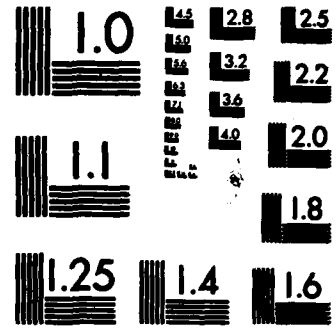
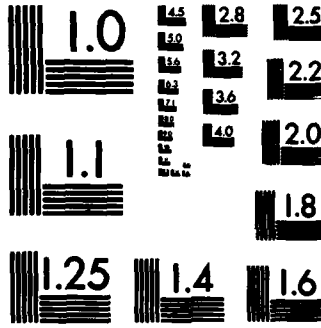


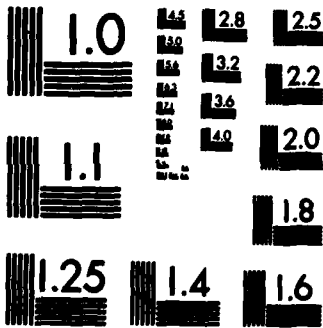
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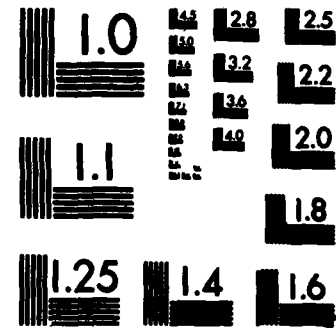
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5 OCT 1982

July 14, 1982

Final Technical Report
Covering Period: 12 May 1978 through 15 May 1982

MULTIPHOTON DYNAMICS: ENERGY DISPOSAL DURING
DECOMPOSITION OF MOLECULES UNDER STATIC, VERY
LOW-PRESSURE, AND MOLECULAR-BEAM CONDITIONS;
SPECIFIC RATE CONSTANTS; AND DISTRIBUTION FUNCTIONS

By: Alan C. Baldwin, Michel Rossi
David M. Golden, and John R. Barker

Prepared for:

DIRECTORATE OF CHEMICAL SCIENCES (NC)
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)
Bolling Air Force Base, Bldg. 410
Washington, DC 20332

Attention: Major W. G. Thorpe
Program Manager
Molecular Dynamics

AFOSR Contract No. F49620-78-C-0107
SRI Project No. 7433

Approved:

M. E. Hill

M. E. Hill, Laboratory Director
Chemistry Laboratory

G. R. Abrahamson, Vice President
Physical Sciences Division

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20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

An energy-grained master equation has been used to model the multiphoton pumping process in SF_6 . It was found that an energy-dependent absorption cross section that was approximately inversely dependent on the level of excitation was needed to reproduce experimental data on the fraction decomposed per pulse.

Intensity, fluence, and wavelength dependence of the collisionless infrared multiphoton dissociation yield for CF_3I have been determined via "titration" of radical photoproducts and molecular-beam-sampling-mass spectrometry. The importance of nonlinear effects in the pumping of this molecule was confirmed.

The infrared multiphoton dissociation of CF_3I is used as a convenient source of CF_3 radicals under very low-pressure conditions. Measurements of thermal absolute rate constants at 298 K for the reactions $CF_3 + Br_2 \rightarrow CF_3Br + Br$, $CF_3 + ClNO \rightarrow CF_3Cl + NO$, $CF_3 + O_3 \rightarrow CF_3O + O_2$, and $CF_3 + NO_2 \rightarrow CF_3O + NO$ yield $(7.8 \pm 1.3) \times 10^8$, $(3.5 \pm 0.5) \times 10^8$, $(5.6 \pm 0.8) \times 10^0$, and $(1.6 \pm 0.3) \times 10^9$ $M^{-1} s^{-1}$, respectively. This new technique shows great promise for production of other free radicals of interest and measurement of thermal absolute rate constants over a wide temperature range.

Continuing efforts focus on:

- (1) Including collisional events in the model.
- (2) Measuring important radical reaction rate constants.
- (3) Understanding photophysical processes of larger molecules.

The intensity, fluence, and wavelength dependence of the collisionless infrared multiphoton yield of a series of perfluorinated alkyl iodides (CF_3I, C_2F_5I, C_3F_7I) have been studied. Continuing work on energy-grained master equation approaches to understanding multiphoton phenomena has provided a powerful method for analyzing and comparing data based on a cumulative log-normal probability distribution for the multiphoton yield.

CONTENTS

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MATTHEW J. KLEINER
Chief, Technical Information Division

RESEARCH OBJECTIVES

→ The objective of this research is to increase ^{the} our understanding of the chemical dynamics of multiphoton processes. The work covers both experimental and theoretical research into both photophysical and photochemical aspects of multiphoton phenomena. The specific tasks of the project are ~~summarized below.~~ ^{to}

Task 1: Study the chemical dynamics of multiphoton processes in a series of prototype molecules under static conditions, ^{AND TO} Particular attention will be given to the effects of varying:

- Substrate pressure
- Buffer pressure and structure
- Laser fluence
- Laser power
- Laser wavelength.

Task 2: Study the chemical dynamics of multiphoton processes in prototype molecules under very low-pressure flow conditions, measuring yields under varying conditions. Variables will include:

- Gas-wall collision frequency
- Gas-gas collision frequency
- Laser fluence
- Laser power
- Laser wavelength
- Reactor wall temperature.



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STATUS OF RESEARCH EFFORT

During this research, we have made great progress in the understanding of infrared multiphoton decomposition of polyatomic molecules and in the use of this phenomenon to generate free radicals whose reaction rates may be studied under a variety of conditions.

The thermochemistry of the t-butyl radical ($t\text{-C}_4\text{H}_9$) has been the subject of a major controversy for the past several years. Laser generation of the t-butyl radicals provides an excellent method for studying kinetics and thermochemistry. Our first attempts at generating $t\text{-C}_4\text{H}_9$ were based on CO_2 laser photolysis of a suitable precursor: $t\text{-C}_4\text{H}_9\text{-N}_2\text{-CF}_3$. In this molecule, the CF_3 group acts as a chromophore to absorb light from the laser. Unfortunately, photolysis yields were low and a second approach was found to be satisfactory. The second approach employed an excimer laser operating at 351 nm (XeF) to photolyze $(t\text{-C}_4\text{H}_9)_2\text{N}_2$ and produce the radicals.

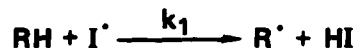
Using laser photolysis to produce $t\text{-C}_4\text{H}_9$ radicals, the reaction



was studied to determine its activation energy. The results of this successful study are presented in the following section.

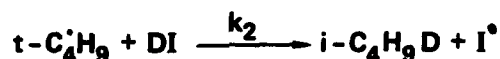
I INTRODUCTION

Many bond strengths of organic molecules have been determined using the iodination technique where the kinetics of the rate-determining step was measured:



Together with the estimated Arrhenius parameters for the reverse reaction (k_2) this method yielded $\Delta H_{1,2}^{\circ}$ and $\Delta S_{1,2}^{\circ}$ and therefore $\Delta H_f^{\circ}(R^{\bullet})$ and $S^{\circ}(R^{\bullet})$ in view of the known thermochemistry of RH, I^{\bullet} and HI.

The standard heat of formation, as well as the standard entropy, of t-butyl radical ($t-C_4H_9^{\bullet}$) is still a matter of debate. We present results on the Arrhenius parameters of the fast metathetical reaction:

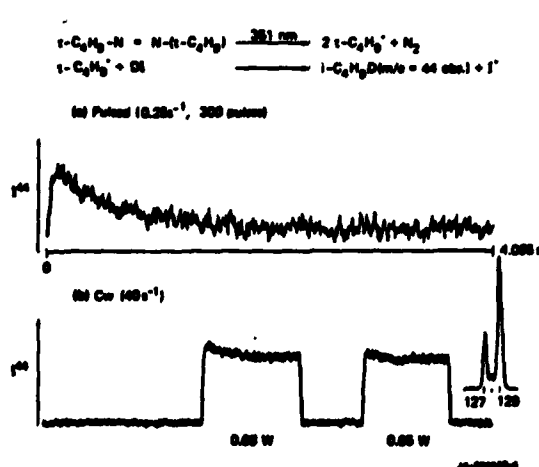


These parameters yield second-law values for $\Delta H_f^{\circ}(t-C_4H_9^{\bullet})$ and $S^{\circ}(t-C_4H_9^{\bullet})$ when combined with the Arrhenius parameters for the reverse reaction by Teranishi and Benson.

