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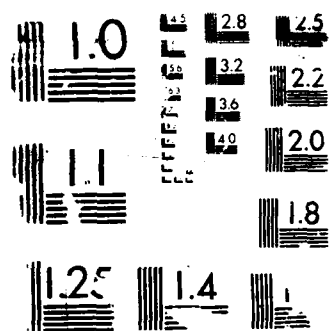
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Under the previous grant, research has been carried out on translation-to-vibration, rotation (T-V,R) transfer excitation processes and reactive events of photolytically-produced "hot" atoms which have kinetic energies of 1-3 eV. We describe the past accomplishments of laser and infrared probing in systems such as $H + NO$, $H_2D + HF$, and collisional dissociation of $Br_2(B,v',J')$. We then discuss recent successful efforts to construct an apparatus to produce even more highly energetic neutral atoms and radicals by laser ablation techniques and the first results in obtaining translationally fast molecular and radical species.

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Accomplishments Under ARO Grant No. 21970-PH

Several years ago, our group, along with several others, discovered a highly utilitarian laser-based photolysis method to probe the dynamics of "hot" atom collisions.¹ The method has been used primarily to study collisions of translationally fast H and D atoms, which are produced with 1-3 eV in the laboratory frame by excimer laser photolysis of precursor molecules such as H₂S, HI, HBr, and HCl (designated H). The large disparity between the mass fragments in the photolysis ensures that most of the excess photon energy is deposited into translation of the H atom. The amount of translational energy in the H atoms is sufficient to produce substantial vibrational and rotational excitation upon collisions with molecules (T-V,R excitation). In addition, the high translational energy can also overcome reaction barriers. Since it is possible to generate high number densities of fast H atoms by the laser technique, the products of both reactive and inelastic collision events can be studied in great detail. Studies of fast atom dynamics are relevant to the rapid reactions of detonation phenomena and the combustion of energetic fuels.

A variety of methods have been used by various groups to probe the resulting product states, including laser-induced fluorescence, infrared fluorescence, coherent anti-Stokes Raman spectroscopy, and diode laser probing. A thorough review of all the experiments has recently appeared,² and thus only a brief mention of several of the categories of experiments which have been carried out will be given here.

Some of the earliest investigations involved explorations of the T-V transfer probabilities of fast H and D atoms with molecules. Work from our group investigated for example H,D + HCl,^{1,3} H,D + CO,⁴ and H + NO.^{5,6} Work from the Flynn and Weston groups studied H + CO₂ and H + CH₃F.² In addition

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to the pure T-V excitation, in our studies of $\text{H} + \text{HCl}$, as reported in the previous three year grant renewal, we also investigated reactive exchange probabilities and the vibrational excitation resulting from both the T-V and exchange events. The Flynn and Weston groups have pioneered rotational state observations in the T-V transfer.² Other groups also invested efforts in reactive events, such as demonstrated by the numerous studies on $\text{H}, \text{D} + \text{H}_2, \text{D}_2$ ^{7,8} and $\text{H} + \text{CO}_2$.^{9,10}

As a result of the many high quality experimental measurements that became available to elucidate the dynamics of these hot atoms collisions, there has been a tremendous surge of theoretical interest in these problems as well. The theoretical studies extend from the simplest $\text{H} + \text{H}_2$ ¹¹ to the more complex $\text{H} + \text{CO}$ ^{12,13} and NO .^{14,15}

Here we review some of the accomplishments in this field of research which have been carried out with the last three years' support from ARO. These consist of detailed studies of the T-V and R inelastic excitation of NO by fast H atoms,⁶ the inelastic and reactive vibrational excitation of HF by fast H and D atoms¹⁶ and the companion theoretical work by G. C. Schatz on the same subject,¹⁷ and a new type of study, the investigation of the probabilities of collision-induced dissociation of excited bromine molecules by translational impact.¹⁸ At the end of this section we give a cumulative list of the publications that have resulted from our ARO grant.

Our first studies on the $\text{H} + \text{NO}$ system were carried out by infrared fluorescence and provided detailed vibrational distributions and overall efficiencies for the T-V collisional excitation.⁵ Because of the very high velocity of the H atoms, the collision frequency was too fast to isolate the effects of just the first collision, given the relatively slow response of the infrared detectors. This is a difficult problem not only for the infrared

detection, but for many experiments performed by other techniques as well. In order to clarify the extent to which the observed vibrational distributions might be a result of multiple collisions of the fast H atoms and also to extract the detailed rotational populations that accompany T-V excitation, we performed an experiment using time-gated laser-induced fluorescence (LIF) to study the T-V,R collisions of $\text{H} + \text{NO}$.⁶

In the time-gated LIF experiment, a thermal sample of NO and H_2S is photolyzed with a pulse from an excimer laser to produce fast H atoms. Figure 1 shows the experimental arrangement for these experiments, which consists of a photolysis laser and a tunable, frequency-doubled dye laser for detection of the NO states. The time between photolysis and detection is varied, along with the pressure, to ensure that the results are representative of just the first collision of the H atoms with NO.

In Fig. 2 a plot of the rotational populations versus time after the creation of the fast H atoms is shown. It can be seen that the rotational population distribution does change slightly, but only at very long times. Two effects contribute to the rotational state changes; these are collisions of NO molecules with H atoms that have been slowed and collisions of vibrationally and rotationally excited NO molecules with other NO molecules. The latter effect is a negligible contribution because of the much slower velocity of the NO molecules. We estimate that under the best conditions that we achieved (100 ns gate delay and the lowest pressure used while still retaining a good signal), there remains a considerable probability that the H atoms have undergone 2 collisions. Thus, some of the NO may have been excited by an H atom which has already been slowed. The fact that the rotational distributions are not changing dramatically from a 100 to 200 ns delay suggests that the H atoms must not be slowed markedly.

