaxation and photoevaporation of molecules adsorbed at the surface of solids [14]. Here, the open questions are: What are the linewidths of the vibrational absorption on surfaces? What is the photodissociation yield for a molecule sitting on the surface of a cluster? What is the probability of photoevaporation versus that of dissipation of the energy into the surface phonon bath? The connection with the problem of the linewidths in the IR spectrum of van der Waals molecules, which has been very actively investigated in recent years [5b], is quite clear. Also, in this field there is a strong need for experiments on "simple" systems, where the interactions are known and theories can be tested. The surface of extended noble gas crystals would, of course, be a suitable environment. However, experiments carried out with noble gas crystals are full of technical difficulties. The surface of noble gas clusters accessible via the pick-up technique, although admittedly more irregular, may provide a viable alternative.

The main disadvantage of cluster experiments, which should be carried out in a molecular beam, is that the time available for the study is of the order of one millisecond. The shortness of this time can, however, be an advantage when experiments are carried out on the cluster surface. Indeed, in a normal UHV apparatus, a vacuum better than 10^{-10} torr is needed to keep a stationary surface clean during an experiment (~a day) whereas in a cluster spectrometer, a vacuum of only $\sim 10^{-6}$ torr is needed to keep a cluster surface clean (1 ms for each freshly formed cluster).

Clusters and Glasses

Are argon clusters, formed in supersonic jets, solid, liquid, or glasses? What type of phase transitions happen in clusters? Is it possible to make argon glass? How much local order is present in glasses?

This series of questions shows the logical connection between the subject of glasses and that of clusters. However, experimentally, the connection is much more difficult to make.

In 1983, we measured the IR spectrum of SF_6Ar_n as a function of cluster size, finding evidence that the region around $n = 10$ shows larger line widths than both regions of smaller and larger clusters [15]. In the latter region, the spectrum tends towards the SF_6 spectrum in a solid Ar matrix. The larger (intermediate region) linewidth was initially attributed to the presence in the beam of a wide distribution of masses and a relatively rapid change of the spectral line position with mass in that mass range. However, recently Eichenauer and LeRoy [16] have put forward the hypothesis that the linewidth versus pressure plots in these spectra could be used to confirm the existence of phase bistability (or isomer bistability as preferred) in clusters of intermediate size. More work is required to test this hypothesis.

Focusing now on larger clusters, we note that it is apparently established that simple atomic clusters, generated by supersonic expansion with large cooling rates ($\sim 10^9$ K sec^{-1}), exhibit icosahedral structures [17] (as opposed to the hexagonal close packed structure of bulk crystals). However, for really large clusters the solid structure is recovered [18]. The connections between the questions raised and the more fundamental aspects of material science are, at this point, quite evident. Indeed, recently, crystals and quasi-crystals of icosahedral symmetry [19] have been the subject of a large number of studies, and the theoretical and experimental activity aimed at the study of glasses has been quite strong [20] as well. It appears that, with the rapid quenching rates available in computer simulation studies, argon can also be made to become a glass (a fact which has, so far, not been reproduced experimentally), while other substances with more complicated interaction potential become glasses much more easily [20].

The influence of the potential on the glassification of materials is an issue which by no means can be considered settled. We submit that the study of simple clusters, carried out on the shoulders of all the knowledge on intermolecular forces accumulated in the last twenty years by molecular beam scattering and small cluster spectroscopy, may give a sound contribution towards the solution of several of the problems listed above.

Chemical Dynamics and Physisorption: An Overdue Marriage

Order, disorder, and phase transitions in overlayers physisorbed at the surface of single crystals have been studied for a number of years and with a variety of techniques [21]. The issues addressed so far concern mostly monolayers (while interest in multilayer phenomena is more recent) and have dealt primarily with the molecular physics aspects of the problem. This is because molecules of chemical interest (most of them highly polar) do not easily form ordered physisorbed structures and, moreover, tend to decompose under electron impact, electrons being by far the most widely used surface probe.

The advantages of low energy atomic scattering for the probing of surface phenomena are well known. Atomic probes are sensitive, nondestructive, very surface-specific and, most important, amenable to quantitative theoretical analysis.

The application of atomic scattering to the study of physisorbed overlayers is relatively recent but has already enormously increased our understanding of these systems [22]. During the last few months, in our laboratory, we have been able to show that well-ordered layers of strongly polar molecules (CH_3F, CH_3Cl, and HCl for instance) may be obtained under carefully chosen layer growth conditions [23]. For example, in Figure 4-3 we show the helium diffraction patterns of three different monolayers: (a) xenon on graphite; (b) CH_3F on graphite; and (c) CH_3F adsorbed on a layer of Xe predeposited on graphite. Both Xe and CH_3F adsorbed on graphite produce commensurate $(\sqrt{3} \times \sqrt{3})R30°$ regular lattices while CH_3F on Xe coated graphite also shows a superstructure (notice the doubling of the diffraction peaks) which arises from the coupling of the dipoles in adjacent rows of molecules.

The possibilities offered by these ordered layers of molecules for the study of the effect of molecular orientation on reactivity are quite clear. Reaction rates may be monitored, following the time behavior of the surface coverage under bombardment by a constant flux of reactive atoms. These rates will be a function of the reacting atom beam energy, angle of incidence, and type and degree of ordering of the surface.

Since most of the interactions involved are relatively well-known, a full theoretical treatment of the problem is possible and may deliver interesting information on both the angular dependence of reactivity and the main differences between gas-phase and adsorbed-phase reaction mechanisms. The level of quantitative sophistication reached by modern molecular physics in describing complex systems is best illustrated by the comparison of the prediction of the structure of a layer of CH_3Cl molecules adsorbed on Xe coated graphite with our experimental results, carried out recently by M.L. Klein and M. Moeller [24].

The structure is uniaxial and incommensurate, with rows of parallel dipoles having alternate dipole orientations and opposite sign displacements with respect to an average plane parallel to the graphite surface. Both experimental and theoretical results are preliminary, but intermolecular distances in the same row are 4.26 Å in the experiment and 4.15 Å in the simulation, while the distance between molecules in adjacent rows is 3.18 Å in the experiment and 3.46 Å in the simulation. No potential optimization was carried out in the theory, the interactions having been derived with a well-educated guess inspired from the solid state properties of CH_3Cl, quantum chemistry calculations, and common potential parameter combination rules. Notice that the calculations have been made easier by the presence of the Xe substrate which makes the poorly known CH_3Cl-graphite potential almost irrelevant to the problem.

We are convinced that the study of ordered molecular layers of this type are going to give a substantial contribution not only to our knowledge of molecular reactivity, but also will add rapidly to our understanding of many-body interactions in solids and the fundamental properties of layered compounds. For instance, is the different vertical displacement from the surface of different molecular rows typical of the surface of polar solids? If not, how many layers will it take to produce a flat surface? As in the case of clusters, we are enjoying the possibility of smoothly going from the atomic to the continuum, solving problems that only ten years ago would have been thought much more difficult, if not impossible, to crack.

Chemistry with a Hammer and the Pressure Effect on Catalysis

As the last example of the power of beam techniques for giving us a better understanding of the behavior of matter in finite size systems, I would like to describe a recent experiment carried out by S. Ceyer and her co-workers at MIT on the collision-induced dissociative chemisorption of CH_4 on the (111) face of Ni crystals [25].

In these experiments a layer of CH_4 is physisorbed on the (111) face of a Ni crystal at relatively low temperatures, and a beam of energetic Ar atoms is made to impinge on it. The amount of carbon permanently bonded to the surface as a consequence of the Ar bombardment is then measured. Below 0.8 eV Argon kinetic energy, no carbon is found to bind to the surface. At 0.8 eV the dissociative chemisorption probability becomes appreciable, while doubling of the energy increases this possibility by two orders of magnitude. The implications of these results for high pressure surface chemistry and catalysis are, of course, important, because now the pressure of buffer gases, and therefore the number of collisions that these make with the surface, should be seen under a completely new light.

In summary, we hope that these few examples have shown to the reader that molecular beam techniques are going to be as useful in the study of condensed matter problems as they have been for the study of gas-phase phenomena and interactions.

Acknowledgments

It is a pleasure to thank my co-workers, D. Levandier, J. McCombie, R. Pursel, P. Rowntree, J. C. Ruiz, and J. Xu for having been instrumental in shaping the ideas described in this paper. It is also a pleasure to thank M. L. Klein and M. Moeller for having shared with me their unpublished results on an overlayer simulation. The part of the work described here which was carried out in our laboratory enjoyed the financial support of the National Sciences and Engineering Research Council of Canada and The Petroleum Research Fund of the American Chemical Society.

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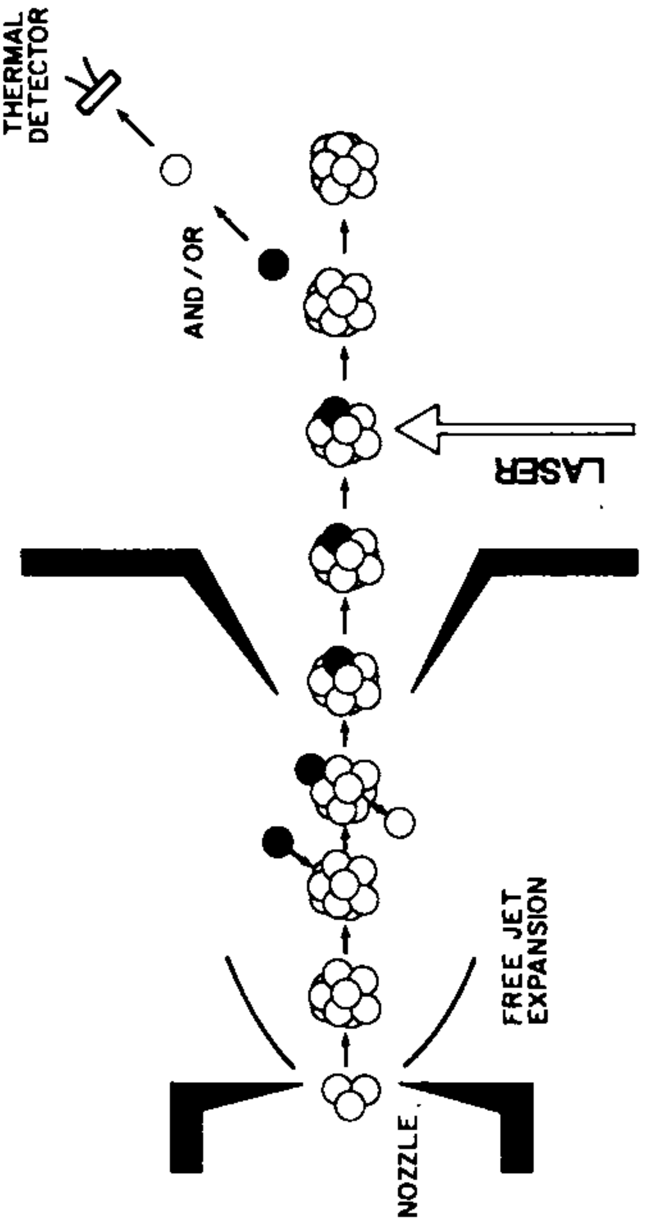

FIGURE 4-1 Schematic description of the pick-up technique introduced to obtain IR spectra of species deposited on the surface of large noble gas clusters. The black circles represent the chromophore. In both cases, the cluster beam ends up against a beam block while the evaporated fragments (either the deposited molecule or a few of the noble gas atoms) strike the thermal detector (a semiconductor bolometer cooled below 2 K).