II EXPERIMENTAL

2,2'-Azobisopropane was photolyzed by a high power excimer laser at 351 μm at low pressures (VLP ϕ -method: very low pressure photolysis).

The two-aperture Knudsen cell (Figure 1) was characterized by the following parameters: $V = 105 \text{ cm}^3$, $k_o^S = 0.832 \cdot (T/M)^{1/2} \text{ s}^{-1}$, $k_o^B = 3.381 \cdot (T/M)^{1/2} \text{ s}^{-1}$, where k is the escape rate constant of a species of molecular weight M and S and B refer to the small and large aperture. The pulse repetition rate of the laser was



3

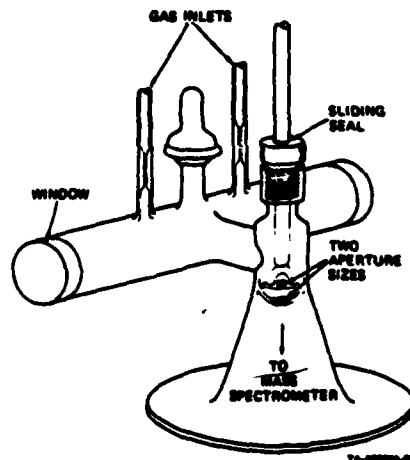
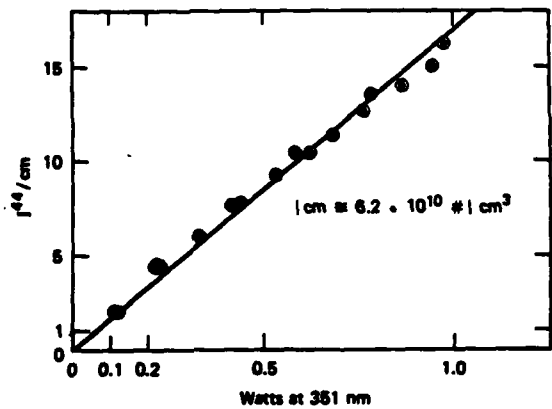


FIGURE 2 REACTION VESSEL

either very low (0.25 s^{-1}) so that after each UV-pulse the products would leave the reaction cell and the next UV-pulse would photolyze a fresh sample (Figure 2a), or high ($10 - 50 \text{ s}^{-1}$) to produce a steady-state concentration of t-butyl radicals (Figure 2b).

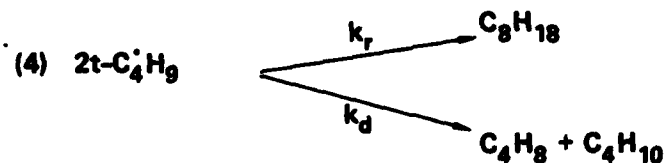
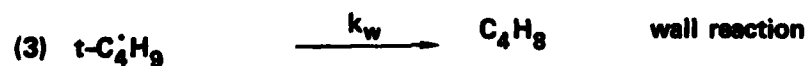
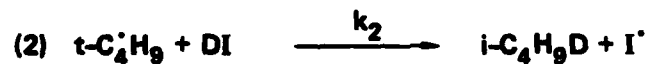
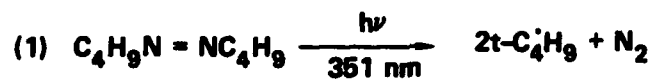
The t-butyl radicals then reacted with DI to yield i-C₄H₉D which was monitored at $m/e = 44$. Figure 3 shows that the yield of t-butyl radicals is linearly proportional to the power of the laser radiation in the CW-mode (Figure 2b) of the experiment.



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III RESULTS

The kinetic scheme relevant to our reaction system is as follows:



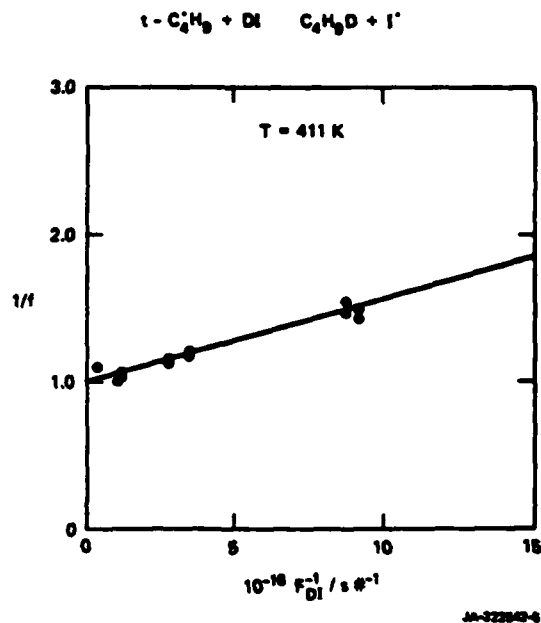
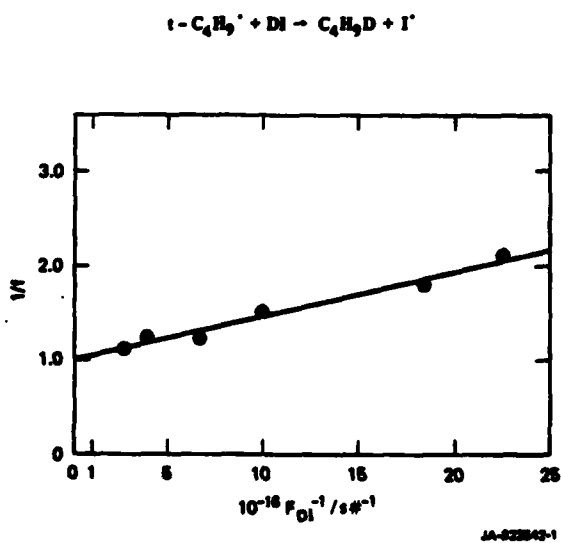
(5) Escape of C₄H₉N = NC₄H₉, C₄H₈, t-C₄H₉, C₄H₁₀ and DI.

In the presence of DI the rates of reactions (3) and (4) were not competitive with (2), because no isobutene, isobutane and tetramethylbutane could be detected. The rate constant k_2 was determined by measuring the yield of $i\text{-C}_4\text{H}_9\text{D}$ at $\phi/e = 44$ as a function of the flow rate of DI into the reactor in the CW-irradiation mode.

The functional dependence of the fraction of radicals titrated (f) on the flow rate of DI (F_{DI}^i) has the following form:

$$(6) \quad 1/f = 1 + \frac{k_0^{\text{C}_4\text{H}_9} \cdot k_0^{\text{DI}}}{k_2 \cdot F_{\text{DI}}^i}$$

Typical $1/f$ versus F_{DI}^i plots are shown in Figure 4 ($T = 303 \text{ K}$) and Figure 5 ($T = 411 \text{ K}$).



The following table presents the rate constants k_2 determined in the small aperture reactor in the CW-irradiation mode.

T/K		$k_2/M^{-1} s^{-1}$	T/K	$k_2/M^{-1} s^{-1}$
303	} coated reactor	$1.55 \cdot 10^8$	302	$2.06 \cdot 10^8$
303		$1.55 \cdot 10^8$	407	$2.76 \cdot 10^8$
303		$1.93 \cdot 10^8$	361	$2.25 \cdot 10^8$
303		$2.07 \cdot 10^8$	411	$3.70 \cdot 10^8$
302		$1.80 \cdot 10^8$		

The absence of wall reactions of t-butyl radical could be established by the absence of isobutene and isobutane at the lowest flow rates of DI used to establish the fraction of radicals titrated (Figure 4 and 5). Furthermore, the results are consistent with the large aperture reactor data.