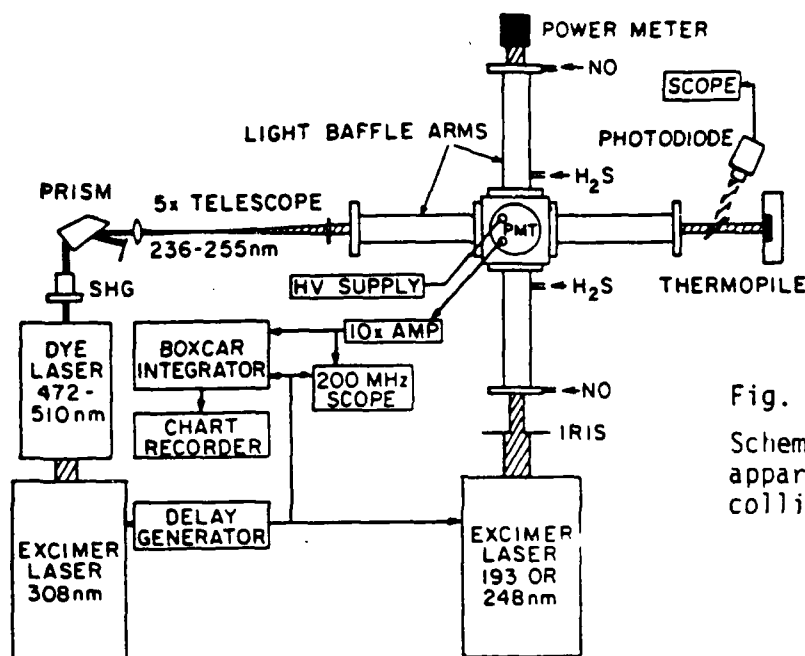


Fig. 1.

Schematic of experimental LIF apparatus for $\text{H} + \text{NO}$ T-V collisions.

Table 1.

Comparison of vibrational distributions of $\text{H} + \text{NO}$ by infrared and LIF methods.

ν	IR fluorescence ^a ($E_H = 2.2$ eV)	LIF ^b ($E_H = 2.2$ eV)	LIF ^c ($E_H = 0.95$ eV)
1	1.00	1.00	1.00
2	0.44 ± 0.05	0.59 ± 0.25	0.42 ± 0.25
3	0.13 ± 0.05	0.45 ± 0.25	...
4	0.09 ± 0.05	...	...
5	0.07 ± 0.04	...	...
6	0.05 ± 0.04	...	...

^a Reference 8; includes contributions from a number of collisions at successively lower collision energies.

^b This work; pulse/probe delay of 100 ns except $\nu = 3$ at 200 ns.

^c This work; pulse/probe delay of 200 ns.

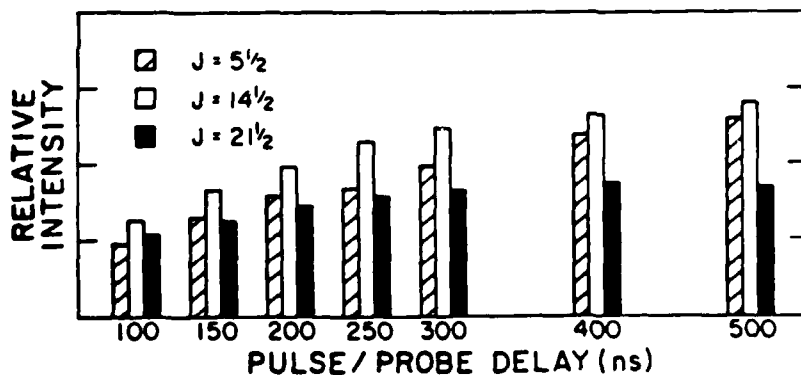


Fig. 2.

Variation of NO rotational populations as a function of gate time.

Table 1 provides a comparison of the vibrational distributions which have been extracted in the inherently slower infrared fluorescence experiments⁵ and the short-time LIF results.⁶ It can be seen from the table, once again, that the effects of multiple collisions are apparent in the infrared experiments, but do not alter the overall results dramatically. As expected, there is a tendency to observe somewhat colder vibrational distributions with the slower time observations of infrared fluorescence. Thus, it appears that the qualitative appearance of the vibrational results obtained by the infrared emission method are in fact reasonable.

The most exciting details to come out of the LIF experiments of $\text{H} + \text{NO}$ are the rotational distributions that accompany the T-V excitation as a function of vibrational level and kinetic energy. Several dramatic features are observed and are partly confirmed theoretically. The rotational excitation in three vibrational levels, $v=1,2,3$, was studied at a c.m. collision energy of 2.2 eV. The extent of rotational excitation is almost identical for all three states (Fig. 3). In addition, when the collision energy is varied from 2.2 to 0.95 eV, there is only a slight decrease in the rotational excitation of the $v=1$ state, from an approximate Boltzmann temperature of 1275 K to 1050 K (Fig. 4).