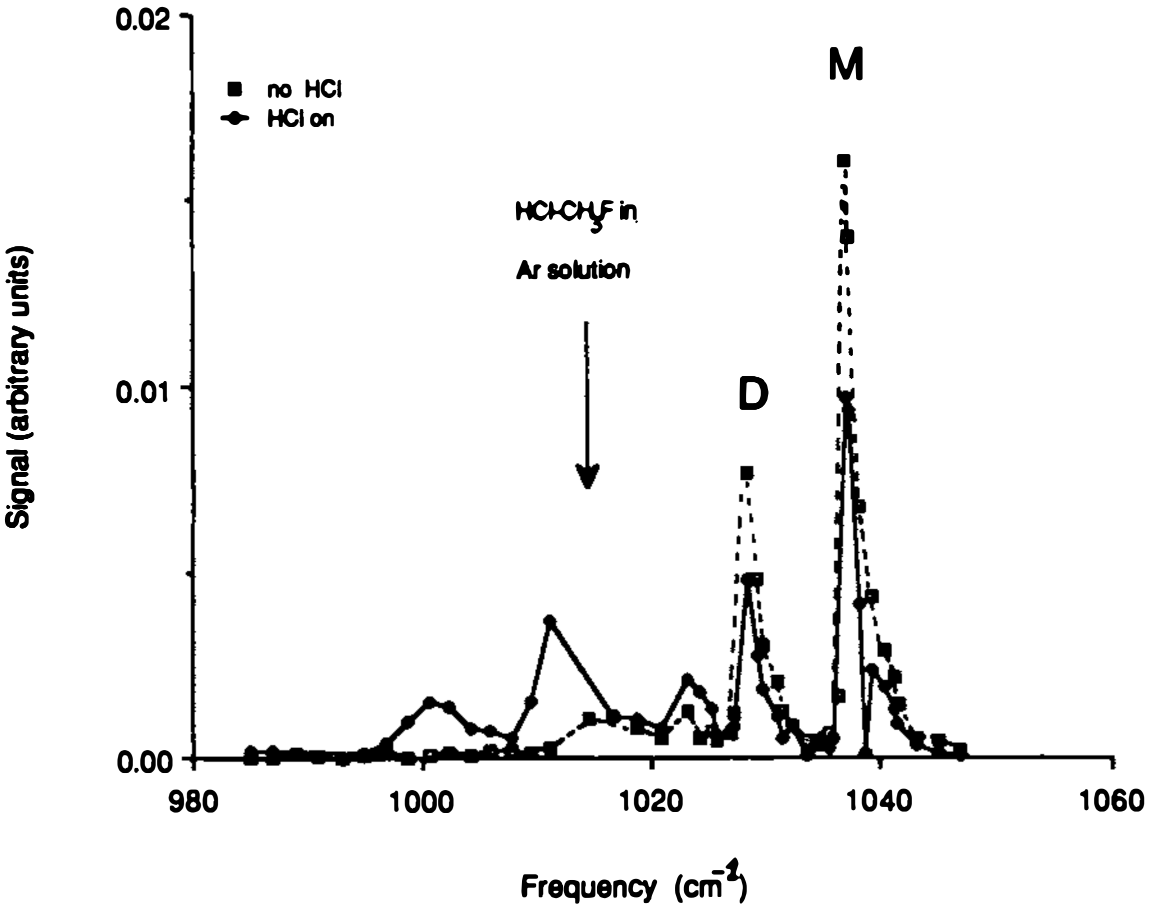

FIGURE 4-2 These are optothermal detection spectra produced with 0.1% CH_3F/Ar mixture expanded at 1034 kPa, either with or without a HCl cross flux, as indicated. The first peak from the right (M) is due to the CH_3F monomer solvated in the Ar cluster while the second (D) is due to the CH_3F dimer in the same environment. The arrow marks the peak position of the HCl-CH_3F complex in liquid Ar at 95 K. The two peaks at the left of the arrow are due to the products of the complexation reaction between CH_3F and HCl in the cluster.

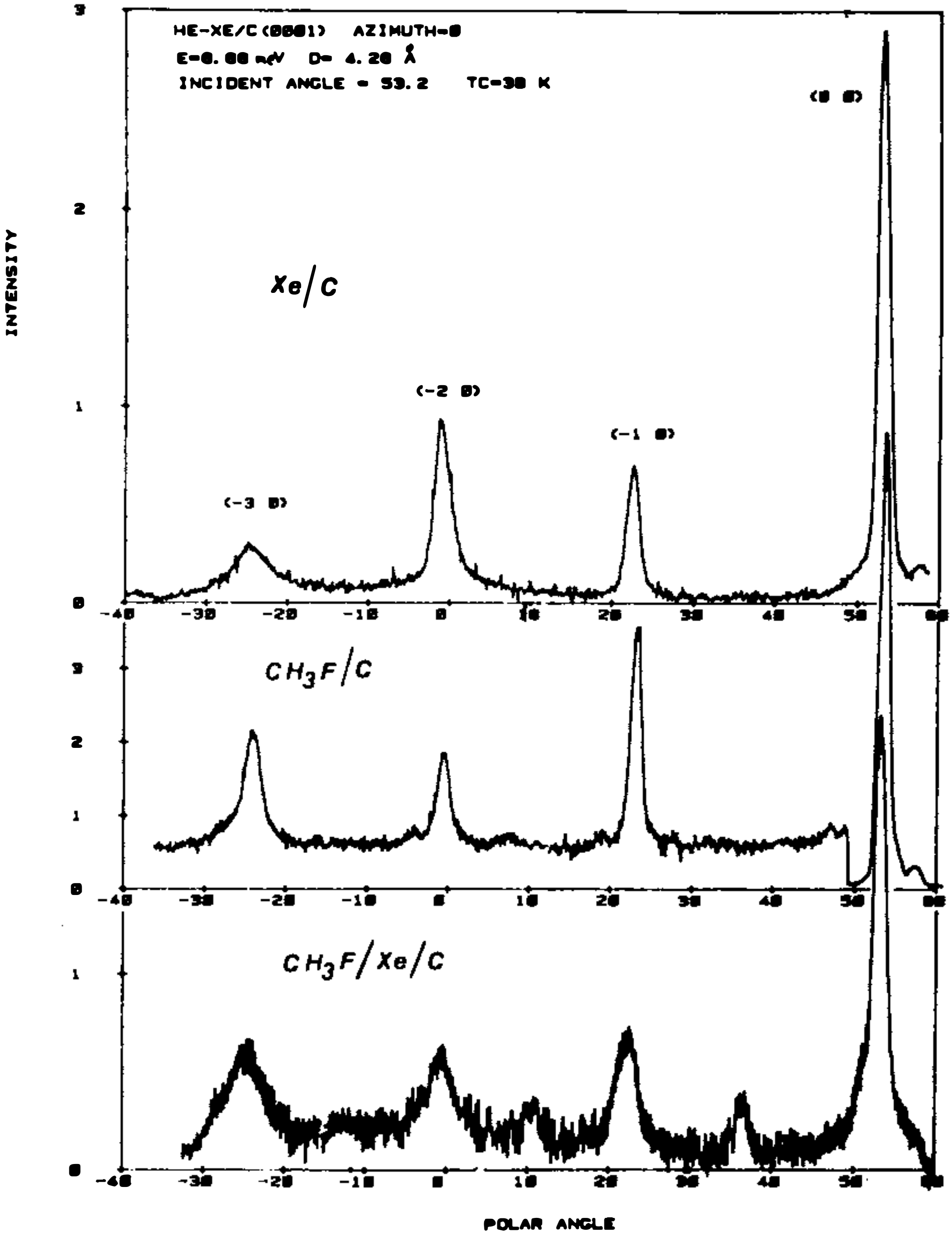

FIGURE 4-3 He beam diffraction patterns of overlayers on graphite. CH_3F on bare graphite forms a layer in registry with the substrate as shown by the diffraction peaks occurring in the same position as for Xe. When CH_3F is deposited on Xe coated graphite the layer also shows a superstructure (see extra peaks indicated by arrows in the figure) which is similar to that described in the text for CH_3Cl.

5

VIBRATIONAL SPECTROSCOPY OF CLUSTER IONS: TWO NOVEL METHODS

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Introduction

Studying the vibrational spectroscopy of cluster ions, such as the hydrated hydronium ions, $H_3O^+\cdot(H_2O)_n$, is inherently difficult. Although one may study these species in the liquid phase or in a gas cell where their densities are relatively high, these methods have the disadvantage of ambiguity in assigning absorption features to a given species. The recently developed velocity modulation technique[1] in gaseous discharge plasmas has provided important information on high resolution infrared absorption spectra of molecular ions, but weakly bound ionic clusters are not abundant in high temperature plasmas. Using an ion beam has the advantage of mass selection capability, but at the expense of orders of magnitude in ion density. This makes traditional absorption spectroscopy nearly impossible. Thus, one has to depend on the observation of the consequence of photon absorption rather than the attenuation of photon intensity due to absorption.

For very weakly bound ionic clusters such as H_5^+, H_7^+, H_9^+, etc., excitation of vibrational degrees of freedom induce the dissociation and one can use the vibrational predissociation process to obtain vibrational spectra as has been done in the investigation of neutral molecular clusters. But there are many cluster ions, such as the hydrated hydronium ions, whose binding energy far exceeds the energy of vibrational quanta, and the vibrational predissociation process will not take place by exciting the fundamental molecular vibration. In our recent ion beam study of the hydrated hydronium ions, we have overcome these obstacles by utilizing two complementary techniques. Both methods take advantage of the inherently high sensitivity of ion detection.

The first approach is to attach a H_2 molecule to the hydrated hydronium ions. Because the original goal was to study the hydrated hydronium ions, the attached H_2 is hoped to have only a small effect on the spectrum. After an O-H stretch of the cluster ion has been excited, it vibrationally predissociates, losing the H_2. In a sense, the H_2 is a messenger that indicates when an absorption has taken place. By monitoring the dissociation product as a function of laser frequency, the absorption spectra of these $H_3O^+\cdot(H_2O)_n\cdot H_2$ ($n = 1, 2, 3$) ions have been found.[2]

The second approach is to detect the vibrationally excited $H_3O^+\cdot(H_2O)_n$ ($n = 1, 2, 3$) ions using an infrared multiphoton dissociation process. The procedure is to first excite from $v = 0$ to $v = 1$ in the O-H stretch using a tunable IR laser. We then make use of the fact that the density of states near $v = 0$ and $v = 1$ are very different, and the vibrationally excited ionic clusters, which contain many low frequency vibrations, are likely to be in the quasicontinuum region for the sequential excitation by a fixed frequency laser. This means that one can distinguish between ground state and vibrationally excited $H_3O^+\cdot(H_2O)_n$ by using a multiphoton dissociation

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(MPD) process to selectively dissociate the latter using a CO_2 laser. Once again, we monitor the dissociation product ion signal as a function of the excitation frequency of the first laser to get the absorption spectra of the $H_3O^+ \cdot (H_2O)_n$ ions. This paper will concentrate on $H_3O^+ \cdot H_2O$ as an example of these two novel experimental techniques.

The spectrum of $H_5O_2^+$ from 3550 to 3800 cm^{-1} is presented and compared to the spectrum of $H_5O_2^+ \cdot H_2$, which was reported previously.[3] A comparison with vibrational frequencies calculated using *ab initio* methods by Remington and Schaefer[4] is also made and implications regarding the structure are discussed.

Experimental Approach

The ions are created in a high pressure corona discharge source as shown in Figure 5-1. Typical discharge conditions behind the nozzle are 1.2 kV from cathode to anode and 200 torr of H_2 gas containing trace amounts of H_2O. The beam containing various ionic clusters is formed by expanding the plasma through a 75 μm nozzle. The ions pass through two differential regions of pumping, in which they are skimmed and focused, before initial mass selection in a 60° sector magnet. This capability of mass selection allows us to eliminate the background ions completely as well as to unambiguously ascertain the identity of the ion being studied. In order to facilitate the interaction with the lasers, the ion of interest is then bent 90° by an electrostatic field and sent into a 50 cm long radio-frequency octopole ion trap. While the ions are trapped, they interact with a tunable infrared laser. A schematic of the apparatus is shown in Figure 5-2.

Two different laser schemes were needed depending on the approach taken. When studying $H_3O^+ \cdot (H_2O)_n \cdot H_2$, a single tunable infrared laser was needed. The system used was a Quanta-Ray infrared wavelength extender (IR-WEX), which is a difference frequency laser. The IR-WEX generates infrared at the difference between the fundamental of an yttrium-aluminum garnet (YAG) laser and the output from a pulsed dye laser. The laser path between the output of the tunable infrared laser and the entrance of the machine was enclosed and continually flushed with dry nitrogen to reduce atmospheric water absorptions. In spite of this precaution, atmospheric water absorption was still a problem, accounting for much of the noise in the spectra introduced during the normalization by laser power. The laser path was flushed in both laser schemes.

The second laser scheme consists of two lasers and is used to investigate the more strongly bound $H_3O^+ \cdot H_2O$. The first laser is a Burleigh cw F-center laser, which is scanned from 3550 to 3800 cm^{-1} with a linewidth of 0.5 cm^{-1}. This is the region of an O-H stretching vibration. The second laser, used to multiphoton dissociate the vibrationally excited $H_5O_2^+$ ions, is an MPB Technologies Inc. continuous-wave (cw) CO_2 laser. The frequency and intensity of the CO_2 laser is determined by trying to reach the ideal situation where none of the ground state $H_5O_2^+$ ions absorb enough photons to dissociate, but those in $v = 1$ do dissociate into H_3O^+ and H_2O. In $H_5O_2^+$, as opposed to $H_7O_3^+$ and $H_9O_4^+$, which will be discussed in a future paper, the ground state ions do not readily absorb enough photons to dissociate. Therefore, the CO_2 laser is run full power (~6 W in the interaction region) on R(24) of the 00°1-02°0 transition. Since a cw CO_2 laser is used, the length of time the $H_5O_2^+$ ions reside in the octopole ion trap is a third variable which is optimized to achieve a low H_3O^+ background from those $H_5O_2^+$ ions that don't absorb an IR photon from the F-center laser and a high H_3O^+ signal from those $H_5O_2^+$ that do. In this case, 100 ms was found to be optimal. The residence time of the ions and the laser intensity together determine the energy fluence of the laser irradiation of the ions in the trap.