Mass Balance. A typical mass balance is as follows:

At 505/35 μ m the degree of photolysis was 3.21%.

With $F_{\text{azo}}^i = 2.50 \cdot 10^{15} s^{-1}$ this results in $F_{C_4H_9}^i = 1.80 \cdot 10^{14} s^{-1}$. The flow of i-C₄H₉D extrapolated to 100% titration gave $F_{C_4H_9D}^o = 1.52 \cdot 10^{14} s^{-1}$. In the absence of DI the following flows were measured:

$$F_{C_3H_{18}}^o = 2.04 \cdot 10^{12}, F_{C_4H_{10}}^o = 1.52 \cdot 10^{13}, F_{C_4H_8}^o = 1.25 \cdot 10^{14}.$$

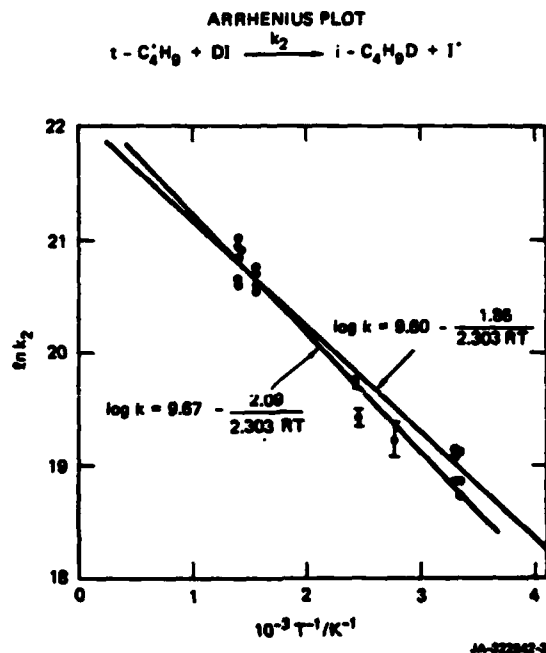
The mass balance equation is, therefore,:

$$(7) F_{C_4H_9D}^o = F_{C_3H_{18}}^o + F_{C_4H_8}^o + F_{C_4H_{10}}^o + (F_{C_4H}^o)_w$$

IV CONCLUSIONS

Together with previously determined rate constants at high temperature (644 - 722 K) using the same technique (VLPP), the present set of rate constants yield the following Arrhenius parameters (Figure 6).

$$(8) \log k_2/M^{-1} s^{-1} = 9.60 - \frac{1.86}{2.303 RT}$$



In combination with Teranishi and Benson's Arrhenius parameters for the forward reaction $(\log k_1/M^{-1} s^{-1} = 10.88 - \frac{21.4}{2.303 RT})$ we obtain for reaction system (9) neglecting the small isotope effect of 1.5:



$$300 \text{ K: } \Delta H_{1,2}^\circ = 21.4 - 1.9 = 19.5 \text{ kcal/mol}$$

$$300 \text{ K: } \Delta S_{1,2}^\circ = 2.303 R \log A_1/A_2 = 5.85 \text{ Gibbs/mol}$$

$$\Delta H_f^\circ(t-C_4H_9) = 6.9 \pm 0.5 \text{ kcal/mol}$$

$$S^\circ(t-C_4H_9) = 70.2 \pm 1.0 \text{ Gibbs/mol}$$

PUBLICATIONS

apers prepared or published during this project are listed below:

Infrared Multiphoton Chemistry: Comparison of Theory and Experiment. Solution of the Master Equation, by A. C. Baldwin, J. R. Barker, D. M. Golden, R. Duperrex, and H. van den Bergh, Chem. Phys. Lett., 1979, 62, 178.

Infrared Multiphoton Dissociation Yields via a Versatile New Technique. Intensity, Fluence, and Wavelength Dependence for CF_3I , by Michel Rossi, John R. Barker, and David M. Golden, Chem. Phys. Lett., 1979, 65, 523.

Infrared Multiphoton Generation of Radicals: A New Technique for Obtaining Absolute Rate Constants. Application to Reactions of CF_3 , by Michel J. Rossi, John R. Barker, and David M. Golden, J. Chem. Phys., 1979, 71, 3722.

Infrared Multiphoton Decomposition: A Comparison of Approximate Models and Exact Solutions of the Energy-Grained Master Equation, by John R. Barker, J. Chem. Phys., 1980, 72, 3686.

Application of a New Technique to Infrared Laser Multiphoton Dissociation of Molecules, by John R. Barker, Michel Rossi, Alan C. Baldwin, and David M. Golden, Proceedings of the International Conference on Lasers '79, December 17-21, 1979, pp. 251-257.

Infrared Multiphoton Decomposition: Photochemistry and Photophysics, by David M. Golden, Michel J. Rossi, Alan C. Baldwin, and John R. Barker, Accounts of Chemical Research, 1981, 14, 56.

IR Photochemistry: A Unified Approach for Single-Channel Reactions. I. Theory and Computational Examples, by Alan C. Baldwin and John R. Barker, J. Chem. Phys., 1981, 74, 3813.

IR Photochemistry: A Unified Approach for Single-Channel Reactions. II. Treatment of Experimental Data, by Alan C. Baldwin and John R. Barker, J. Chem. Phys., 1981, 74, 3823.

Infrared Multiphoton Photophysics: Decomposition of $C_nF_{2n+1}I$ ($n = 1,2,3$) by Michel J. Rossi, John R. Barker, and David M. Golden, J. Chem. Phys., 1982, 76, 406.

IR Photochemistry: A Unified Approach for Single-Channel Reactions. III. A Simple Approximate Solution of the Master Equation, by Alan C. Baldwin and John R. Barker, Chem. Phys. Lett., 1982, 86, 55.

- Laser-Induced Chemical Kinetics: Absolute Rate Constants for the Reactions $C_2F_5 + Br_2 \rightarrow C_2F_5Br + Br$ and $n-C_3F_7 + Br_2 \rightarrow n-C_3F_7Br + Br$, by M. J. Rossi, J. R. Barker, and D. M. Golden, *Int. J. Chem. Kinetics*, 1982, 14, 499.

Review papers, which are in part concerned with work undertaken here, are:

- Experimental and Theoretical Examples of the Value and Limitations of Transition State Theory, by David M. Golden, *J. Phys. Chem.*, 1979, 83, 108.
- Measurement and Estimation of Rate Constants, by David M. Golden, in Dynamics and Modeling of Reactive Systems, Warren E. Stewart, W. Harmon Ray, and Charles C. Conley, Eds. (Academic Press, New York, 1980), pp. 315-331.
- Thermochemistry and Kinetics of Aromatic Radicals, by D. M. Golden, in Frontiers of Free Radical Chemistry, William A. Pryor, Ed. (Academic Press), New York, 1980, pp. 31-41.
- Measurement and Estimation of Rate Constants for Modeling Reactive Systems, in Modeling of Chemical Reaction Systems, Proceedings of an International Workshop, Heidelberg, Fed. Rep. of Germany, 1-5 September 1980. K. H. Ebert, P. Deuflhard, and W. Jager, Eds. (Springer-Verlag, Berlin, 1981), pp. 148-161.