One theoretical treatment finds that the rotational excitation in $\text{H} + \text{NO}$ is relatively low and independent of vibrational state and gives good agreement with experiment. The results are explained by the fact that relatively "direct" hits are necessary to excite the vibration, resulting in little accompanying rotational excitation.¹⁵ However, another more complete study using all the electronic potential surfaces of the $\text{H} + \text{NO}$ system finds dramatic low and high temperature rotational components,¹⁴ which are not observed experimentally. Our experiments provide an important case for

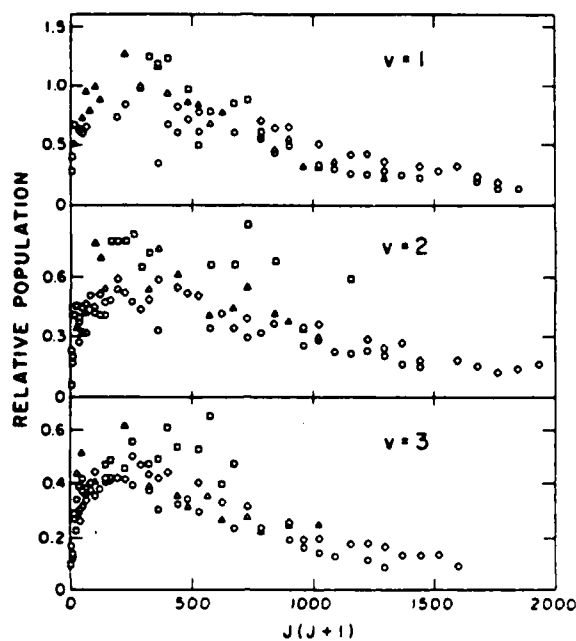


Fig. 3. Rotational populations in levels $v=1,2,3$ of NO.

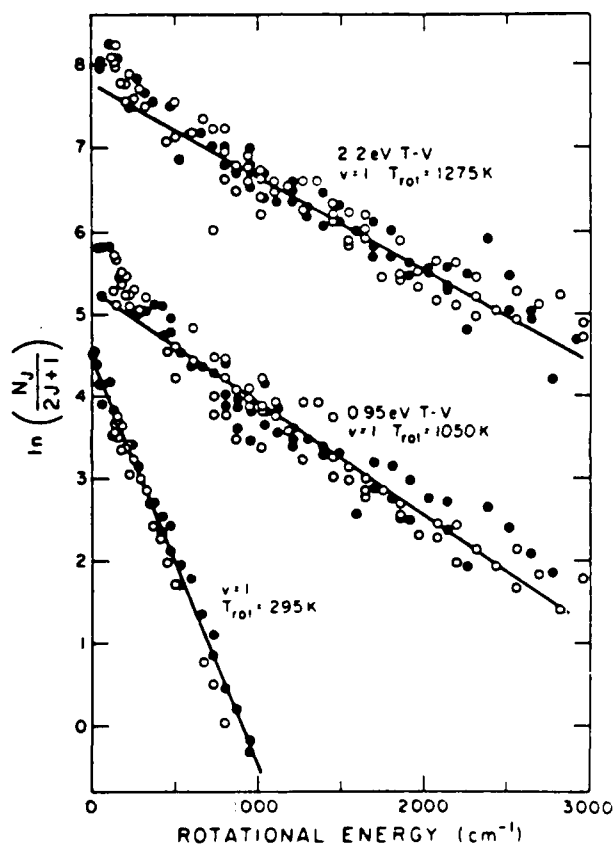


Fig. 4. Variation of rotational excitation in NO($v=1$) with $\underline{H}$ atom energy.

further testing of the exact features of the multiple electronic potential surfaces used to represent the complicated $H + NO$ system.

Our earlier investigations of the T-V transfer and reactive exchange of $H, D + HCl$, DCI revealed intriguing differences in the degree of vibrational excitation, depending on whether the reactive exchange or the direct inelastic excitation pathway was detected.³ By far, the most efficient vibrational excitation was observed for the case of H on HCl . Because of the large number of electrons in the HCl system, it is difficult to obtain accurate potential energy surfaces for these collisions. We therefore carried out a collaborative study with G. C. Schatz of Northwestern University, to investigate the T-V and reactive pathways of H, D with HF . Our experimental results were compared to Schatz' exact trajectory calculations on the best available potential energy surface. The results show remarkably good agreement and provide excellent explanations for the observed behavior.^{16,17}

Since infrared fluorescence is still the only readily available technique to detect vibrationally excited HF and DF , this is the method of choice in our experiments. The vibrational distributions are acquired for the excitation of $HF(v)$ in collisions of $H + HF$ at 2.2 eV and for the HF and DF products of $D + HF$. The detailed relative efficiencies of all pathways are obtained as well. Collisions of $H + HF$ are found to be three times more efficient than $D + HF$ at producing HF vibrational excitation. The $D + HF$ T-V channel deposits approximately two times as much energy in the HF molecules as the reactive exchange channel disposes in the newly formed DF product. Figure 5 shows a summary plot of the vibrational distributions for the two cases, which have been normalized for overall efficiency. In the plot, the HF and DF product pathways for $D + HF$ have been summed. It is clearly seen that the $HF(v=1)$ pathway for $H + HF$ is more efficiently populated than any other state. This