After the laser irradiation, ions are ejected from the exit lens of the rf ion trap. It is the fragment ions, not the parent ions, which are mass selected by an extranuclear quadrupole mass filter and sent into a Daly-type ion detector. Specifically, when studying $H_5O_2^+ \cdot H_2$, the quadrupole mass filter selects $H_5O_2^+$ fragment ions; when studying $H_5O_2^+$, the H_3O^+ ions are mass selected. By monitoring the fragment ion signal as a function of the tunable IR laser frequency, the vibrational spectrum is obtained.

Results and Discussion

The *ab initio* calculations on the structures and frequencies of the hydrated hydronium ions, $H_3O^+ \cdot (H_2O)_n$ (n = 1,2,3), have been carried out by Remington and Schaefer.[4] For $H_5O_2^+$, the proton in the center is shared by two H_2O molecules, but for larger clusters, the H_3O^+ unit forms the core, which is solvated by H_2O in strong hydrogen bonds. Kebarle[5] has measured the binding energies to be 31.6, 19.5, and 17.9 kcal/mole for n = 1, 2, and 3, respectively.

The two lowest energy structures of $H_5O_2^+$, which are shown in Figure 5-3, are the C_2 and C_S structures. At the CISD level of theory, using a DZ+P basis set, they differ in energy by less than 0.2 kcal/mole, with the symmetric structure being lower. This structure agrees with our vibrational spectrum shown in Figure 5-4. The dashed lines in the figure indicate the predicted vibrational frequencies and intensities for the C_2 structure where the central H atom is equidistant between the two oxygen atoms.

Contrast the $H_5O_2^+$ spectrum with that of $H_5O_2^+ \cdot H_2$ shown in Figure 5-5. Rather than two principle absorptions, four are now evident. This indicates a loss of symmetry and consequently a splitting of the degenerate vibrations. The dashed lines in Figure 5-5 correspond to the frequencies and intensities predicted for $H_5O_2^+$ at the SCF level of theory for the asymmetric C_S geometry where the central H is closer to one of the oxygen atoms. The presence of the H_2 on the H_3O^+ core stabilizes the asymmetric C_S structure causing it to be the dominant structure. Although the H_2 messenger is bound very weakly, its presence has a tremendous impact on the vibrational spectra.

The two features of the spectrum of $H_5O_2^+$ from 3550 to 3800 cm^{-1} are due to O-H stretches. The feature near 3609 cm^{-1} is assigned to the symmetric O-H stretch of the H_2O units and is broad and featureless. The more striking feature centered at 3696 cm^{-1} corresponds to the antisymmetric O-H stretch of the H_2O units and is shown resolved into a perpendicular band progression of Q-branches. The separation of the Q-branch positions is ~11.6 cm^{-1}. This agrees with the spacing predicted by the theoretical C_2 structure, although the significance of this agreement is not known due to the nonrigidity of the molecule. High resolution spectra have been resolved under the central Q-branches and are in the process of being analyzed.

We also are able to take Doppler limited high resolution spectra as shown in Figure 5-6, by operating the F-center laser single mode. The Doppler width arises from the motion of the ions traveling back and forth in the octopole ion trap, giving a linewidth of 0.02 cm^{-1}. This band is the antisymmetric O-H stretch of the solvent H_2O moieties in $H_9O_4^+$. The apparent structure on the sides has a separation of 0.18 cm^{-1} which seems to be due to the end over end rotation of the $H_9O_4^+$ ion.

Concluding Remarks

We have briefly discussed two sensitive techniques for obtaining vibrational spectra of cluster ions. Although H_2 may not be the ideal choice for a "messenger" due to its perturbation of the spectra, the feasibility of the technique has been demonstrated, warranting further development of this approach. The second method, which makes use of MPD, has been proven capable of obtaining high resolution spectra of low density cluster ions. In fact, this technique is ideally suited to study cluster ions because of the abundance of low frequency modes in cluster ions making the multiphoton dissociation process more facile.

Acknowledgments

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The F-center laser was on loan from the San Francisco Laser Center, a National Science Foundation Regional Instrumentation Facility, NSF Grant No. CHE79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University. We also thank R. Remington, and H. Schaefer for providing us with results of unpublished calculations.

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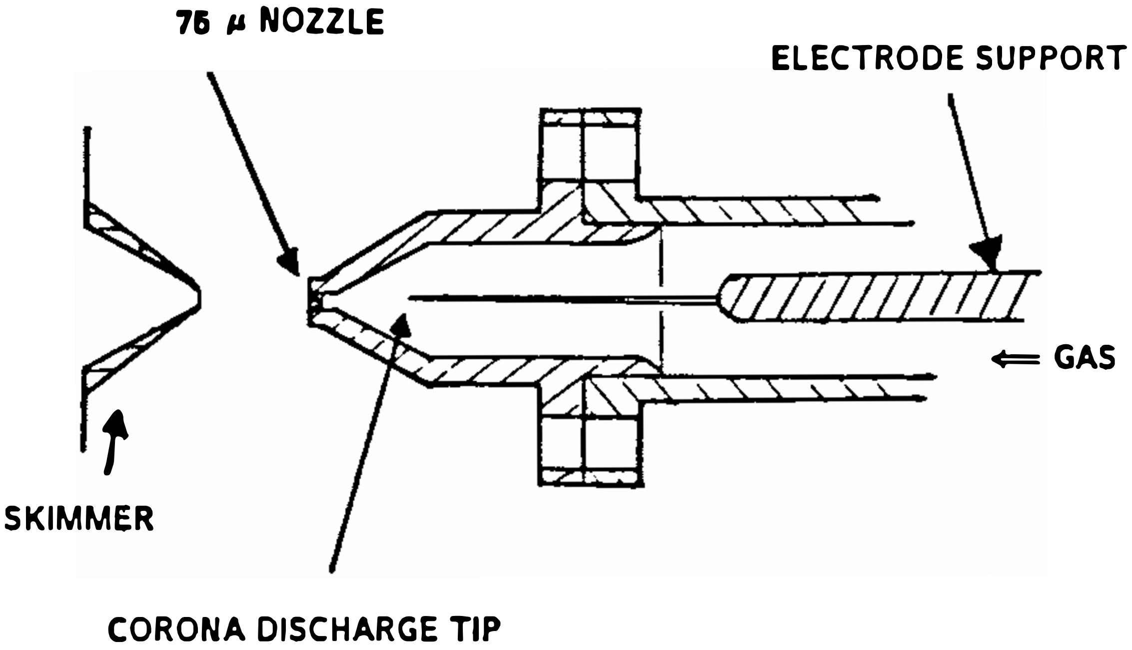

FIGURE 5-1 Schematic of the corona discharge ion source.

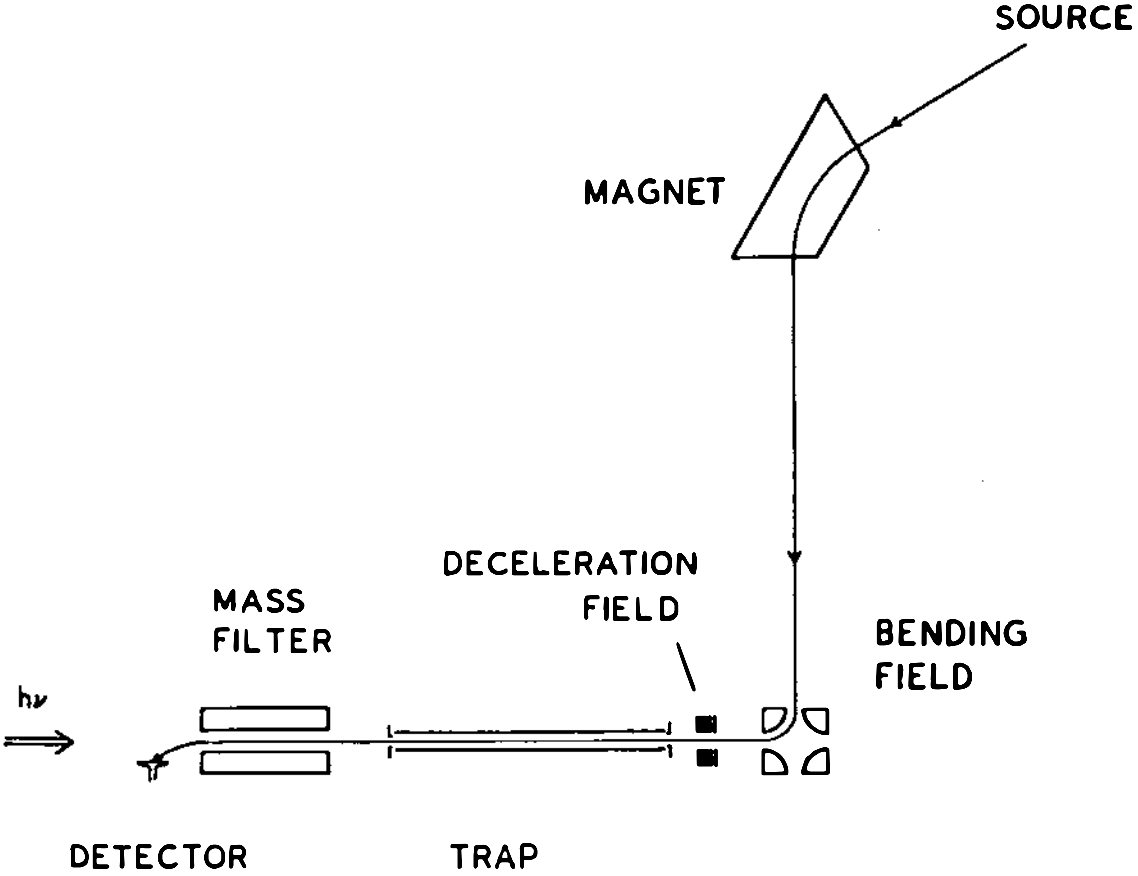

FIGURE 5-2 Schematic of the tandem mass spectrometer and octopole ion trap.

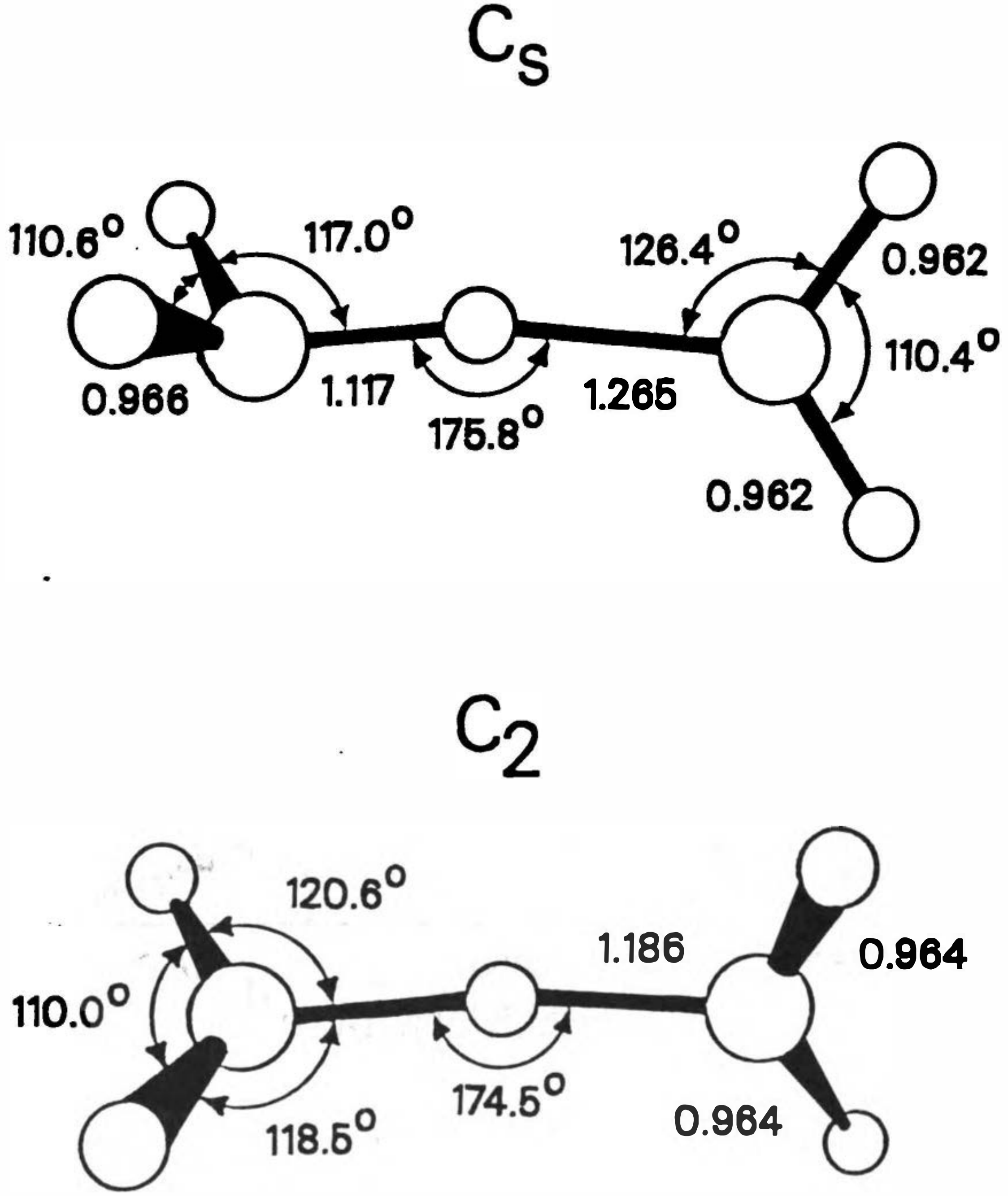

FIGURE 5-3 Two lowest energy structures for $H_5O_2^+$ using a DZ+P basis set and configuration interaction with single and double excitations.