INTERACTIONS

Invited Talks

David M. Golden

- NBS-sponsored Current Status of Kinetic and Elementary Gas Reactions, Gaithersburg, MD, 18-21 June 1978. Invited paper.
- Western Regional American Chemical Society Meeting, San Francisco, CA, 2-7 September 1978. Invited paper.
- Stanford University, Bay Area Combustion Group, 7 December 1978. Invited paper.
- University of Colorado, Boulder, 8 December 1978. Invited talk.
- University of Pittsburgh, Pittsburgh, PA, 8 February 1979. Invited talk.
- Louisiana State University, Baton Rouge, LA, 9-11 April 1979. Invited talk.
- Gordon Conference on Organic Photochemistry, Andover, NH, 23-27 July 1979. Invited speaker.
- AFOSR Contractors' Meeting, Colorado Springs, 3-5 October 1979.
- AFOSR Contractors' Meeting, Alexandria, VA, 28 January-1 February 1980.
- University of California, Berkeley, 8-9 April 1980. Invited speaker.
- Workshop on Modeling of Chemical Reaction Systems, Heidelberg, Germany, 1-6 September 1980. Invited talk.
- Workshop on Fundamental Research: Directions for Decomposition of Energetic Materials, University of California, Berkeley, 19-22 January 1981. Invited speaker.
- Naval Research Laboratory, Washington, DC, 29 January 1981. Invited talk.
- Princeton University, Princeton, NJ, 17 February 1981. Invited talk.
- CAS Ad Hoc Panel on Atmospheric Chemistry, Boulder, CO, 13-15 October 1981.
- Combustion Contractors' Meeting on Basic Energy Sciences, Sandia Laboratories, Livermore, CA, 25-28 October 1981. Invited talk.
- AFOSR/AWL Molecular Dynamics Conference, Albuquerque, NM, 9-11 November 1981. Invited talk.

- Conference on Chemistry and Mechanism in Combustion and Flames, University of Southern California, Los Angeles, 16-17 November 1981. Invited talk.
- Department of Chemistry, University of California, Irvine, 1 February 1982. Invited talk.
- Air Products Corporation, New Jersey, 26 March 1982. Invited talk.

M. J. Rossi

- American Chemical Society Meeting, Honolulu, Hawaii, 1-6 April 1979. Presented paper.
- Informal Photochemistry Conference, April 1980. Presented paper.
- Institute fur Physikal Chemie, University of Basel, Switzerland; Laboratorium fur Physikal Chemie, ETH, Zurich, Switzerland; Institute fur Chimie Physique, EPFL, Lausanne, Switzerland. July 1980. Presented informal seminars.
- 6th International Symposium on Gas Kinetics, Southampton, UK, 14-17 July 1980. Presented paper.
- Symposium on Laser Photochemistry in Large Molecules and Solids, IBM Research Laboratory, San Jose, CA, 20-22 August 1980. Invited talk.

John R. Barker

- Naval Research Laboratory, May 1979. Invited speaker.
- Redstone Arsenal, May 1979. Invited speaker.
- International Conference on Lasers '79, December 1979. Presented paper.
- Informal Photochemistry Conference, April 1980. Presented paper.
- Western Spectroscopy Association Meeting, Asilomar, CA, 28 January 1981. Presented paper.
- Combustion Contractors' Meeting for Basic Energy Sciences, Sandia Laboratories, Livermore, CA, 25-28 October 1981. Invited talk.
- AFOSR/AWL Molecular Dynamics Conference, Albuquerque, NM, 9-11 November 1981. Invited talk.
- CLEO '82, Phoenix, Arizona, 15 April 1982. Invited talk.

Alan C. Baldwin

- EPFL, Lausanne, Switzerland, October 1979. Invited speaker.
- University of Gottingen, W. Germany, October 1979. Invited speaker.

Consultative and Advisory Functions

We were retained as consultants to U.S. Army MIRADCOM (W. Wharton, Redstone Arsenal) in the general area of laser-induced chemistry. The expertise required was developed, in part, as a result of this contract (1979-1981).

INVENTIONS

There have been no inventions under this contract.

Appendix

INFRARED MULTIPHOTON DECOMPOSITION: PHOTOCHEMISTRY AND PHOTOPHYSICS

by

David M. Golden, Michel J. Rossi, Alan C. Baldwin, and John R. Barker

This review article was published in *Accounts of Chemical Research*,
1981, 14, 56.

Infrared Multiphoton Decomposition: Photochemistry and Photophysics

DAVID M. GOLDEN,* MICHEL J. ROSSI, ALAN C. BALDWIN, and JOHN R. BARKER*

Department of Chemical Kinetics, SRI International, Menlo Park, California 94025

Received August 15, 1980

Chemical kineticists often search for experimental tools that allow the preparation and study of molecules with energy distributions other than thermal. Thus, experiments using photochemical and chemical activation are common. Also sought are techniques whereby short-lived species, such as free radicals, may be created under conditions where their reactions may be studied. In this Account, we report on some experiments in which we have employed an infrared laser to achieve both of these results.

In the past 10 years,¹⁻³ experiments have indicated that polyatomic molecules can be decomposed when subjected to radiation from a high-power infrared laser under conditions where no molecular collisions are possible. Infrared optical pumping is thus a nonthermal energization process.

Three aspects of this phenomenon have been of great interest. First, the molecular decomposition can lead to reactive species, such as free radicals, and thus is a rapid method for preparing such species for chemical and physical study. Second, the optical pumping process may be mode specific, i.e., as many photons are absorbed, they may excite a given molecular vibration to a continually greater degree. This is quite different from collisional excitation which is statistical. Because of this difference, it is conceivable that chemistry induced by laser excitation would be considerably dif-

ferent from that induced by thermal collisional excitation. Finally, since similar molecules with different isotopically substituted molecules absorb infrared radiation of different frequencies, the infrared laser-induced dissociation process is a natural method for isotopic separation. Indeed, these last two points have furnished the major impetus for recent research in this area.

Kinetic Model

A model for infrared laser pumping of molecules which has received general acceptance is illustrated in Figure 1. In this particular case, the first two photons are absorbed in a given isolated vibrational mode with the anharmonicity being compensated for by $\Delta J = \pm 1$, leading to allowed transitions. In Figure 1 we depict a situation where the coupling of energy from $v = 2$ of the isolated vibrational mode to the other quantum states of the molecule at this energy is sufficiently strong that we describe the molecule in terms of an energy level, rather than a specific state. At this energy and higher, the density of levels is so great that the resonant absorption of the specific laser photon is assured. This energy region is called the quasicontinuum. Above some barrier to chemical decomposition, a true continuum exists and molecules have lifetimes given by $(k(E))^{-1}$, where $k(E)$ may be computed via RRKM theory or other models for unimolecular decay. The exact nature of pumping in any given molecule is thus strongly dependent on energy-level and wave-function details. If we desire to understand the time history of population in the molecular quantum states, we need to solve the time-dependent Schrödinger equation. It is well-known⁴ that under certain conditions the

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Dr. Barker was born in Tennessee and studied at Hampton-Sydney College and then at Carnegie-Mellon University, where he received his Ph.D. in 1968.

(1) R. V. Ambartzumian and V. S. Letokhov in "Chemical and Biochemical Applications of Lasers", Vol. 3, C. B. Moore, Ed., Academic Press, New York, 1977.

(2) N. Bloembergen and E. Yablonovitch, *Phys. Today*, 21, 23 (1978).

(3) P. A. Schultz, Aa. S. Sudbo, D. J. Krajnovich, H. S. Kwok, Y. R. Shen, and Y. T. Lee, *Ann. Rev. Phys. Chem.*, 20, 379 (1979).

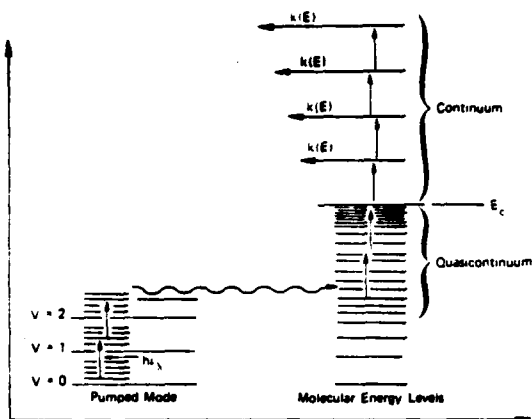


Figure 1. Energy level structure of a polyatomic molecule excited by monochromatic radiation of energy $h\nu_\lambda$.