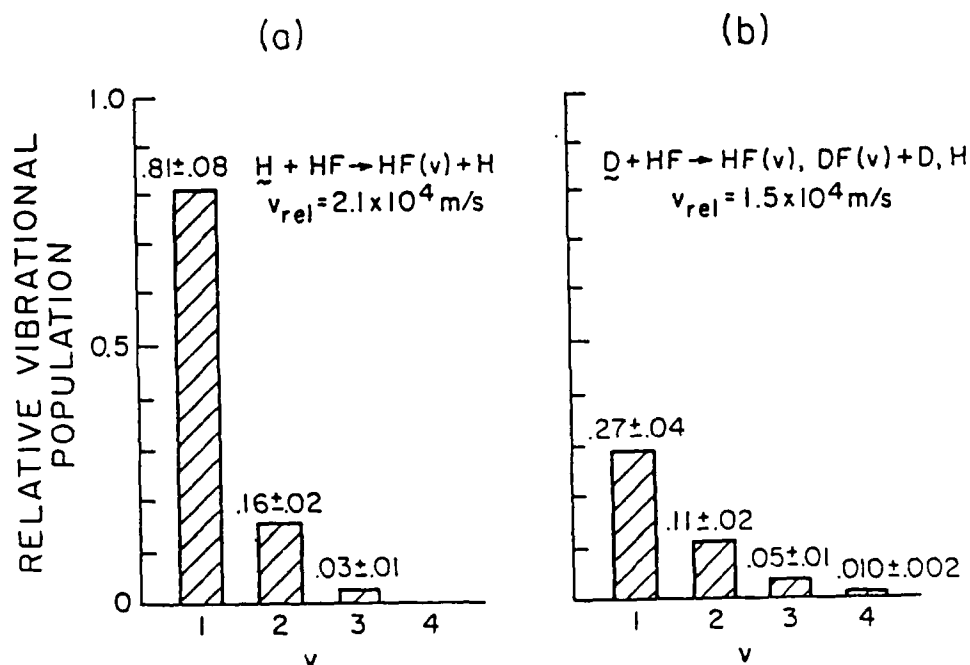


Fig. 5. Normalized vibrational population distributions for $\text{H} + \text{HF}$ and $\text{D} + \text{HF}$.

v	$\text{H} + \text{HF} \rightarrow \text{HF}(v) + \text{H}$		$\text{D} + \text{HF} \rightarrow \text{HF}(v) + \text{D}$		$\text{D} + \text{HF} \rightarrow \text{DF}(v) + \text{H}$	
	Expt ^a	Calc ^b	Expt ^a	Calc ^b	Expt ^a	Calc ^b
1	0.81 ± 0.08	0.88	0.65 ± 0.09	0.69	0.55 ± 0.09	0.49
2	0.16 ± 0.02	0.08	0.25 ± 0.05	0.21	0.25 ± 0.04	0.26
3	0.03 ± 0.01	0.04	0.10 ± 0.02	0.10	0.14 ± 0.04	0.19
4					0.06 ± 0.01	0.06

^aThe experimental results may be skewed to lower v 's by the multiple collision nature of the experiments.

^bRef. 24. Calculated at 2.3 eV relative translational energy.

The theoretical values for the first few states are normalized to compare directly to the experimental vibrational state distributions. Small populations in higher v -levels are also present.

Table 2. Comparison of experimental and theoretical (Schatz) vibrational populations for $\text{H} + \text{HF}$ and $\text{D} + \text{HF}$.

effect is fully explained by the Schatz calculation, where it is found to be due to a much higher probability of T-V excitation, particularly for the $v=1$ channel, when the higher velocity H atom is used compared to the D atom.

Equally interesting is the propensity of $\underline{D} + \text{HF}$ to populate higher v levels than that of $\underline{H} + \text{HF}$. This might appear at first to be in contradiction with simple impulsive models, which predict that the less efficient energy transfer process should correspond to a vibrationally colder state distribution. Schatz' calculations¹⁷ show that the slow D atoms have insufficient velocity to impart T-V excitation by impulsive collisions, but that the excitation comes about as a result of unsuccessful exchange reactions. This demonstrates that in systems in which chemical forces are important the excitation must involve both reactive and nonreactive parts of the potential surface. The particle velocity therefore plays a significant role in which mechanism dominates.

Table 2 shows a detailed comparison of our experimental results and the Schatz calculations. The agreement is excellent. Although the experiments are susceptible to multiple collisions, we believe that the high frequency of the HF vibration precludes any significant additional excitation by H atoms which have been slowed by one or more collisions. This can account for the generally better agreement with theory than might have been expected. From Schatz' calculations, we not only have detailed vibrational distributions, but also rotational populations and results for all the isotopic variants of the $\underline{H} + \text{HF}$ system. The trajectories have been "binned" to reveal which sorts of trajectories, incoming angles, and impact parameters result in T-V excitations and reactive exchanges. The excellent agreement with the experiments allows the body of theoretical results to be of high value, and the combined effort has resulted in a major understanding of the

dynamics of these processes.

As a further investigation of T-V processes in general, a new experiment was performed to probe the collisional dissociation of a diatomic molecule. Instead of using translationally hot atoms, the initial vibrational energy of the molecule below the dissociation limit is varied. This problem has been termed "collisional release" in the literature when applied to Br_2 and I_2 molecules. Our interest is to understand the concept of vibrational ladder climbing and the absolute probabilities with which a molecule will be collisionally dissociated to radical species. The results of such a study might then be generalized to consider also hot atom collisions that result in collisional dissociation.