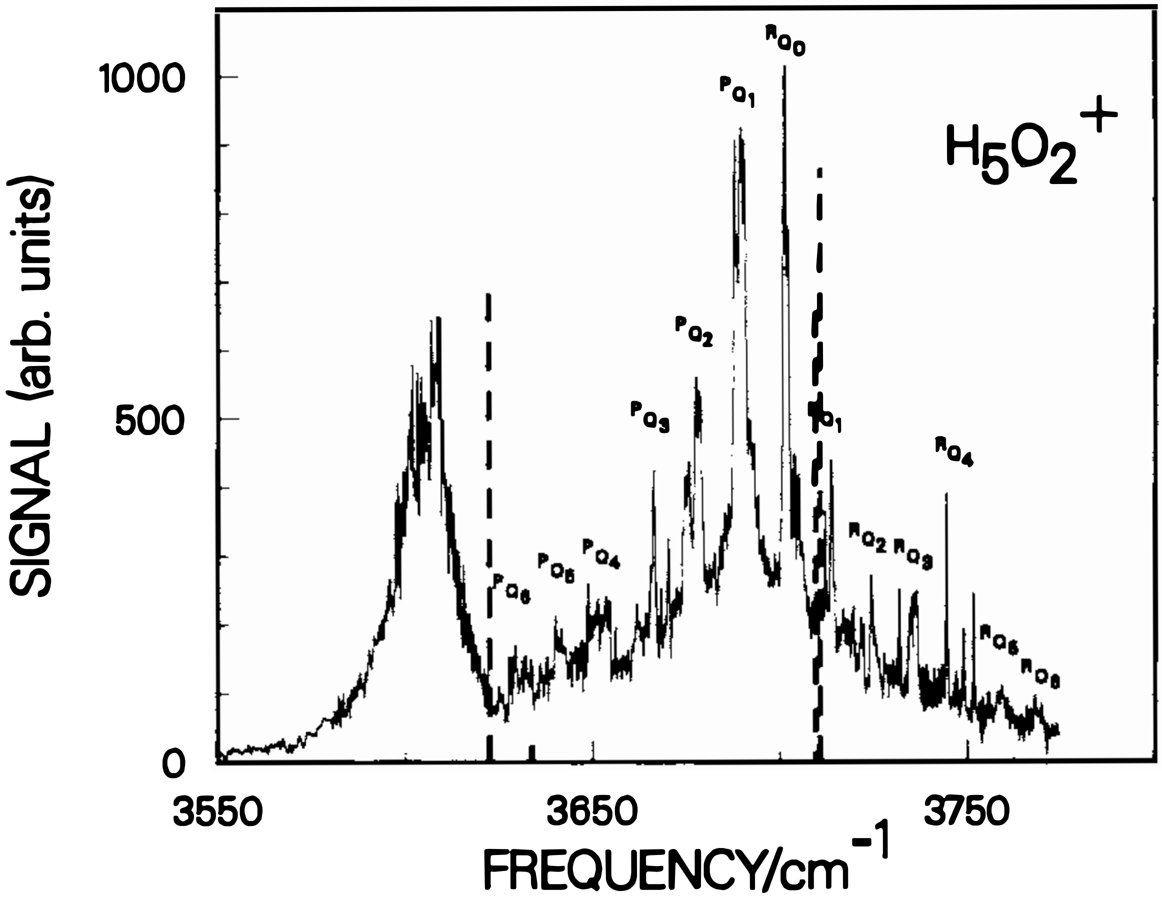

FIGURE 5-4 Infrared spectrum of $H_6O_2^+$ taken with the two laser scheme and detecting the H_3O^+ dissociation product. The linewidth of the F-center laser was 0.5 cm^{-1}. The dashed lines correspond to the *ab initio* CISD frequencies and intensities for the C_2 geometry.

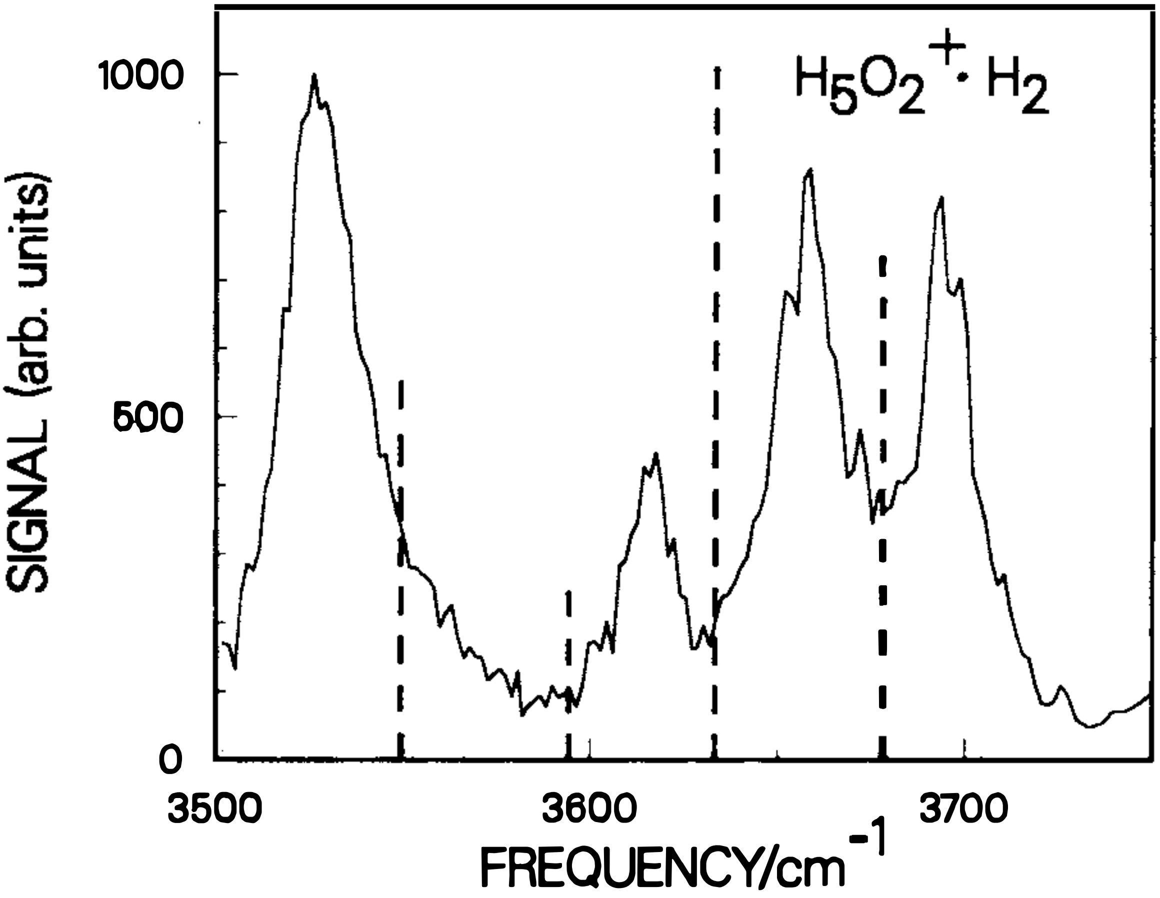

FIGURE 5-5 Infrared spectrum of $H_5O_2^+ \cdot H_2$ taken using the Quanta-Ray IR-WEX ($\Delta\nu \sim 1.2$ cm^{-1}) and detecting the $H_5O_2^+$ dissociation product. The dashed lines correspond to the *ab initio* SCF frequencies and intensities for the C_S geometry.

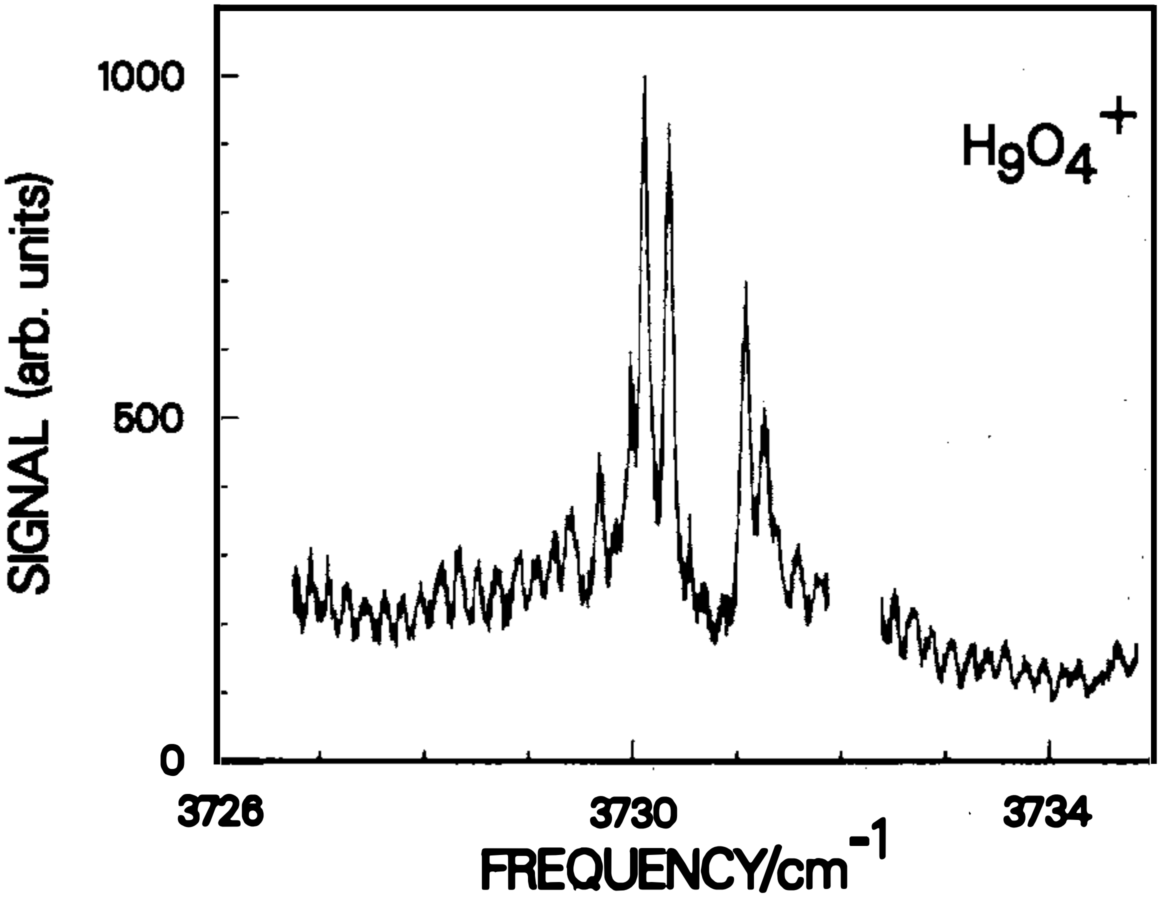

FIGURE 5-6 Infrared spectrum of $H_9O_4^+$ taken with the two laser scheme. The F-center laser was operated with its intracavity etalon giving it a theoretical linewidth of 3 x 10^{-5} cm^{-1}. The Doppler width due to the motion of the trapped $H_9O_4^+$ moving back and forth in the ion trap was 0.02 cm^{-1}. $H_7O_3^+$ dissociation product was monitored as a function of the F-center laser frequency.

6

SPECTROSCOPY OF IONIC CLUSTERS

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Introduction

Researchers involved in a variety of subdisciplines of molecular science are currently exploring cluster techniques as a means of creating well defined ensembles which mimic properties of complex condensed phase systems.[1] For example, one might wish to prepare an ensemble of microparticles containing a specific number of molecules to study its reaction chemistry, electronic properties, catalytic activity, and physical state. Such an ensemble is not however, easily obtained, as each particle would usually consist of weakly bound components in an unsaturated valence state, leaving it unstable with respect to disproportionation unless locked inside a cryogenic matrix.