Schrödinger equation can be approximated by a coupled set of differential rate equations, a "master equation".

Variables at the disposal of researchers include the usual environmental parameters such as temperature and pressure, molecular parameters, such as density of states (entropy), and reaction barrier heights. In addition, there are several laser parameters that may be varied. These include wavelength, intensity (photon flux = photons $\text{cm}^{-2} \text{s}^{-1}$), fluence (energy dose = energy cm^{-2}), and the temporal profile of the laser pulse. The properties intensity and power, which is just intensity multiplied by the energy of the photon, are often interchanged. Thus, fluence is the time integral of power and is often written $\phi = \int_0^t I dt$.

The question of applicability of master equation representations for infrared multiphoton collisionless decomposition has been extensively treated,⁵ and it has been shown that such approaches are applicable here. Thus we write

$$\frac{dN_m}{dt} = C_{m-1}^a N_{m-1} + C_m^a N_{m+1} - (C_m^e + C_{m-1}^e + k_m) N_m \quad (1)$$

to describe the time history of the population of the m th level, where N_m is the population density of level m , C_m^a is the effective first-order rate constant for absorption from level m to $m+1$, and C_m^e is that for stimulated emission from level $m+1$ to m . k_m is the rate constant for chemical decomposition from level m and is identically zero if the energy of level m is below the barrier for reaction. Since the level separation is just the photon energy, the numerical solution for this equation is obtained with the natural "grain" size. This is often called an energy-grained master equation (EGME).

The Einstein relation⁶ allows us to compute the emission rate constant from the absorption rate constant according to detailed balance:

$$\frac{C_m^e}{C_m^a} = \frac{g_m}{g_{m+1}} \quad (2)$$

(4) W. Pauli, *Festschrift Zum 60 Geburtstag A. Sommerfelds*, Hirzel, Leipzig, 1928, as quoted in ref 5.

(5) M. Quack, *J. Chem. Phys.*, **68**, 1282 (1978); *Ber. Bunsenges. Phys. Chem.*, **83**, 787 (1979).

(6) J. I. Steinfeld, "Molecules and Radiation: An Introduction to Modern Molecular Spectroscopy", MIT Press, Cambridge, MA, 1978, pp 24-30.

where g_m is the molecular density of states at energy $mh\nu$.

The master equation may be an acceptable description of the pumping process for many possible functional forms of the rate constants. We may define an absorption cross section by considering the situation when light of intensity I_0 is incident on a gas sample and induces a molecular transition from level m to $m+1$. The light intensity is attenuated according to the Beer-Lambert law, $I = I_0 e^{-\sigma_m N_m l}$, where σ_m is the absorption cross section and l is the length of the absorbing gas layer. The effective first-order rate constant for absorption of photons is⁶

$$C_m^a = \frac{\sigma_m I}{h\nu} \quad (3)$$

In this simple case, every term in eq 1 except $k_m N_m$ is linearly dependent on intensity. In general, k_m is small, except for the highest few levels, and thus we see that the decomposition yield would depend on fluence. If this description were completely adequate, we could compare experimental yields with ab initio computed yields for determination of the cross section, so we assume a simple power law dependence on internal energy:⁷

$$\sigma_m = \sigma_0 (i+1)^n \quad (4)$$

where σ_0 is the $0 \rightarrow 1$ cross section, i is the number of laser quanta in the molecule, and typically $n < 0$. This reduces the problem to a one-parameter fit. There are two expected complications. First, the cross sections may be intensity dependent in the strong laser field, and thus rigorous fluence scaling is lost. Second, a molecule might have more than one populated level that interacts with the laser field. If the cross sections are different for each set of pumped levels, we will need an EGME for each. The overall yield will then correspond to a combination of EGMEs. Thus experimental model verification requires the determination of yields as a function of fluence, intensity, and wavelength for molecules with a range of cross sections and densities of states under different conditions of pressure and temperature. This requires a general technique, and we discuss such an experiment in this Account.

Experimental Approach

The need for a universal detector for the study of infrared laser dissociation of polyatomic molecules under collisionless conditions encouraged us to adapt a familiar technique to the study of infrared photochemistry and photophysics. We have been using an experimental technique called very low pressure pyrolysis (VLPP) for a number of years.⁸ In this flow technique we use a heated Knudsen cell reactor at low pressures coupled with molecular-beam-sampling mass spectrometric detection to study the gas-phase unimolecular decomposition of organic molecules, and the rapid reactions of subsequently formed free radicals at pressures in the micrometer range and at temperatures from below ambient up to $\sim 1000^\circ\text{C}$. We have found this technique to be applicable to the study of unimolecular processes, radical-molecule reactions, radical-radical

(7) J. R. Barber, *J. Chem. Phys.*, **72**, 2686 (1980).

(8) S. W. Benson, D. M. Golden, and G. N. Spehar, *Angew. Chem. Int. Ed. Engl.*, **12**, 664 (1973).

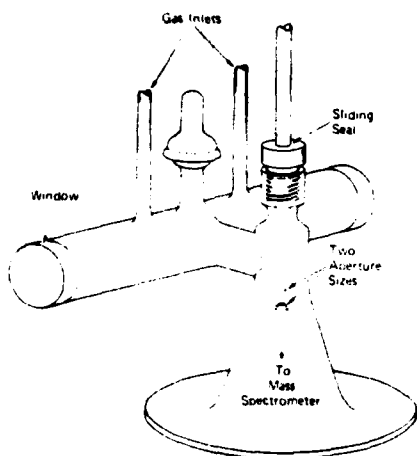
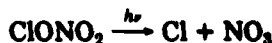


Figure 2. The two-aperture Knudsen cell reactor.

reactions, some equilibrium constants, and catalysis. In some recent work,⁹ the general technique has been extended to enable the determination of photoproducts of



irradiated by a Xe arc.

For the work described in this Account, we have modified a VLPP experiment to replace thermal collisional energization with infrared laser energization. We have suitably modified the hardware to collect data in a pulsed rather than steady-state mode.

The basic VLPP molecular-beam-sampling apparatus has been described in detail elsewhere.⁹ Briefly, the effusive molecular beam is mechanically chopped in the second (differentially pumped) chamber before it reaches the ionizer of the quadrupole mass filter. The signal is demodulated by a lock-in amplifier whose output is stored in a signal averager (PAR 4202), which also triggers the laser. The two-aperture Knudsen cell (Figure 2) is fitted with KCl windows and has an optical pathlength of 20.5 cm and a volume of approximately 105 cm³. The cell is coated with Teflon by rinsing with a finely dispersed Teflon slurry in a water/aromatic solvent mixture (Fenton Fluorocarbon, Inc.) and curing at 360 °C. The cell is characterized by the following escape rate constants (two apertures) for a molecule of molecular weight, *M*, at temperature, *T*: $k_1 = 2.943(T/M)^{1/2} \text{ s}^{-1}$, $k_2 = 0.883(T/M)^{1/2} \text{ s}^{-1}$.

The Lumonics TEA laser (Model K-103) is operated at a pulse repetition frequency of ~0.25 Hz, slow enough to permit >99% of the reaction products to escape from the cell before the next laser shot. The output of the laser consists of a pulse of approximately 6 J, directed through the photolysis cell after being weakly focused by a concave mirror (*f* = 10 m), which gives a beam cross section of 2.67 cm² at the KCl entrance window of the cell (1/e²-criterion).