The molecule we chose to study is Br_2 , which can be excited to the $\text{B}^3\Pi(0^+_u)$ state in selected vibrational and rotational energy levels. The energy of the vibration-rotation states can be varied from the dissociation limit to more than 1000 cm^{-1} below the dissociation limit. The molecular dissociation caused by thermal energy collisions (208 cm^{-1}) is then detected by monitoring the $\text{Br}^*(^2\text{P}_{1/2})$ electronically excited atoms produced. The experiments require a complicated series of measurements (Fig. 6): the relative and absolute yields of Br^* are measured, the total quenching rates of each v,J state are determined, high resolution absorption spectra of single isotopes of Br_2 are obtained with the tunable dye laser, and the absolute absorption cross sections are measured.¹⁸ These are the first results to interrogate single rovibronic states in the Br_2 system.

Figure 7 shows the summary of the results of many determinations to extract the efficiency of collisional dissociation for several collision partners, Ar, Xe, and Br_2 . The results are shown as a ratio, indicating the fraction of quenching events that produce collisional dissociation "upwards"

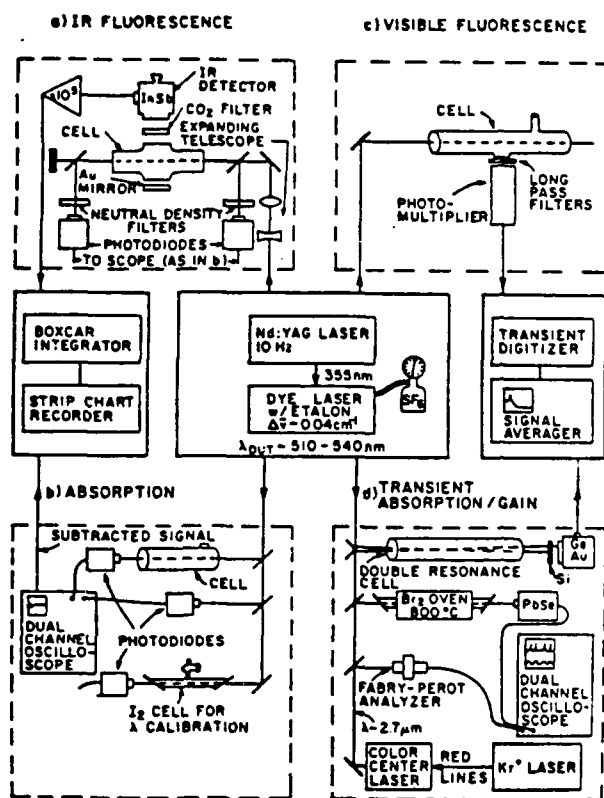


Fig. 6.
Apparatus for collisional
dissociation studies.

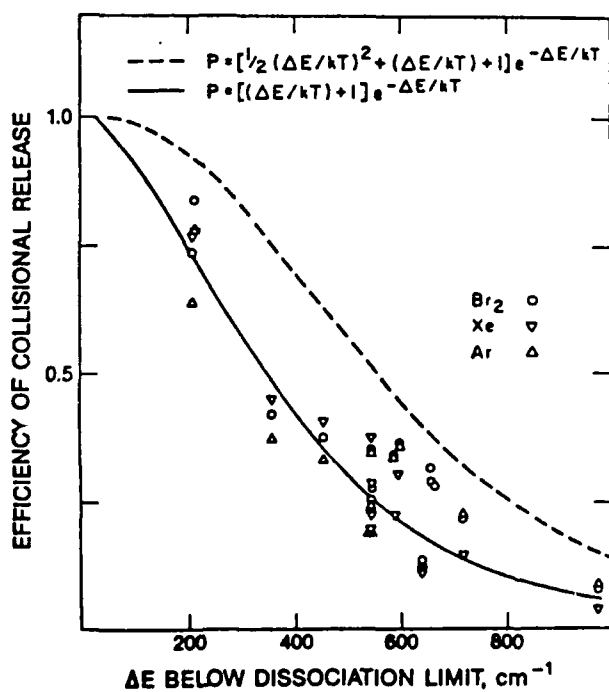


Fig. 7.
Efficiency of collisional
dissociation as a function of
state energy below dissociation.

in energy. It can be seen that at the energies nearest to dissociation the probability of collisional release is almost unity. Even at 5 kT below dissociation, the probability is large, 5-10%.

The most striking result in Fig. 7, however, is the fact that all of the collision partners behave identically; the results fit extremely well to a simple model for collisional dissociation based on total energy considerations. Past speculation has suggested that the release process may involve reactions to form complexes, e.g. $\text{Br}_2(\text{B}, \text{v}', \text{J}') + \text{Br}_2 \rightarrow \text{Br}_3 + \text{Br}^*$, which enhance the dissociation via their exothermicity. We see no evidence for the role of reactive product formation, as deduced from the similarity of our observed results for species of disparate polarizability. These results provide definitive new information on the mechanisms of collisional dissociation and will encourage new theoretical studies of these events.

With support from the present ARO grant, we recently completed construction of a new apparatus to study the formation and collisions of a variety of translationally fast atoms and radicals other than H atoms. Our emphasis is to use laser ablation techniques, which have been pioneered by various groups over the years,¹⁹⁻²⁸ to produce reactive atoms, radicals, metal vapors and other compounds with kinetic energies of 1-10 eV in the lab frame.

Laser ablation techniques have been used recently to study material removal properties for electronics fabrication.²⁵⁻²⁸ Because of the tremendous interest in dry etching for production of smaller and smaller semiconductors, the interaction of atoms, ions, and photon beams with surfaces and the mechanisms of removal of materials from solids are subjects of intense investigation.^{29,30} Our basic time-of-flight mass spectrometry investigations of the characteristics of laser ablation will be of interest in the fields of selective removal and deposition of materials.