The method of choice for generating clusters of unstable species involves cooling the molecular components in a supersonic expansion.[2] Here, the expanding gas supercools to a few degrees Kelvin and begins to condense, but condensation is left incomplete owing to the rapidly decreasing density. This type of source creates a distribution of cluster sizes containing up to several hundred atoms or molecules. The major difficulty with such experiments at present is that associated with selecting a single, specific cluster from this ensemble for detailed investigation. The study of ionic clusters has long been recognized as an alternative that allows both identification and cluster selection by mass spectrometry. In the past few years, experiments have begun to appear that utilize mass analysis of cluster ions for selection prior to further study. In this report, we describe briefly some experiments that use charged clusters[3] so that a specific species aggregate can be isolated by mass spectrometry. In one set of experiments, Cu_n^- clusters are thermalized by collisions with helium buffer before mass selection to establish the temperature of the ensemble. Photoelectron spectra are recorded for each n, $1 < n < 11$, yielding information on the electronic structure of the neutral copper clusters. An important extension of this technique uses pulsed ion beams, a pulsed photodetachment laser and time of flight photoelectron energy analysis. This method has been applied to the $[N_2O_2^-]$ system, where PES is used to explore the properties of three different isomers with this stoichiometry. Finally, we present recent results from photodissociation experiments aimed at understanding the detailed effect of solvent molecules on reactions in condensed phases. In this study, Br_2^- ions, which have been surrounded by a specified number of carbon dioxide molecules, are photodissociated, and the strength of this CO_2 cage is probed by observing its effectiveness in facilitating recombination of the dissociated atoms. A dramatic increase in caging efficiency is observed for clusters containing approximately 12 CO_2 molecules, indicating especially stable structures in this size range.

High Resolution PES With a Flowing Afterglow Ion Source

A major problem in many cluster experiments is characterizing the physical state of ions isolated at a specific mass. In one solution to this problem, a flowing afterglow, fast-flow reactor has been configured as an ion source whose negative ion beam could be injected into a high resolution continuous-wave (cw) laser photoelectron spectrometer.[4,5] The advantages of the afterglow source include its great versatility in creating ions via controlled reaction sequences and the control it offers over the internal energy of the ions. [Ions are thermalized for many milliseconds in the He flow (several torr) before extraction.] A dramatic example of the cooling afforded by the afterglow was seen in the photoelectron spectrum of CH_2^-, where vibrational hot bands, ubiquitous in the spectrum obtained with discharge sources, are absent after cooling in the afterglow.[5] This source, with adaptation of a sputtering region,[7] has proven to be a simple source of bare metal cluster ions. It has been employed to obtain[6,7] visible photoelectron spectra of Fe_2^-, Co_2^-, Re_2^-, and Cu_n^- with $1 < n < 11$.

Leopold et al.[7] have obtained high resolution (~10 meV) photoelectron spectra of Cu_n^- from $n = 1$ to 10 at 488 nm (2.54 eV) with the results displayed in Figure 6-1. The inherent resolution of the continuous device is evident in the sharp feature in Cu^- and the resolved vibrational structure in the dimer spectrum. Higher clusters show an overall increase in electron binding energy with cluster size-dependent features. There is a rapid alternation of electron binding energies between consecutive even and odd clusters, with odd numbered clusters having larger binding energy, similar to the trend observed by the Smalley group[8] using threshold photodetachment. For the clusters $n = 4$, 5, 7, and 10, there are two well resolved features in the spectra showing the location of some electronically excited states in the Cu_n *neutral* cluster. The ability to obtain information on electronic states of selected neutral cluster species is one of the greatest appeals of this technique.

The success of this study portends a rich area of research as a variety of pure and metal, alloy and semiconductor clusters are probed via photoelectron spectroscopy (PES). This cw laser photoelectron technique is particularly promising as a high resolution tool to characterize those species with electron affinities less than 3.5 eV or when one is primarily interested in the low-lying electronic structure of the neutral species. The application of PES either to systems with higher electron affinity or to probe deeper into the neutral electronic structure, however, requires photodetachment with hard ultraviolet light and falls in the domain presently only covered by pulsed lasers. Extensions of photoelectron techniques to incorporate such laser sources are described in the following section and in Smalley's contribution to this report.

Pulsed Photoelectron Spectroscopy of Mass Selected Negative Ions

While it has been evident for some time that the pulsed supersonic expansion is an easily implemented means of achieving high density, internally cold molecular beams,[9] such expansions have only been used as cluster ion sources in the past few years. In 1984, it was shown[10] that ionization of a pulsed expansion with a high energy (1 keV) electron beam formed a dense, transient plasma, which can be controlled to create cluster ions by nucleation onto monomer ions. The essential feature of this source is that the direct ionization process generates cations and slow secondary electrons in addition to scattered high energy electrons. The slow electrons are thermalized in the ambient temperature of the expansion and neutralize the plasma. This medium is ideal for synthesizing negative ion clusters since the dissociative electron attachment process

$$e^- + A_n \rightarrow A_m^- + (n-m)\,A \qquad (6.1)$$

is quite efficient at low temperature.[11] Thus, simply ionizing a pulsed free jet with an electron beam serves to create an intense pulsed source of negative ions. In 1986, Posey, DeLuca, and Johnson[12] demonstrated an apparatus that efficiently overlaps the pulsed ion with a pulsed laser beam to carry our PES in the ultraviolet. Their apparatus is shown in Figure 6-2, and uses time-of-flight to mass separate and spatially focus parent ions. The laser is timed to intercept a specified mass at the focus, and photoelectrons are energy analyzed by field-free time-of-flight. A magnetic TOF photoelectron spectrometer with very high collection efficiency and operable with pulsed ultraviolet light sources has been developed by Smalley,[13] and promises new opportunities in the study of the growth of bulk electronic structure.

Typical TOF photoelectron spectra from this source are shown in Figure 6-3, where an O_2^- calibration spectrum is displayed in the upper trace and the spectrum from the $O_2^-{\cdot}N_2$ cluster is shown in the lower trace. The spacing of the peaks in the lower spectrum matches that of the O_2 molecule, allowing a definitive assignment of the structure of this ionic cluster as the ion-molecule complex $O_2^-{\cdot}N_2$, and the separation of the origins gives an estimate of 0.27 eV for the binding energy of N_2 to O_2^-. Posey and Johnson[12] have systematically investigated whether one can prepare the analogous clusters $O^-{\cdot}N_2O$ and $NO^-{\cdot}NO$, and they find that three distinct species can be selectively formed with stoichiometry $[N_2O_2^-]$. One of these species has an unresolved photoelectron spectrum and also photodissociates to NO^-, detected via its photoelectron spectrum. This ion behaves as expected for a resonance stabilized $NO^-{\cdot}NO$ dimer anion. A third ion can be synthesized starting from O^- and N_2O, but this ion only photodissociates below 3.5 eV to O^- product ions, analogous to the behavior observed for the isoelectronic CO_3^- molecular ion.

The capability of isolating cluster ions in different isomeric forms is interesting since these forms can correspond to intermediates in ion molecule reactions. In the $N_2O_2^-$ case, two of the above clusters exist at minima on the potential energy surface of the

$$O^- + N_2O \rightarrow NO^- + NO \qquad (6.2)$$

reaction. Since the reaction complex can be captured at specific points along the surface, one can envision triggering the reaction to occur with a laser and thereby to investigate the reaction dynamics evolving from well-defined initial conditions. As a first attempt to study photoinduced reactions using the cluster environment, we have investigated the recombination of halogen atoms photodissociated within a cluster as a function of cluster size as described in the next section.

Recombination of Br_2^- Photodissociated Within Mass Selected Ionic Clusters

Over the past 15 years, several groups have been intrigued by the role of the solvent cage in the dynamics of chemical reactions in solution. A very productive approach has been to determine the rate of atom recombination using picosecond pump-probe techniques.[14,15] Typically, the time dependence of a diatomic absorption feature is monitored after the diatomic is dissociated with a short laser pulse. An important question only indirectly addressed in such studies is what fraction of the atoms break outside the solvent cage and migrate away as free atoms. Using cluster techniques, photodissociation can be carried out within clusters of a particular cluster size, and the quantum yield for diatom dissociation determined directly. As a prototype system, we have chosen Br_2^-, which can be dissociated via a charge transfer continuum absorption covering the range 700 to 300 nm. The unsolvated Br_2^- ion is first produced by electron beam interaction with a free jet of 1% Br_2 in CO_2, and the larger clusters $Br_2^- \cdot (CO_2)_n$ $(0 < n < 24)$ are grown by subsequent ion-molecule reactions in the expansion. The Br_2^- moiety is photoexcited above its dissociation limit, and the relative quantum yield for the two processes,

$$\begin{aligned} Br_2^- \cdot (CO_2)_n + h\nu &\rightarrow Br_2^- \cdot (CO_2)_m + (n-m)\, CO_2 \quad \text{"uncaged"} \qquad (6.3) \\ &\rightarrow Br_2^- \cdot (CO_2)_p + (n-p)\, CO_2 \quad \text{"caged,"} \end{aligned}$$

are measured for each n. The fraction of ionic fragments which contain two bromine atoms is a direct measure of the quantum yield for separation of the atoms outside the solvent cage. In this fashion, the quantum yield for caging at 820 nm, 700 nm, and 355 nm [1.5, 1.8, and 3.5 eV, respectively] has been measured[16] with the results displayed in Figure 6-4. Note that the bond energy of isolated Br_2^- is ~1.2 eV so that these wavelengths are above the dissociation energy. A dramatic increase in caging efficiency occurs around $n = 12$ at each wavelength, with complete caging above $n = 12$ at the two red wavelengths. It is interesting that caging is still ~60% efficient with 3.5 eV excitation (355 nm), which requires dissipating 2.3 eV of initial recoil energy. This efficiency is remarkable in light of the relatively weak binding energy of the CO_2 monomers onto the ionic cluster (~0.25 eV). These results evidence a structural property of the $n = 12$ and higher clusters where the diatomic bromine core is surrounded by a complete solvent shell of CO_2 molecules.

Having demonstrated that clusters can be used to explore the role of solvent molecules in this prototype chemical reaction, a new direction for this research is opening, where one can explore the timescale of the recombination using picosecond pump-probe techniques on the ion beam. Such time-resolved experiments appear feasible and have the potential to provide qualitatively new information on chemical reaction dynamics in a microsolvent environment.

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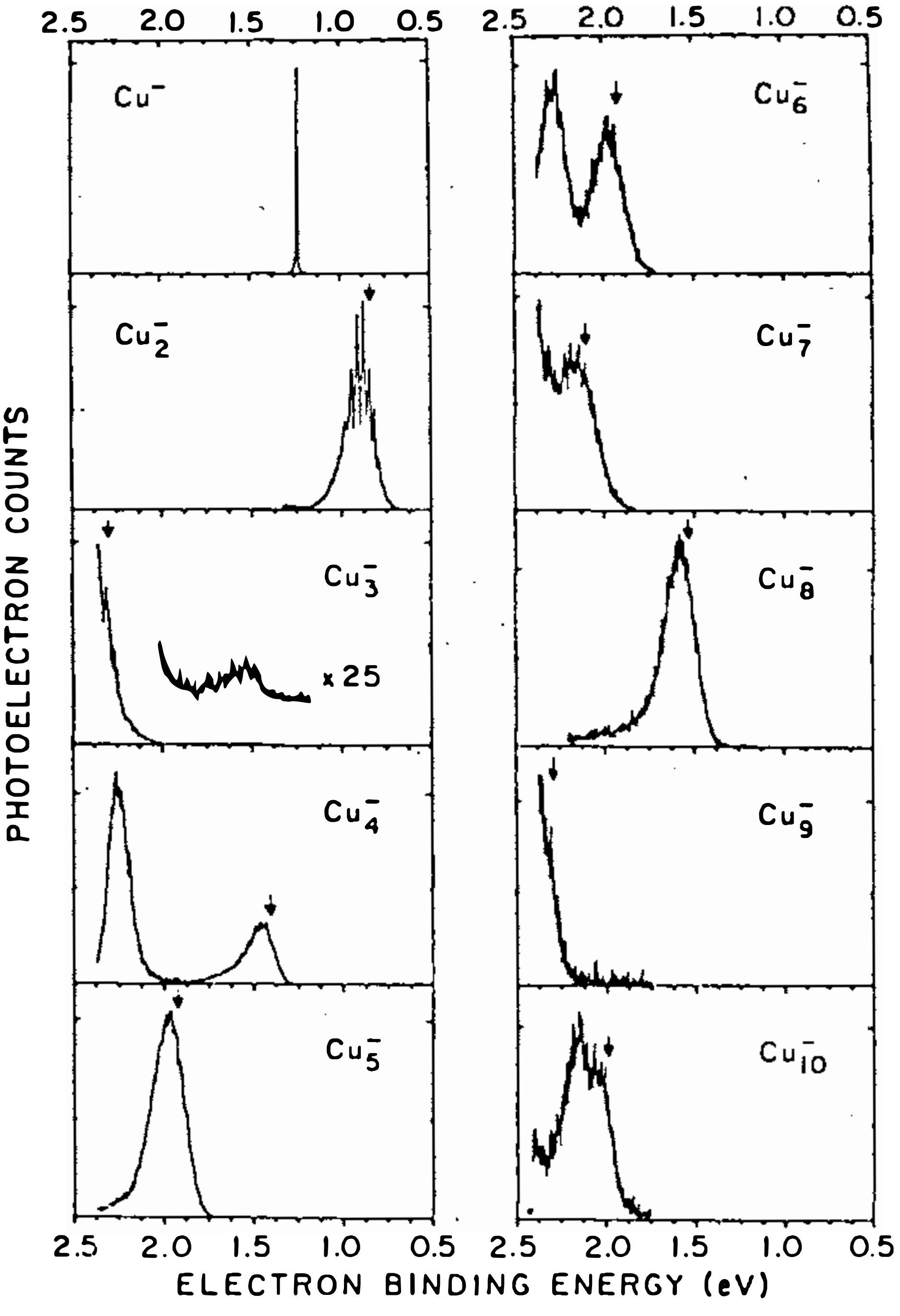

FIGURE 6-1 Photoelectron spectra of Cu$_n^-$ obtained[7] at 488 nm (2.540 eV) or 458 nm (2.707 eV) with an electron energy resolution of <10 meV. Vibrational structure is resolved for Cu$_2$ only. The arrows indicate positions of adiabatic electron affinities; for Cu$_3^-$ and Cu$_9^-$, the arrows show minimum values. Transitions to excited electronic states of the neutral Cu$_4$, Cu$_6$, Cu$_7$ and Cu$_{10}$ clusters are also apparent as a second peak to the left of the ground state feature.