Detection of free-radical products by electron-impact mass spectrometry is made difficult by the fact that parent species often have daughter peaks of the same masses as the radical fragments. Thus we have chosen to detect radical species by causing their rapid reaction with a scavenger molecule. Figure 3 shows the signal

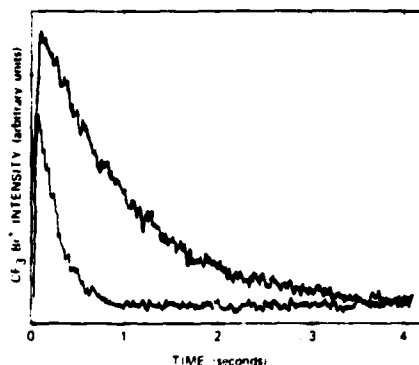


Figure 3. Mass spectrometer signal due to CF₃Br product.

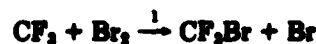
from the CF₃Br product (148/150 amu) arising from the reaction of CF₃ radicals and Br₂. The CF₃ radicals were created from the infrared photolysis of the precursor, CF₃I.¹⁰ The two curves in Figure 3 reflect the two apertures of the reactor.

A typical experiment consisted of averaging the time-dependent mass spectroscopic signal intensity of the products for a number of laser shots (10–100) as a function of the flow rate of the reactant gases at constant precursor flow rate and constant energy per pulse. Although experiments can be performed on a single-shot basis, the signal/noise ratio is improved by averaging the results of a number of laser shots. The total yield of product formed in the reaction of interest is determined by integrating the accumulated time-dependent signal of the signal averager on the strip-chart recorder fitted with an electronic integrator. The signal is calibrated by using known flow rates of products to obtain absolute yields per laser pulse.

Photochemistry

We use the term photochemistry to describe experiments in which laser radiation is used to produce species (usually free radicals) whose thermal rate constants we wish to measure. The modified VLPP technique is well suited for these studies because, regardless of their internal energy upon formation, laser-produced species will collide with the walls of the reactor with a collision frequency of ~10⁴ s⁻¹, thus assuring thermalization (and requiring an awareness of the possibility of heterogeneous reactions).

The following chemical reaction mechanism is appropriate for data interpretation when CF₃ radicals react with Br₂ in our experiments:



The secondary reaction of CF₃I + Br is not included because it is too slow at the concentrations of CF₃I used in the present study, and no evidence for it is observed. Similarly, no heterogeneous first-order reaction of CF₃ to produce CF₃Br is included, since the data interpretation does not suggest it. As in the usual data treatment of VLPP studies, each molecular and radical species escapes from the reactor with a characteristic

(9) J. S. Chang, J. R. Barber, J. E. Deavenport, and D. M. Golden, *Chem. Phys. Lett.*, **69**, 285 (1979).

(10) M. J. Rossi, J. R. Barber, and D. M. Golden, *J. Chem. Phys.*, **71**, 3722 (1979).

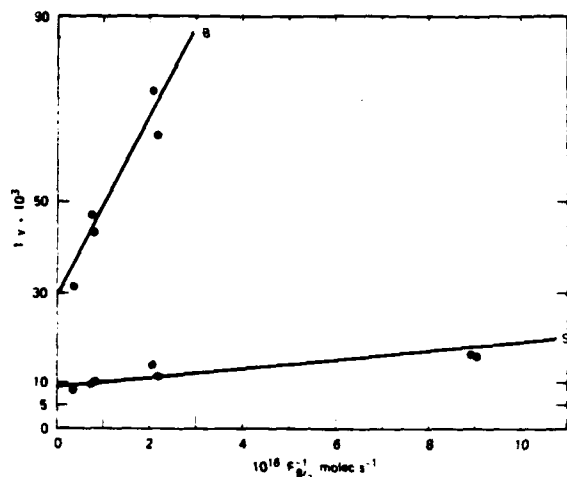


Figure 4. Experimental data for the reaction $C_2F_7 + Br_2 \rightarrow C_2F_7Br + Br$.

first-order escape rate constant; for CF_3I , Br_2 , CF_3 , and CF_2Br , the escape rate constants are k_2 , k_3 , k_4 , and k_5 , respectively.

Analysis of the reaction mechanism and solution of the appropriate differential equations (using Laplace transforms, for example) give an expression for the time-dependent mass spectrometer signal due to CF_2Br .¹⁰ The total yield of CF_2Br (Y) is related to the rate constants as follows:

$$Y^{-1} = (\alpha\beta V[CF_3I]_0)^{-1} \left[1 + \frac{k_4 + k_w}{k_1[Br_2]} \right]$$

when pseudo-first-order conditions are maintained. In this expression, α is a mass spectrometric sensitivity factor, β is the fraction of the initial CF_3I that is dissociated by the laser pulse, and V is the volume of the cell. The initial $[CF_3I]_0 = F_{CF_3I}/(Vk_2)$, where F_{CF_3I} is the flow rate of CF_3I into the reactor; similarly, $[Br_2] = F_{Br_2}/(Vk_2)$. For each F_{Br_2} , two escape apertures can be used, giving two different values for the escape rate constants, corresponding to the "big" and "small" apertures, thus creating two independent data sets. Plots of Y^{-1} vs. $F_{Br_2}^{-1}$ give two straight lines with intercepts c_s and c_b (small and big apertures), given by

$$c_i = \frac{k_w}{\alpha\beta VF_{CF_3I}} \quad i = s, b$$

The slopes of the straight lines are given by

$$m_i = \frac{c_i V(k_4 + k_w)k_2}{k_1}$$

The analytical form remains the same when precursors and "titrants" are changed. Data for CF_3 radicals have been published;¹⁰ Figure 4 shows representative plots for C_2F_7I as precursor for C_2F_7 radicals and Br_2 as titrant.

The rate constants studied in detail up to this time include those in Table I.¹⁰ The reactions of per-fluoroalkyl radicals are of some interest, but a reaction of wider interest is



The Arrhenius parameters for this reaction can be combined with those of the reverse reaction to give

Table I

reaction	$k(300 \text{ K})/M^{-1} \text{ s}^{-1}$
$CF_3 + Br_2 \rightarrow CF_2Br + Br$	7.8×10^8
$C_2F_5 + Br_2 \rightarrow C_2F_4Br + Br$	1.8×10^8
$n\text{-C}_4\text{F}_9 + Br_2 \rightarrow C_4F_8Br + Br$	2.0×10^8
$CF_3 + NOCl \rightarrow CF_2Cl + NO$	3.5×10^8
$CF_3 + O_2 \rightarrow CF_2O + O_2$	5.8×10^8
$CF_3 + NO_2 \rightarrow CF_2O + NO$	1.6×10^8
$CF_3 + O_2 \rightarrow CF_2O + F$	
$CF_3 + NO_2 \rightarrow CF_2O + NO$	
$CF_3 + O_2 \rightarrow CF_2O + F$	

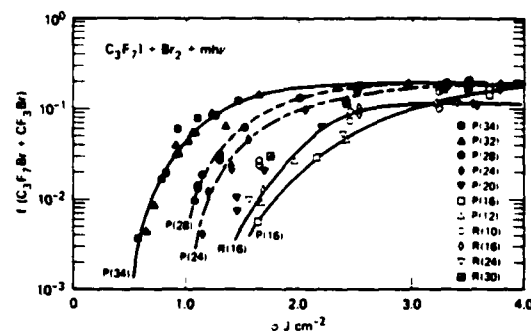


Figure 5. The yield of C_2F_7 from the MPD of C_2F_7I at various wavelengths.

values for both ΔH_f° and S° of t -Bu-radical. This reaction is currently under investigation using the molecule $CF_3N=N-t\text{-C}_4\text{H}_9$ as precursor.

Photophysics

We use the term photophysics to describe the interaction of the laser field and the molecules of interest. For example, the multiphoton decomposition yields depend on the fluence. Indeed, the yield of the MPD process is obtained from integrated areas under curves such as shown in Figures 3 and 4 when the scavenger concentration is sufficient to trap virtually all the radicals. Thus, yields as a function of laser parameters can be obtained in a universal manner. We have studied yields as a function of laser fluences, intensity, and added gas pressure. Results¹¹ for C_2F_7I at various exciting frequencies are shown in Figure 5. Here the results are displayed as the logarithm of the fraction reacted vs. fluence.