The experiments of Friichtenicht²⁰ are most relevant to our work with the newly constructed apparatus. This apparatus is designed to produce translationally fast particles by laser vaporization of materials from surfaces. In a series of articles²⁰⁻²⁴, Friichtenicht and Wicke showed that atomic metals and other elements such as B, C, Mg, Si, Ti, Cr, Mn, Fe, Co, Cu, Ge, Mo, In, Sn, Ba, La, Ce, Nd, Ho, Au, Pb, Rh, and U could be formed with kinetic energies of 1-10 eV by laser vaporization of films that had been deposited on quartz slides. The high power pulsed laser was directed through the quartz to vaporize the film on the other side. This configuration produces primarily neutral fragments; ions are removed by collecting grids. By depositing fluorine-containing crystalline compounds on an epoxy film, reactive F atom beams of similarly high kinetic energies were achieved.²⁰ Various reactions of metal atoms with oxidants were carried out as a function of collision energy in their work.

Our apparatus is designed to improve upon the capabilities demonstrated in the early work on laser vaporization. In particular, we have built in sources to deposit materials continuously on the quartz window through the use of in situ metal ovens. The quartz window can also be cryogenically cooled to allow continuous condensation of volatile molecules on the window between laser pulses. Figure 8 shows the apparatus as it will be configured for the surface scattering, etching, and deposition experiments. We presently have the capability to create fast atoms and radicals, to measure their velocity distributions by time-of-flight, and to determine the composition of ablated particles by mass spectrometry.

The apparatus works as follows. A quartz window or other semi-transparent material is mounted in a differentially pumped chamber. Molecules or atoms are condensed continuously on the window by either cryogenic

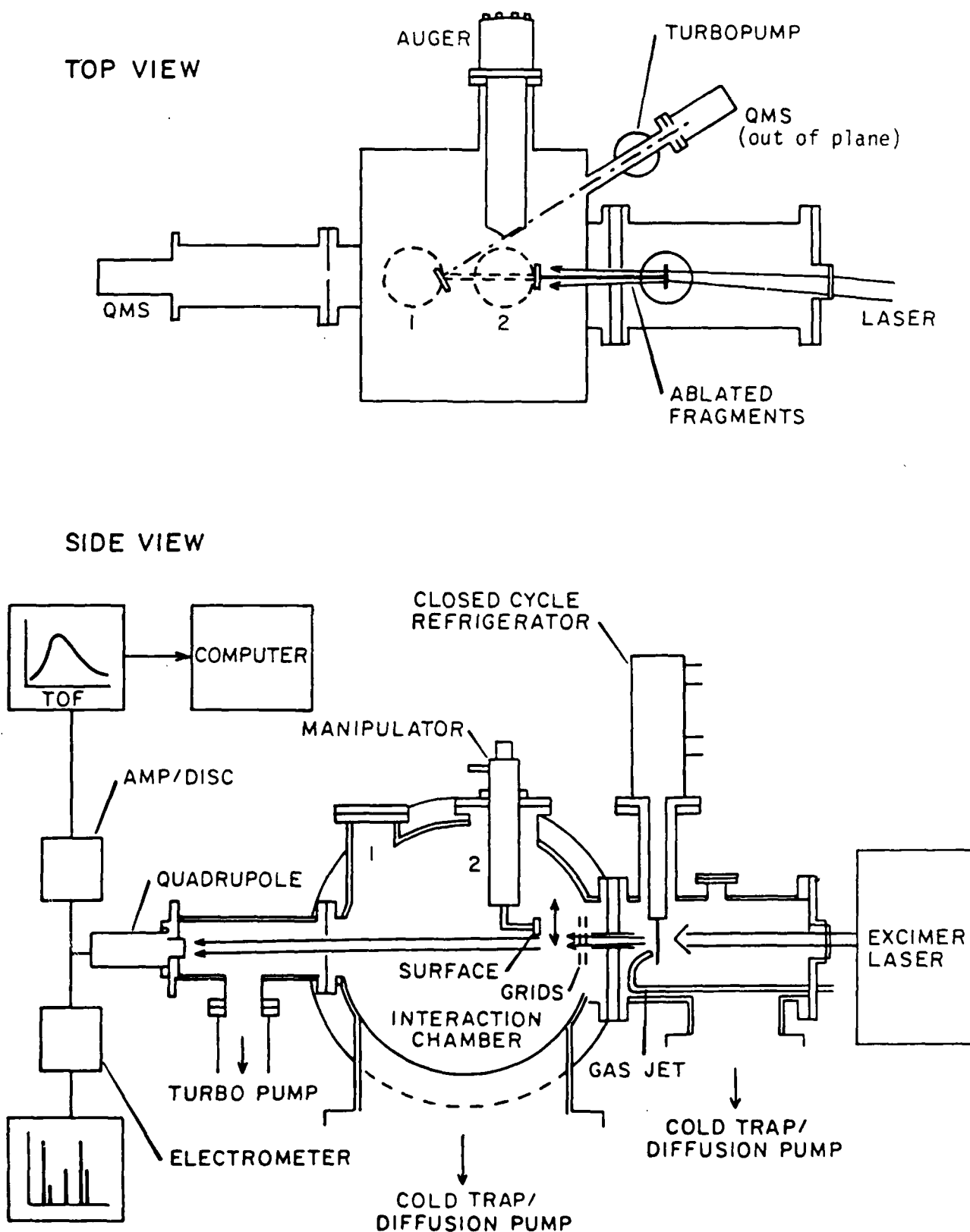


Fig. 8 Apparatus for laser ablation surface collision studies.