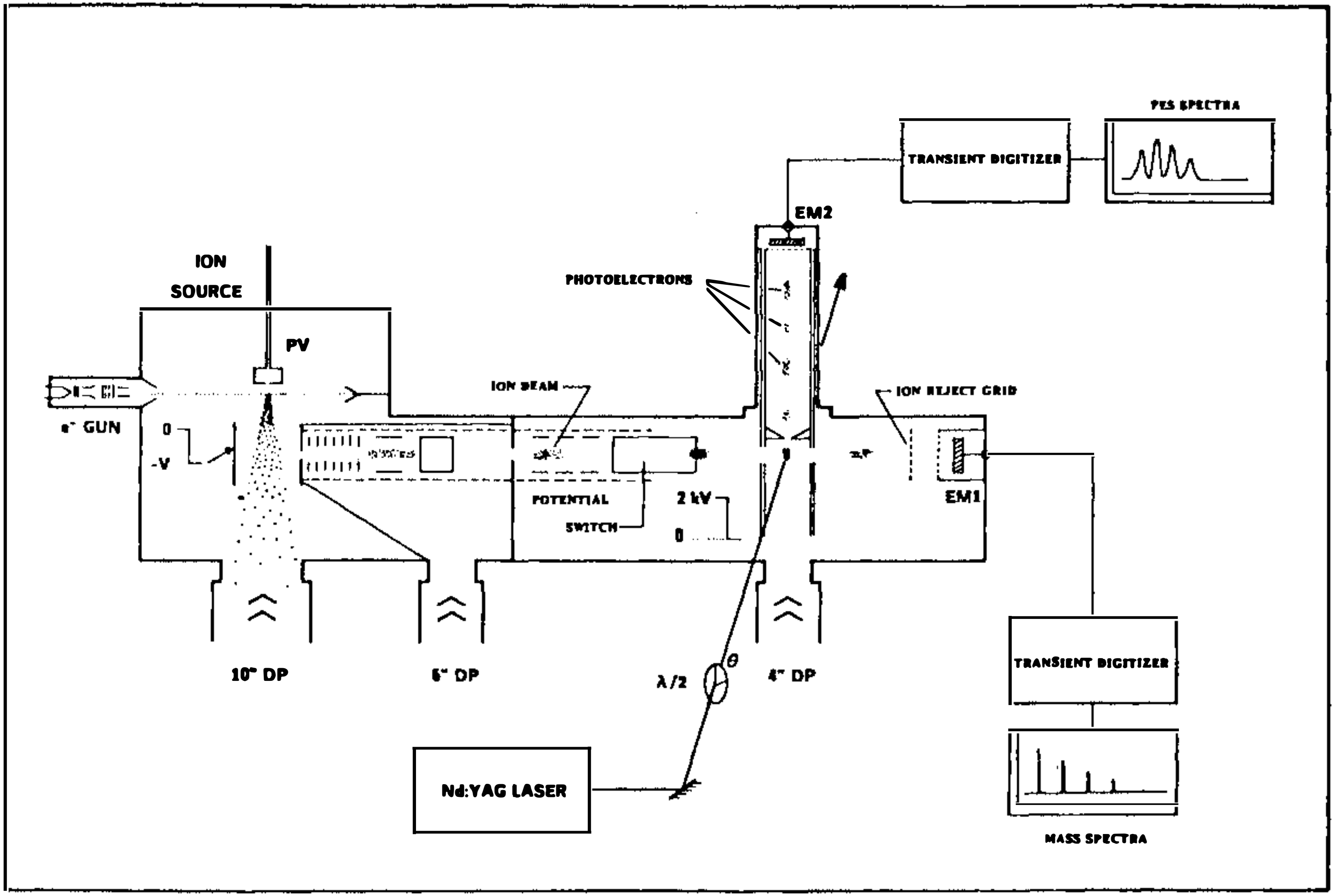

FIGURE 6-2 Schematic diagram of the Pulsed Negative Ion Photoelectron Time-of-Flight spectrometer developed[12] by Johnson and coworkers.

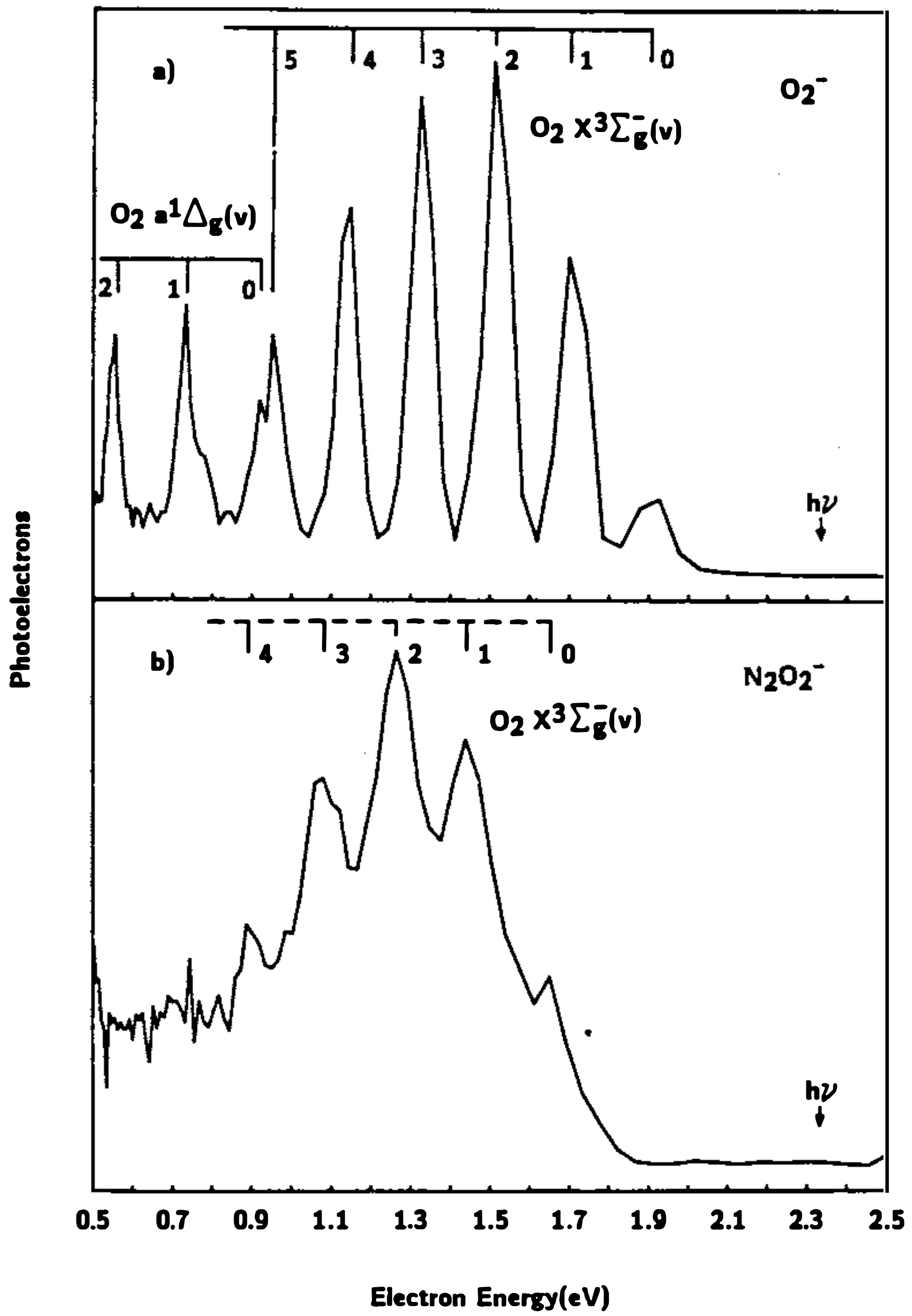

FIGURE 6-3 Time-of-flight photoelectron spectra of O_2^- and $N_2O_2^-$ obtained[12] with the apparatus shown in Figure 6-2. The spectra show that this particular $N_2O_2^-$ isomer is of the form $O_2^- \cdot N_2$.

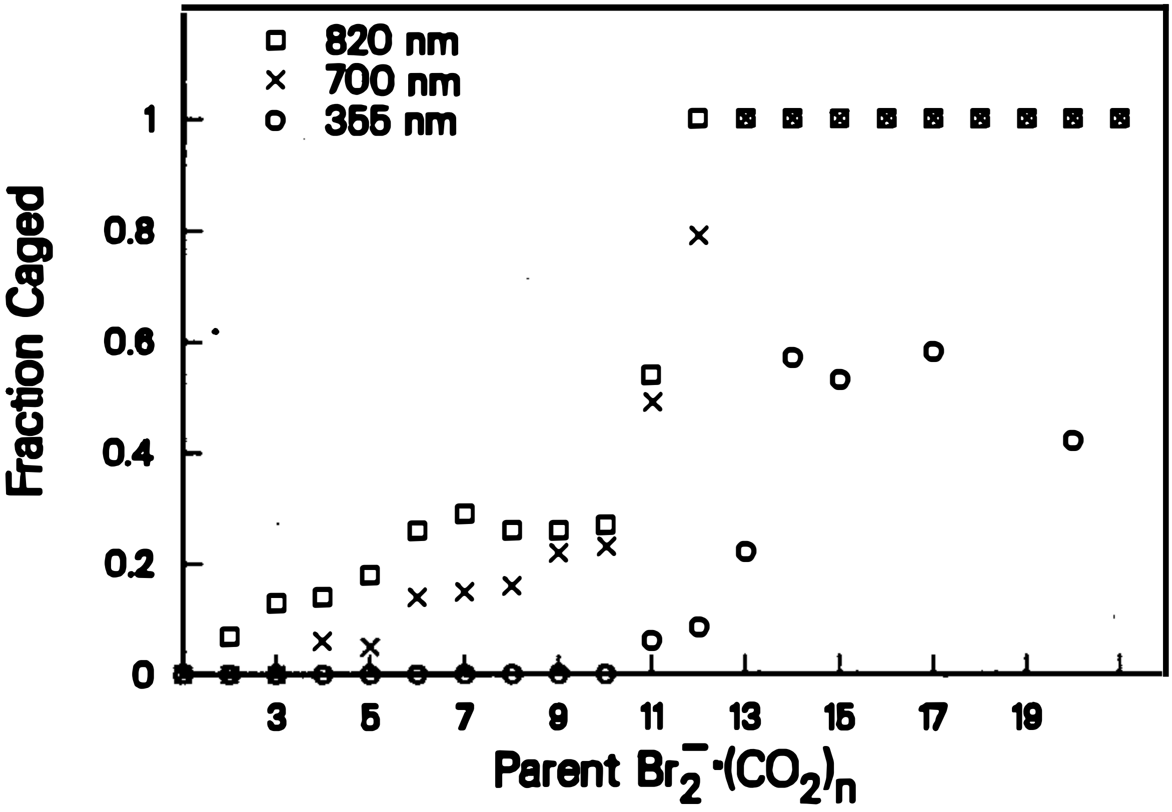

FIGURE 6-4 The caged fraction of $Br_2^-\cdot(CO_2)_n$ photodissociation products as a function of cluster size, n. The different wavelengths correspond to dissociation energy releases of approximately 0.3, 0.6, and 2.3 eV, respectively.

7

ADVANCES TOWARD A MOLECULAR SURFACE SCIENCE

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Introduction

In recent years a rather remarkable evolution of molecular beam experiments has taken place. This evolution is remarkable not so much in the high level of the technology involved, or the increasing level of intricacy and sophistication. Such technical evolution has been proceeding fairly continuously ever since the first crude experiments several decades ago. What is remarkable is that a qualitative change is taking place in the very subject matter of these experiments.

Rather than being limited to the study of intrinsically atomic or small molecule phenomena, the newest molecular beam machines are quite at ease with quite large assemblies of atoms--at times extending to species where the atom count runs into the hundreds. Although these species are still molecular in the sense that they contain a definite number of atoms bound in a particular way, the physics and chemistry of these species is often quite distinct from the small molecule realm. In many respects these objects are nearly macroscopic.