To investigate the assumption that fluence is the most important independent variable, we performed two types of experiments.¹² These experiments take advantage of the fact that the laser output is actually a train of partially mode-locked sharp peaks. If part of the beam is delayed relative to another part, these peaks are split and delayed as depicted in Figure 6. The recombination of the delayed and undelayed beam creates a pulse of the same fluence as the initial beam, but with less intensity, while causing no significant change in the overall pulse envelope. In the simplest experiment, Figure 7a, the transmitted beam is reflected upon itself. By changing the reflecting mirror position with respect to the sample cell, we can vary the instantaneous beam intensity while maintaining a constant fluence. This arrangement has the added advantage that it increases the available fluence by about

(11) M. J. Rossi, J. R. Barber, and D. M. Golden, to be published.

(12) M. J. Rossi, R. Nazman, J. R. Barber, D. M. Golden, and R. N. Zare, to be published.

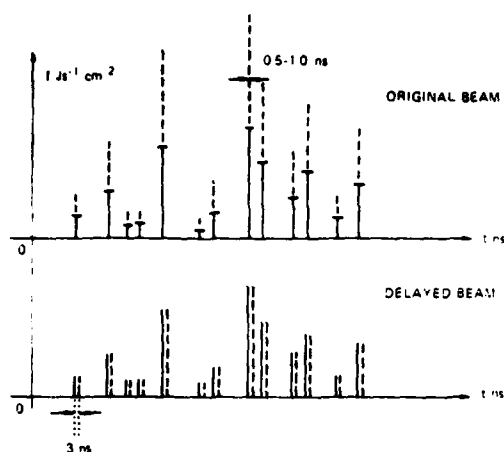


Figure 6. Schematic representation of the experimental intensity profiles.

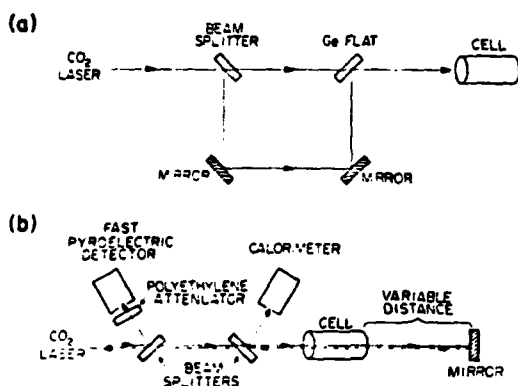


Figure 7. Experimental configuration for varying the intensity at constant fluence.

a factor of 2, and the optical arrangement is simple, although the phase difference between incident and reflected pulses varies over the cell length.

Another method for achieving the same results is the optical delay technique shown in Figure 7b. The pulsed output from the CO₂ laser passes through a beam splitter; one beam is delayed with respect to the other; then the two beams are recombined.

We performed experiments of the first type with both CF₃I and C₂F₇I. The results for the latter, using the method of Figure 7a, are shown in Figure 8. The CF₃I results are similar for both methods of beam delay, illustrating that in both cases intensity effects are clearly observable.

Treatment of Yield Data

In the search for a convenient way to display and analyze data concerning multiphoton yield as a function of fluence, we find¹³ that numerical solutions to the EGME over a wide range of physically reasonable parameters (i.e., cross section, density of states, chemical barrier height, and decomposition rate constants) show a regularity that can be used in data interpretation. Typical behavior of the system is shown in Figure 9. After the laser field is turned on, the ensemble of molecules is excited and the average internal energy increases monotonically toward a steady-state level. Figure 9c shows the approach to steady state, defined

(13) A. C. Baldwin and J. R. Barber, *J. Chem. Phys.*, in press.

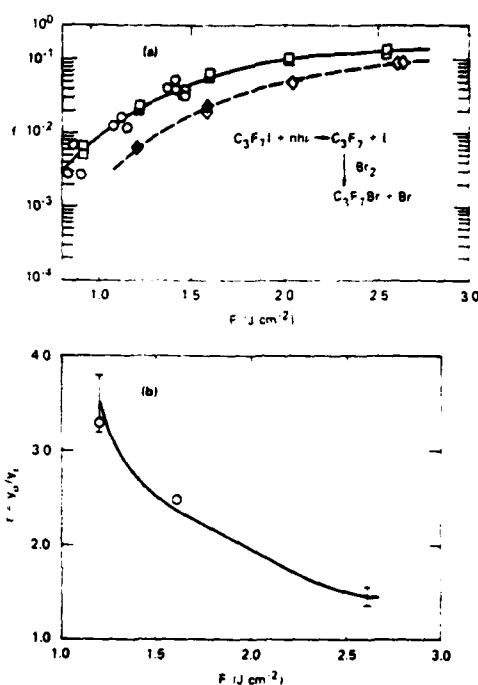


Figure 8. Experimental data on the MPD of C₂F₇I as a function of intensity at constant fluence. (a) (O) Experiments without mirror; (□) experiments with the mirror as close as possible to the sample cell; (◊) experiments with the mirror 30 cm from the cell, causing an average delay of 3 ns with respect to the center of the cell. Filled symbols refer to consecutive experiments in which all conditions remained constant except for the mirror position. (b) The ratio of the results given by the filled symbols in (a).

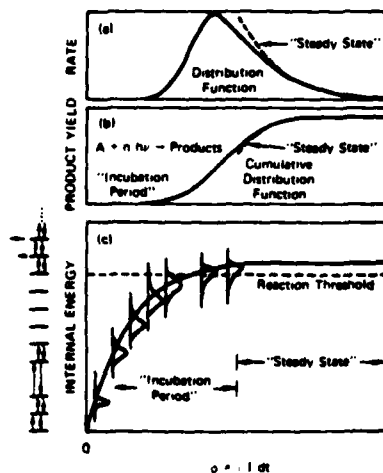


Figure 9. A schematic representation of the behavior predicted by the EGME.

in terms of internal molecular energy, and Figure 9a shows that during this same time the rate of decomposition or the probability that a molecule will decompose in time t to $t + dt$ (i.e., $P(t)dt$) first increases to a maximum and then decays. Figure 9b shows that yield, which is the integral of "rate", is an S-shaped cumulative distribution function (CDF). This CDF represents fractional yield vs. time. The abscissa can be scaled to fluence instead of time by recalling that $\phi = \int_0^t I dt$.

An important discovery is that the distribution function $P(t)$ of reaction times shown in Figure 9a can

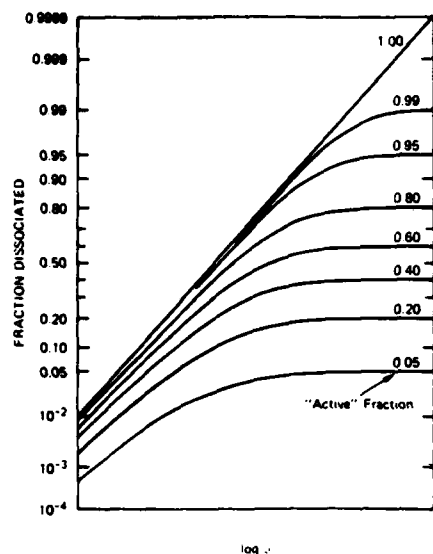


Figure 10. The calculated effect of an inactive population subset on the yield behavior, vs. log fluence.

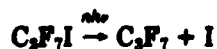
be represented as a log-normal distribution function (LNDF)^{7,13} (μ = mean, σ = standard deviation):

$$P(t) = \frac{1}{\sigma t \sqrt{2\pi}} \exp \left[-\frac{(\ln t - \mu)^2}{2\sigma^2} \right]$$

When the CDF corresponding to this equation is plotted vs. $\log \phi$ (or $\log t$), assuming a time-independent laser intensity, on probability graph paper, the result is a straight line.