deposition from a gas jet or vaporization from an oven source. The choice of molecules is governed by requirements of strong adhesion to the window and high absorption at the ultraviolet wavelengths used for ablation. High energy pulses from an ArF rare gas halide laser (193 nm) are directed through the quartz from the other side of the growing film to ablate the film and eject translationally "hot" radicals and fragments by simultaneous vaporization and photodissociation. This part of the apparatus is intended primarily as a reliable source of translationally fast particles for the surface scattering, etching, and deposition experiments which are carried out in the main interaction chamber. However, it will also be possible to analyze the components of the ablated materials. The mechanisms of the laser vaporization process can be studied by directing the laser onto the front side of a surface material.

By combining highly absorbing molecules with optically transparent molecules in the growing film, a wide variety of translationally fast atoms and radicals can be formed. Candidate systems include the formation of Cl atoms from deposition of Cl_2 molecules, F atoms from CF_4 or NF_3 , CF_3 radicals from CF_3I , and metal vapors from metal films.

The translational energy of the ejected particles are first analyzed by time-of-flight mass spectrometry using a quadrupole mass spectrometer located on the other side of the interaction chamber. The flight distance can be varied from 60-100 cm. Application of electrical potentials to grids placed after the laser ablation region can be used to remove ions created in the vaporization. Our goal is to produce well-defined, reproducible pulsed beams of reactive atom species such as F and Cl, metal vapors for deposition of interconnects, such as W, Al, and Cu, and radical or molecular species such as CH_3 and CF_3 . The desirable range of kinetic energies is 1-10 eV.

In future experiments, the fast beams will be directed onto a substrate material in the main interaction chamber. The substrate cleanliness is checked by Auger spectroscopy and cleaning is accomplished with mild Ar ion sputtering. For high flux studies of etching rates, the surface may be positioned close to the ablation source (position 2 in Fig. 8). For mass spectrometric studies of the etching products and sticking coefficients as a function of kinetic energy, a second mass spectrometer detection system is set to analyze the surface material in position 1 of the figure. If the fluxes are of insufficient intensity for the remote position of the mass spectrometer as shown, provision will be made to bring the mass spectrometer re-entrant into the chamber in order to be close to the surface. Some time resolution of the formation of etching products will also be possible because of the pulsed nature of the ablation process.

In the past several months, our apparatus for laser vaporization of materials from low temperature quartz windows has become operational and the first experiments have been successful. The experiments consist of a continuous deposition of a molecular precursor such as Cl_2 or acetone on the window, which is held at 10-77 K. The 193 nm ArF laser vaporizes the growing film by coming from behind through the window. The flight times of the ejected particles are detected by a quadrupole mass spectrometer.

The first experiments involve the detection of fast Cl atoms and Cl_2 molecules from Cl_2 and C atoms from acetone. Although many tests still need to be conducted, the initial results are very promising and demonstrate that fast particles can be generated repetitively by the laser ablation mechanism.

Figure 9 shows several traces of the time of arrival of Cl_2 molecules at the mass spectrometer under different conditions of laser ablation during condensation of Cl_2 on the window. Each trace is the result of a single laser