For example, consider even a rather small cluster molecule, one composed of 10 atoms of nickel. Techniques have now been worked out that permit beams such metal clusters to be prepared quite routinely.[1] They can be cooled to near absolute zero, and studied either as a neutral, or a cold ion, either positive or negative.[2,3] They can be extracted from the beam and trapped in an inert matrix, or injected into a superconducting magnet and trapped in an electromagnetic field for long periods[4] without "touching" anything.

Since nickel is a fairly refractory metal, one expects the nickel atoms in Ni_{10} to be bound to each other rather strongly. There will be an inside and an outside to such a molecule, and this outside *surface* of the Ni_{10} molecule should be the dominant player in any physical or chemical processes one might wish to study. In this respect Ni_{10} is no different from most medium sized molecules studied by classical organic and inorganic chemists. But in almost all other respects, Ni_{10} is *very* different.

This 10th cluster of nickel is a microscopic piece of metallic nickel. Using the new cluster beam techniques, its surface chemistry is now beginning to be studied, and this chemistry is far more like the catalytic dissociative chemisorption of bulk nickel surfaces than it is like the chemistry of an isolated nickel atom or organo-nickel complex.[5] Most small molecules studied by conventional molecular beam techniques exist in a single well-defined ground electronic state with the first excited electronic state several eV higher in energy. In sharp contrast, Ni_{10} is estimated to have a vast number of excited electronic states within 1 eV of the ground state.

It is instructive to estimate just how vast this number of low-lying excited states can be for even this rather small cluster. The current feeling about the bonding in transition metal clusters on this far right hand side of the periodic table is that they are held together predominantly by interaction of the 4s atomic orbitals. In the case of nickel, each atom comes to the cluster with one 4s electron and nine 3d electrons. The 4s electrons become involved in the bonding, while the $3d^9$ holes remain primarily intact around each atom. For each atom there are (including spin) 10 possible states of the $3d^9$ hole, so the total number of electronic states of Ni_{10} for a given type of 4s bonding is 10^{10}!

For small molecules the paradigm for physical science is that of the atom: find the individual eigenstates and fit their energy patterns to that of a simple Hamiltonian. While this has been a fine formula for successful science in small molecules, it is clearly useless for a molecule with 10^{10} electronic states. Some other approach will be necessary to understand these Ni_{10} molecules, and one obvious place to look is the concepts and machinery of solid state physics and surface science. Instead of talking about individual quantum states and wavefunctions, one is better served to consider bands of states, and the variations in spatial extent and nodal properties with energy.

The Molecular Surface Science Approach

This electronic state catastrophe is just one example of the microscopic → macroscopic transition that is making a qualitative change in the subject matter of modern cluster beam experiments. Other examples include the question of what is the best view of the bonding in the molecule: is it like balls held together with sticks, or a set of smeared out ion cores bound together by a sea of electrons? Or questions of dynamics: e.g., how does one handle the electronic degrees of freedom, or the concept of strain release during fragmentation of a large framework?

However, along with these new conceptional worries comes a whole new set of reasons to be doing such experiments in the first place. Since these clusters act in many ways like a bulk surface, they should serve as excellent "molecular models" of such surfaces.[6] In fact, to many scientists currently involved in this cluster beam field, this molecular model aspect is the principal appeal. Since such small clusters are ideally suited for detailed theoretical treatment at the highest level, the physics and chemistry of such clusters may well turn out to be one of the most critical testing grounds for the development of a truly powerful, predictive surface science.

As an example of the sort of new information that is being revealed by this approach--and a rather different example from that of the nickel clusters just mentioned--a short summary of recent work on carbon is presented below. In this case cluster beam "molecular surface science" has already produced major new insights into how this ubiquitous element handles the problem of forming a surface. Although still quite young, the cluster beam field is extremely active. Many wonderful experiments have been carried out on a wide range of transition metals, semiconductors, and other main-group elements, and there are already many pretty stories to be told. What follows is only a sample.

Laser Vaporization Cluster Beam Source

Perhaps the single most crucial development that has triggered this new field is the cluster source itself. The bulk surfaces one generally wants most to study are those of fairly refractory metals like nickel or iron or platinum, or semiconductors like silicon or gallium arsenide. How can these materials be brought into the gas phase, cooled to form clusters in a controlled way, and formed into a collisionless cold beam suitable for detailed study?

One very general and powerful answer is to use a pulsed laser to vaporize the desired material.[1] With suitably short laser pulse durations and appropriate pulse energies, the vaporization temperature can easily be driven to tens of thousands of degrees in such a short time that no heat transfer occurs to the bulk supporting structure of the source. Any material is therefore easily vaporized without heating large portions of the apparatus.

Figure 7-1 shows a version of such a device as it is currently implemented in our laboratory at Rice. Here a disk of the material to be vaporized (carbon in this case) is mounted so that it can rotate and translate as the focussed laser vaporizes material from a 1-mm diameter spot on its surface. The vaporized atoms and small molecules are entrained in an intense pulsed jet of helium travelling at near sonic velocity down a 2-mm diameter tube passing near the surface of the disk. The helium serves as a thermalizing bath, and prevents diffusional loss of the vaporized atoms and molecules to the walls. As the gas travels downstream through the nozzle, clusters begin to form. By controlling the residence time in the nozzle (sometimes by addition of such devices as the "integration cup" shown in the figure) the extent of clustering can be controlled over a broad range.

In addition to serving to cool the vapor plume produced by the laser and helping the cluster formation and growth, this near-sonic flow of helium serves as the main expansion fluid of an intense supersonic expansion as the gas exits the nozzle and exhausts into a large vacuum chamber. Collimated beams skimmed from these intense supersonic expansions then contain ultracold clusters of the material vaporized off the disk. Under fairly readily achieved conditions, these clusters can be cooled within a few degrees of absolute zero. While in the supersonic beam, the clusters are all travelling in complete absence of collisions in a single direction with a very narrow velocity distribution--a superb environment in which to study their chemical physics.

Carbon Clusters

One of the most striking observations yet made with one of these supersonic cluster beam sources has involved the clusters of carbon. Figure 7-2 shows a section of the time-of-flight mass spectrum of carbon clusters prepared by laser vaporization in a supersonic nozzle such as that just described. The results are really quite bizarre.[7] Here it is clear that some extraordinarily facile process is contriving that only even-numbered clusters of carbon will exist in this mass region of the cluster distribution. Actually, more extended traces of the mass spectrum have shown that under the nozzle conditions pertaining the bottom trace of Figure 7-2, this even-numbered distribution extends well out past 200 atoms.[8] What has happened to the odd clusters?

Even more perplexing is the fact that this even-numbered carbon cluster distribution is strongly dependent on the gas flow conditions in the nozzle at the time of vaporization. As the helium carrier gas density is increased, and as the over-all residence time of the vaporization species is increased in the nozzle by addition of the "integration cup," the C_{60} cluster becomes increasingly dominant. As seen in Figure 7-2, the top trace corresponds to the maximum possible residence time in the nozzle, and here C_{60} is found to be 50 times more abundant than any other cluster in the region, except C_{70}. What is so special about the 60th cluster? Whatever it is, the mass spectrum makes it clear that such clusters as C_{58} and C_{62} have not even a trace of the aspect that favors C_{60}. The 70th cluster is clearly also special, but, ultimately, it too loses out in competition with C_{60}.

As my colleagues and I argued in a short letter in Nature[7] a little over a year ago, one very intriguing possible explanation of this behavior has to do with the symmetry of the number 60. The largest point group possible is the icosahedral group which has 120 symmetry elements. Of these only 60 are proper symmetry operations (i.e., operations which do not involve a simultaneous rotation and reflection). The result is that 60 is the largest number of symmetrically equivalent vertices that can be arranged on the surface of a sphere. When these vertices are connected, the pattern that results is that of a truncated icosahedron--or, more familiarly, a soccer ball. If one arranges 60 carbon atoms in such a pattern, a strikingly beautiful new bonding arrangement of carbon results as shown in Figure 7-3.

Since this structure reminds one of the geodesic domes invented by R. Buckminster Fuller, we (partly in jest) suggested the rather inelegant name of "buckminsterfullerene" for this bizarre structure of carbon. The virtue of this structure is, of course, that it is an exceptionally wonderful way for carbon to solve the problem of forming a surface without generating any dangling bonds. Neither bulk diamond, nor graphite has this ability. The surface dangling bonds of diamond are rendered inert only with the aid of hydrogen atoms, while graphite surfaces are free of dangling bonds only parallel to the hexagonal sheets. At some point these two-dimensional sheets must terminate, and there again one either has dangling bonds or hydrogen atoms to terminate the structure.

This spheroidal structure of C_{60} is topologically an entirely new configuration for carbon. Due to the perfect symmetry of 60, this structure has no edges, no corners, no ends. It is an edgeless molecule.

With no dangling bonds it should be quite inert to further growth and chemical attack. Indeed this inertness has now been verified by a variety of supersonic cluster beam experiments involving fast-flow chemical reactors attached to the end of the cluster-formation nozzle.[8]

Remarkably, this absence of chemical reactivity was found to apply not only to C_{60}, but to all the even numbered clusters in the 40- to 100-atom size range. In retrospect, however, this is easy to understand. Using pentagons and hexagons one can construct an infinite set of increasing large geodesic domes. Each such carbon shell must contain exactly 12 pentagons, but may contain any number of hexagons. In order to be closed, there always must be an even number of carbon atoms. For example, Figure 7-4 shows a reasonable structure for a 72 carbon cluster. This geodesic model therefore has a natural explanation of the occurrence of only even numbered clusters in the mass spectrum.

These structures all appear quite reasonable. In fact a wide variety of quantum chemical calculations have been published now on such forms of carbon, and in each case the quantum methods that work well for other aromatic forms of carbon predict these spheroidal shells to be stable and reasonably tightly bound.[10,11]

But how is it that such special, extraordinarily low entropy forms of carbon jump full-formed out of the laser-vaporization plume over a graphite disk? In thinking about this problem, my colleagues and I have been led to propose a mechanism[9] which may have wide relevance to such diverse problems as the formation of soot in candle flames and interstellar dust in the vicinity of carbon-rich stars. The notion is that as the small carbon radicals begin to grow in the condensing carbon vapor, they pass through the size range, (approximately 1 to 24 atoms) of linear carbon chains and monocyclic rings.[12] As they grow above this size range they begin to sample polycyclic aromatic ring structures--the graphitic sheets. Since the sheets must have edges with a large number of dangling bonds, these are extremely reactive forms.

But, unlike the corresponding polycyclic aromatic hydrocarbons, there is no reason to think that these graphitic sheets will prefer to be flat. In fact, if one of the peripheral hexagonal rings is rearranged to a pentagon, one finds that two things happen: (1) the sheet begins to curl, and (2) a new carbon-carbon bond can now be formed from what were previously two dangling bonds in the original flat sheet.

There is therefore an intrinsic tendency of graphitic sheets to curl back on themselves by the incorporation of pentagonal rings during the growth process. Now as such a curling sheet continues to grow (and curl) its growth edge will ultimately come back around to the vicinity of the opposite edge of the sheet.

Generally one expects that these edges will only rarely be just right to join to each other to form a closed spheroidal shell. More often one edge will simply grow past its counterpart and continue growing and curling. The result will be that one edge will be buried beneath the growing shell of the other. The result is the fascinating structure shown in Figure 7-5, somewhat similar to a snail shell--but it's a snail shell that spirals in three dimensions. The resultant structure of carbon is quite an interesting general model for any environment in which carbon is nucleating and growing to form soot.

The suggested model for these bizarre, large, even clusters of carbon is therefore that they are the closed graphitic spheroids which were "dead-ends" on the growth process to form soot. As such they tend to persist as molecular clusters in the gas phase even after most of the carbon has condensed. The most symmetrical of these, C_{60}, persists longer because its high symmetry distributes the strain evenly over the entire surface, thereby rendering the molecule exceedingly difficult to attack.

Cold Cluster Ion Beams and the Tandem Time-of-Flight

Just recently, further verification of this picture of the surface formation of carbon clusters has come from a new generation of experiments that study the singly charged positive ions of the clusters. It has proved possible to devise supersonic cluster sources where not only the neutral clusters, but also the positive and negative clusters, emerge from the nozzle.[2] Most importantly these charged clusters form a dense plasma, which is perfectly balanced: there are exactly as many negative clusters as there are positive clusters. As a result, there is no net space charge and the cluster ions move through the beam apparatus just as though they were neutral particles. They are therefore cooled by collisions with the helium carrier in the supersonic expansion, and are available at any point downstream whenever cold cluster ions of a particular charge are desired.

Of course, one of the great advantages of the charged clusters is that they can be extracted from the beam and mass-selected by simple electrostatic time-of-flight techniques.[13] A number of groups have now begun to exploit this new technology as a way of making very detailed studies of particular clusters without the fear that their results will be affected by the simultaneous presence of other clusters in the beam.