This general behavior can also be shown by using the theory of Markovian random walks in finite discrete state space and continuous time.¹³ Since the log-normal distribution function is defined by two parameters (μ and σ), we may completely describe the yield behavior of the system by computing analytically the first two moments of the distribution of first passage times of the Markov process without numerically solving the set of differential equations represented by the EGME.¹³

In dealing with real data, several other considerations are important. First, even if an EGME is, in fact, applicable, the spatial profile of the laser must be taken into account. The data shown in Figures 11 and 13 are compared with deconvolutions of this kind. Second, many systems will not exhibit homogeneous behavior, i.e., different groups of molecules will be coupled with the laser field under different conditions (many ladders). A particularly simple version of this effect would be exhibited by a system in which a certain fraction of molecules (active) interact with the laser field, and the rest (inactive) do not. An idealization of such behavior is shown in Figure 10, and a possible example of actual behavior of this type (including spatial profile convolution) from our experiments using the system



with C_2F_7 trapped as $\text{C}_2\text{F}_7\text{Br}$ is shown in Figure 11.

If nonhomogeneity involves the coupling of more than one subset of the ensemble of irradiated molecules with the laser field, a linear combination of LNDFs may be required to fit the data. Figure 12 shows some possible results for the subsets in various combinations, and the

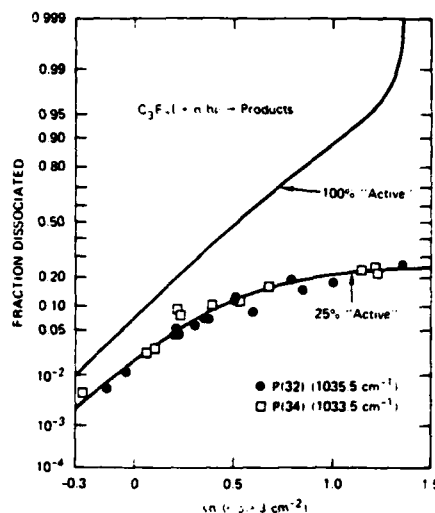


Figure 11. Experimental results (points) for the MPD of $\text{C}_2\text{F}_7\text{I}$, interpreted in terms of a two-population active/inactive case. The calculated lines have been convoluted with the experimental laser spatial profile.

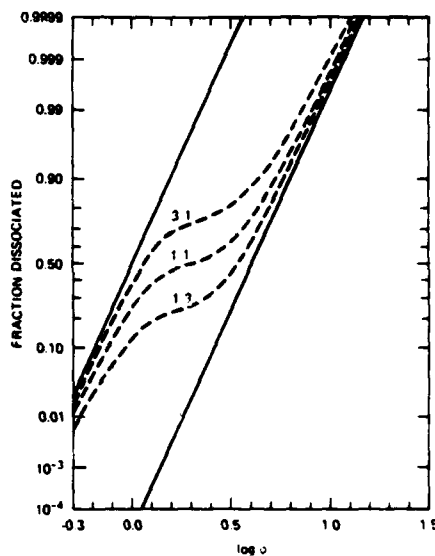


Figure 12. The calculated effect of two active population subsets on the yield behavior, as a function of the relative populations in each subset, plotted on probability graph paper vs. log fluence.

data in Figure 13 labeled R(16) gives a possible example of such a two-population case from some of our experiments on CF_3I (CF_3 trapped as CF_3Br). The data in Figure 13 labeled R(8) may be the result of a simple homogeneous case, or a nonhomogeneous case that mimics the simple one.

Energy Transfer

The EGME, which describes a simple incoherently pumped, homogeneously interacting system, is valid only under collisionless conditions. The effects of collisions can be added to the master equation by adding collisional energy transfer rate constants. These rate constants can be described in terms of the parameter $\langle \Delta E \rangle$, the average energy transferred per collision.¹⁴ If, in fact, we have data for the yield vs. fluence under collisionless conditions such that we have arrived at

(14) J. Troe, *J. Chem. Phys.*, **66**, 4748 (1977).

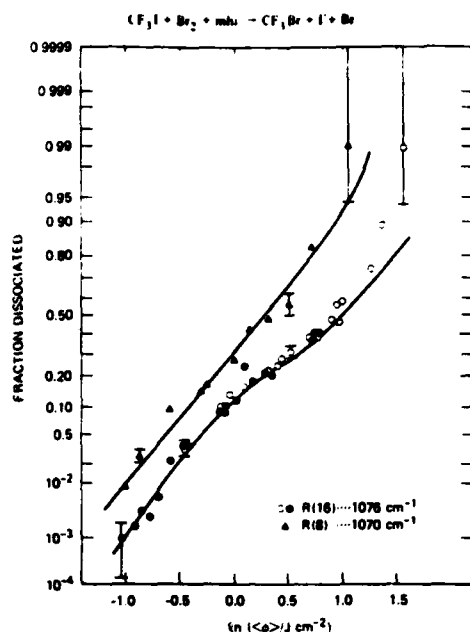


Figure 13. Experimental results (points) for the MPD of CF_2I , interpreted in terms of a simple homogeneous situation R(8) or in terms of two active population subsets, R(16). The calculated lines have been correlated with the experimental laser spatial profile.

suitable values of the absorption cross section and its energy dependence, we may fit the yield as a function of pressure at a given fluence with a value of $\langle\Delta E\rangle$. This value may be compared with values derived from chemical activation (for above threshold) and from low-pressure limit thermal activation (less than or equal to threshold) experiments.

van den Bergh and co-workers¹⁵ have measured the yield of multiphoton decomposition of CF_2HCl as a function of both fluence and pressure of added argon; their data are shown in Figure 14. These data have been simulated as described above,¹⁶ and it was found that a value of $\langle\Delta E\rangle$ of ~ 0.1 kcal mol⁻¹ gives best agreement with the data. Figure 14 shows this fit for three different fluences. (Note that the homogeneous collisionless decomposition fraction is taken from extrapolation to zero pressure.) Introducing collisional terms, which are independent of the laser intensity, into the EGME requires us to consider in detail the exper-

(15) R. Duperrez and H. van den Bergh, *J. Chem. Phys.*, **46**, 275 (1979).

(16) A. C. Baldwin and H. van den Bergh, *J. Chem. Phys.*, in press.

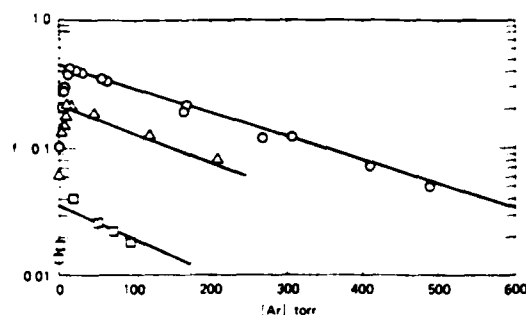


Figure 14. Experimental data (points) on the decomposition of CF_2HCl as a function of fluence and bath gas pressure. The calculated lines are based on an EGME with collisional energy transfer terms included.

imental laser intensity dependence when comparing the EGME predictions with experiment. The good agreement between computed and experimental results in Figure 14 was only obtained by using a parameterized temporal laser intensity profile that approximated the mode-locked spikes of the experimental beam.

Future Directions

We have developed a technique that allows us to extend the experimental range for the determination of rate constants for fundamental processes and at the same time provide data for the detailed physical understanding of the multiphoton decomposition of polyatomic molecules. The photophysical questions raised have occupied much of our effort, but we believe that the photochemical uses of these experimental techniques will prove very interesting and useful to chemists in the long run. We now have the ability to produce reactive species at wall temperatures chosen independently of the production act. Thus, we will be able to extend these rate constant measurements over wide temperature ranges. In addition, we can study average vibrational energy transferred per collision by monitoring the effects of added gases.

A potentially interesting area for future research is the study of branching ratios when more than one reaction pathway exists. Changes in these ratios with laser conditions will be sensitive probes of energy distribution functions and may shed some light on the rate of intramolecular vibrational energy redistribution.

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