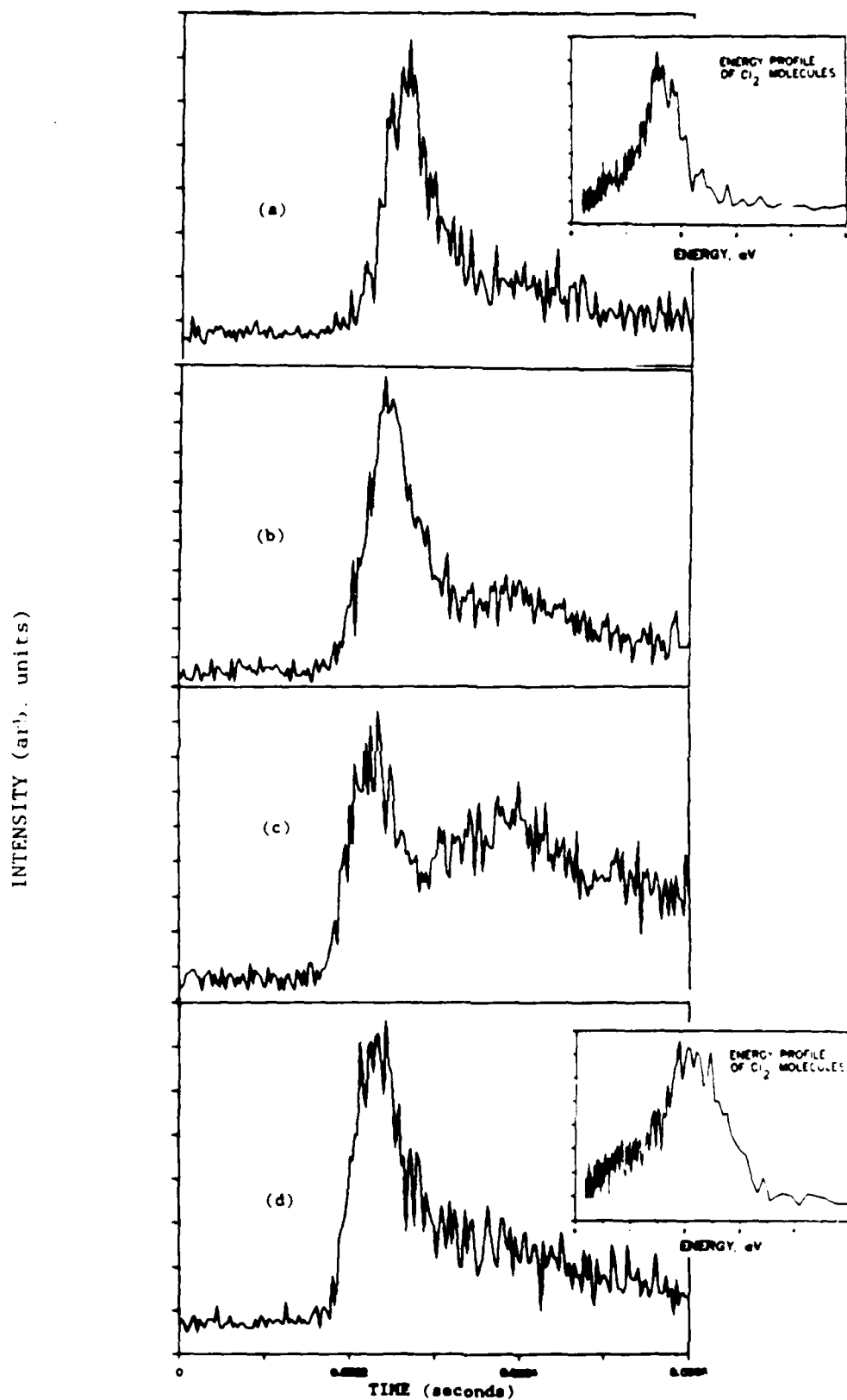


Fig. 9. Cl_2 arrival time distributions from 193 nm laser vaporization of 30K Cl_2 solids. Background pressure of Cl_2 is 5×10^{-6} Torr. Each trace results from a single laser pulse fired at an interval Δt apart. a) $\Delta t=60$ s; b) $\Delta t=60$ s; c) $\Delta t=180$ s; d) $\Delta t=40$ s. The reproducibility is still a factor in the controlled use of the process.

pulse in the continual deposition and repetitive vaporization process. From the distance and flight times, the Cl_2 molecules observed thus far are estimated to have energies between 1 and 7 eV. Further work is in progress to quantify the flight times of both the Cl atoms and Cl_2 molecules and to improve the instantaneous deposition of laser energy so that even higher kinetic energies can be achieved.

There is widespread interest in the elucidation of dry etching processes and gas-surface materials deposition for the manufacture of smaller features in semiconductor devices.^{29,30} State-of-the-art techniques make use of the chemical specificity and affinity of certain radical species to effect selective materials removal, together with the anisotropic characteristics of high energy ion bombardment to produce sharp sidewall profiles.³² A typical example might be the etching of silicon by XeF_2 in the presence of Ar^+ bombardment. The chemical nature of the radical species, in this case F atoms, gives elemental discrimination, providing rapid etching of silicon. Although the ion bombardment shows little selectivity for particular elements, it does provide for directed removal of etching products or for enhancement of other mechanisms involved in the removal rates in the directionally irradiated regions. Etching by species such as F, Cl, and Br alone, which are some of the main etchant radicals in plasma etching, produces little selectivity in direction.^{33,34}

The use of ion bombardment can produce numerous damages, however, which can be undesirable.³⁵ These include displacements of atoms in the semiconductor lattice, formation of electron-hole pairs, surface contamination by redeposition, and incorporation of impurities from the ion source. These damages are particularly troublesome in the limit of ultrasmall devices, in which electrons are confined to dots or wires that are smaller than the

wavelengths of the electron.³⁶ The necessity for ion bombardment to enhance the etching rate in many cases suggests that there are barriers to desorption or in the final reaction to form the volatile end products. Thus, a variety of other energetic particles may provide interesting alternatives to maximize etching rates and anisotropies.

Recently, there have been investigations of etching with both vibrationally excited SF_6 molecules³⁷ and radicals (F , Cl , CH_3) formed by thermal decomposition of molecules in a "hot jet".³⁸ The latter publication is of particular interest to us here, since it shows that "directed" radicals with slightly elevated kinetic energies (0.3 eV) can etch a large variety of materials by themselves. In some cases this occurs with reasonable anisotropies. That work explored the differential etch rates of Si versus SiO_2 with F atoms, demonstrated a practical dry etching of Pb by combining CH_3 reactions with some additional ion bombardment to remove nonvolatile films, and explored the anisotropy of etching GaAs with Cl atoms. From these results, there are very encouraging reasons to consider the possibilities of dry etching with energetic, translationally fast atoms and radicals which can be produced by the laser ablation techniques described above.

A strong case can be made for investigations of the characteristics of materials removal with neutral atoms and radicals at high kinetic energies (1-10 eV). The laser ablation techniques that we described above will allow a variety of atoms and radicals to be produced with high energy. The fast atom beams will provide directionality in etching processes, since the first collision of the fast reactive atom with the etching material will have a very high velocity and subsequent collisions will be slowed dramatically by strong trapping-desorption mechanisms. Such translationally fast atoms and radicals will have substantial additional energy to surmount reactive barriers and to

overcome energetic constraints to desorption, thus allowing product molecules to evolve into the gas phase without the necessity for simultaneous ion bombardment.

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