In the cluster lab at Rice, this cluster ion beam technology has been used to examine the photophysics of such clusters as C_{60}^{+}. Here the cluster ion is extracted from the supersonic beam, mass selected (by time-of-flight), and injected into a second apparatus. Here it is irradiated by an ultraviolet photolysis laser beam. After a delay of roughly 5 μsec, the result of this irradiation is probed by subjecting the clusters to a second time-of-flight mass analysis.

A typical result[14] is shown in Figure 7-6. The C_{60} cluster has so many internal degrees of freedom that it nearly behaves as a macroscopic object. In order to observe any fragmentation at all one must deposit over 20 eV of excess energy into the molecule. In the experiment of Figure 7-6 this has been achieved by multiphoton excitation. The primary photoprocess is loss of C_2 to form the next smallest spheroidal cage structure, C_{58}^{+}. At the high fluence used here, this C_{58} daughter cluster fragments again to form a granddaughter fragment, C_{56}^{+}. This process continues with successive C_2 ejections until C_{32}^+ is formed. This cluster is so highly strained that it explodes into small carbon chain fragments.

Silicon and Germanium Clusters

Once again this stress-induced explosion is another example of how a macroscopic concept proves to be the most relevant for these molecular clusters. A somewhat different but quite similar phenomenon has been found recently in the case of silicon clusters. Unlike carbon, silicon shows no tendency to form spheroidal cages. In the observed cluster distributions from a supersonic silicon cluster source, all possible cluster sizes are found with roughly equal intensity--both odd- and even-numbered clusters. However, when one looks at the photofragmentation of particular large clusters very dramatic results are found. For example, Si_{60}^+ (to pick a random example!) is found to exhibit two competing primary photoprocesses: (1) evaporative loss of an atom to form Si_{59}^+, and (2) stress-induced explosion into at least 6 small pieces.[15] Even more striking is the observation that these small pieces are exclusively found to have between 6 and 11 silicon atoms. This same photofragmentation pattern applies to all silicon clusters, and occurs similarly for germanium clusters as well (although here Ge_{10} loss is by far the most dominant fragmentation channel).

These general observations of explosive fragmentation into 6 to 11 atom pieces may be a vital clue as to how silicon and germanium go about the process of restructuring their surfaces in order to tie up the dangling bonds.

Summary and Outlook

As was mentioned in the introduction, cluster beam techniques are in a sensationally rapid period of development and discovery. Within the past year two other major technological advances unmentioned above have come into operation. One of these is a general technique for injecting the mass-selected cluster ions from a cluster beam source into a superconducting magnet. The chemistry and photophysics happening on the surface of such magnetically trapped clusters can be monitored at sensational mass resolution by the techniques of Fourier transform ion cyclotron resonance. Another major technological breakthrough is a general method for recording the ultraviolet photoelectron spectrum of the clusters through photodetachment of the corresponding negative cluster ion. This will provide a critically important general view of the evolution of the molecular orbital ("band") structure of the clusters as a function of size, surface adsorption, and detailed constitution.

Such continued developments in this young field of cluster beams increase our optimism that "molecular surface science" may not be such a wild idea after all.

Acknowledgments

Research on the properties of bare metal clusters at Rice is funded by the Department of Energy, Division of Chemical Sciences; while that on chemisorbed cluster species is funded by the National Science Foundation. Our studies of semiconductor clusters have been funded by the U.S. Army Research Office. Support particularly for our carbon cluster research has also been provided by the Robert A. Welch Foundation, and the Exxon Education Fund.

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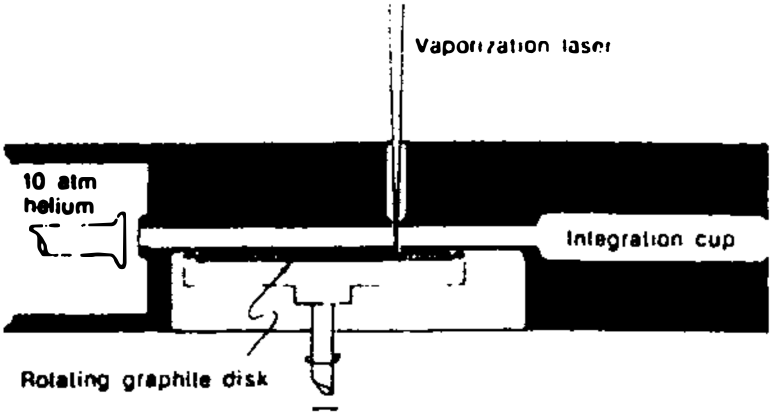

FIGURE 7-1 Rotating disk source used to produce supersonic cluster beams by laser vaporization.

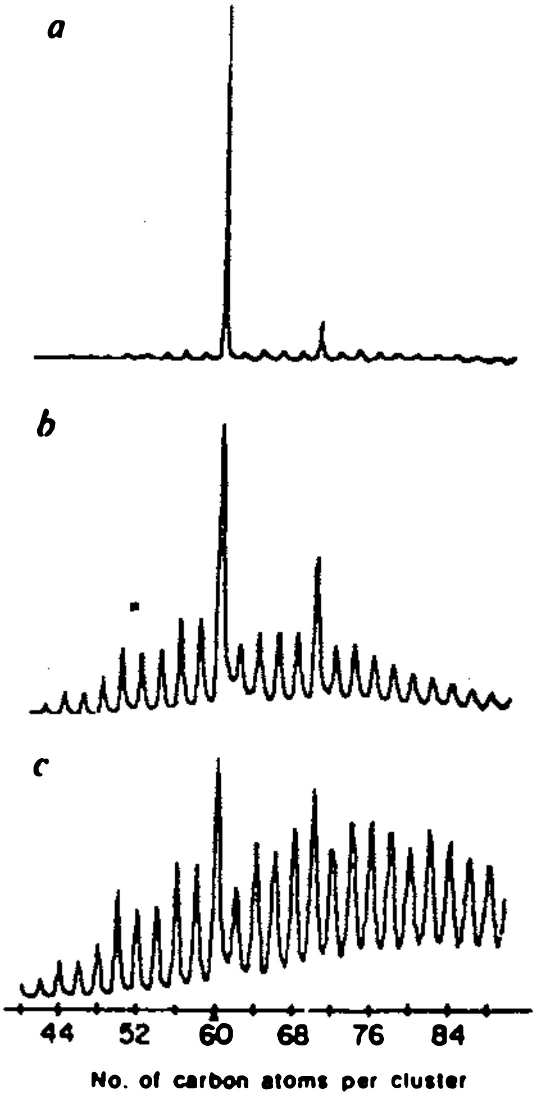

FIGURE 7-2 Section of the time of flight mass spectra of carbon clusters prepared in a supersonic beam by laser vaporization under three different nozzle conditions. Note that only the even numbered clusters are present, and that the 60th and 70th cluster become increasingly prominent in the upper mass spectra.

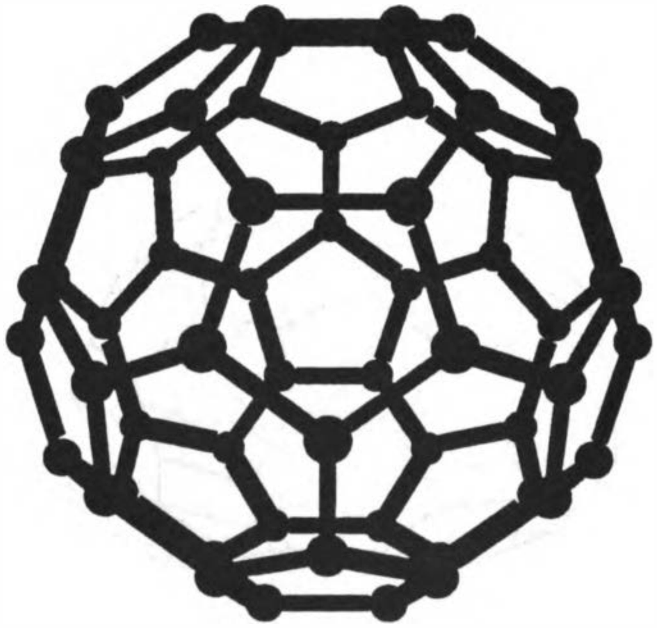

FIGURE 7-3 The proposed "soccer ball" structure for C_{60}.

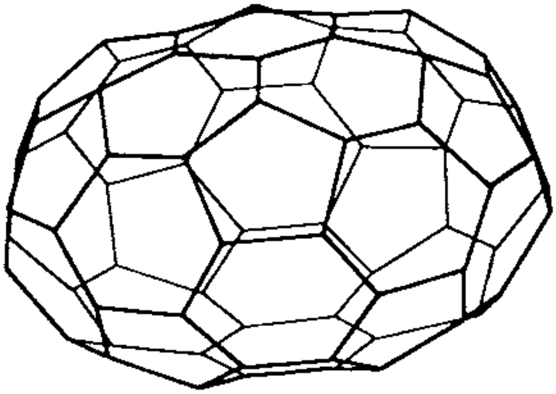

FIGURE 7-4 A "carbon pillow" structure proposed for C_{72}.

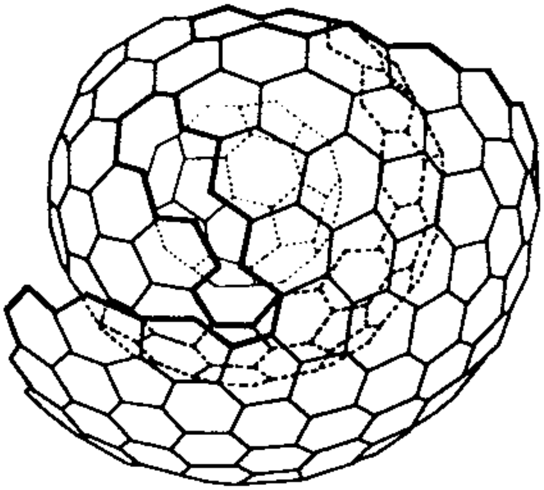

FIGURE 7-5 Spiraling graphitic structure suggested as the nucleus for growing soot particles.

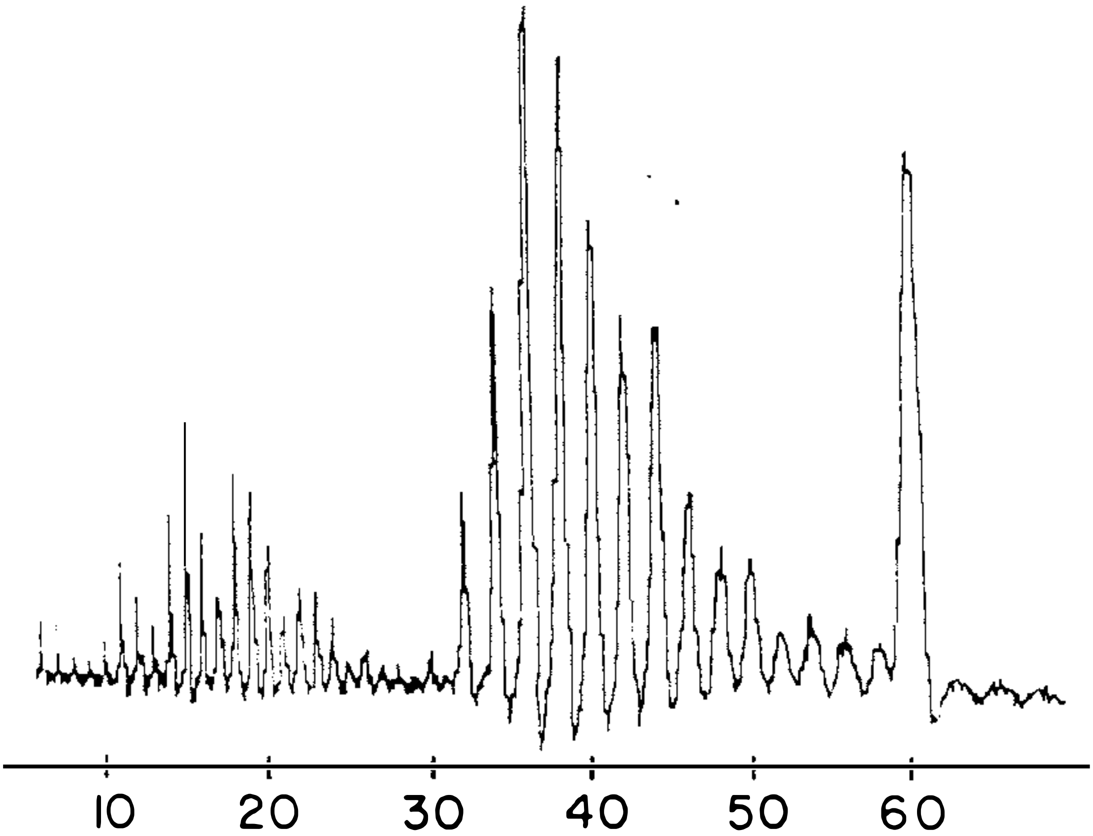

FIGURE 7-6 **Photofragmentation pattern of C_{60}^+ at rather high fluence of a Nd:YAG laser beam at 362 nm.**