

PHOTOSELECTIVE CHEMISTRY

PART 2

Edited by

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ADVANCES IN CHEMICAL PHYSICS

VOLUME XLVII

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PHOTOSELECTIVE CHEMISTRY

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ADVANCES IN CHEMICAL PHYSICS

VOLUME XLVII

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more, and be broadly educated with respect to a large domain of science, has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE
STUART A. RICE

PREFACE

Photoselective chemistry is concerned with the influence of selective optical excitation on the acquisition, storage and disposal of energy and on the reactivity of molecules, in both gaseous and condensed phases. The very considerable recent progress in this field is largely due to the introduction of lasers, both as pumping and as probing devices, and to the intense theoretical effort stimulated by the many new and intriguing experimental findings. Photoselective chemistry is an interdisciplinary research area, blending concepts and techniques from a wide variety of fields. The articles assembled in these volumes describe many of the theoretical and experimental results now in hand, with the goal of contributing to the synthesis of a conceptual framework with which one can understand a broad spectrum of photophysical and chemical processes. The field is too young, and too little is known, to permit compilation of a definitive treatise. Instead, the contributions in these volumes reflect our opinion of the kinds of information which must be accumulated before it is possible to develop an integrated approach to the interpretation of observations already made and to the development and exploitation of these for new approaches to photochemistry. The same (opinionated) point of view guided the Organizing Committee [J. Jortner (Chairman), S. Kimel, A. Levin, R. D. Levine] of the Laser Chemistry Conference, which took place on December 15–22, 1979 at Ein Bokek, Israel, under the auspices of the National Council for Research and Development, Jerusalem, Israel. Indeed the decision to compile these volumes was triggered by the intensive and exhaustive problem-oriented discussions which took place during that Conference. In addition to contributions by participants at the Ein Bokek meeting, we have included many others, the overall goal being to provide an up-to-date set of authoritative reviews spanning the various aspects of photoselective chemistry.

The first article is meant to serve as an introduction to the entire field; it provides an overview of the relevant concepts, problems, ideas and experiments described in the following papers. This introductory article was written after receipt of the other contributions so that cross references could be made. The following articles have been organized in topical groups. Where it was desirable and practical, an introductory article to the given

topic is placed first. The general organization of the material is:

1. Aspects of Intramolecular Dynamics
2. Multiphoton Induced Chemistry
3. Studies of Collision Effects
4. Studies in Condensed Media
5. Other Aspects of Photoselective Chemistry

We have followed the general policy of the *Advances in Chemical Physics* in that the authors have been given complete freedom, our point of view being that the person who pioneered the topic is the best judge of the appropriate mode for its presentation. We believe that the results have more than vindicated our approach and hope that the reader concurs. These volumes offer the newcomer a review of the entire field, yet in each and every direction reach the forefront of the current research effort and even attempt to explore the perspectives and future of photoselective chemistry.

We are grateful to the participants of the Ein Bokek Conference and to numerous colleagues and friends, whose lively and probing discussions convinced us of the merits of this project, and to the staff of Wiley-Interscience for welcoming and supporting it. We thank the authors for their willingness to contribute to this endeavor and for their adherence to a timetable which enabled us to send the manuscripts to the publisher in the Fall of 1979. The wide range of subjects touched on in these volumes bears witness to the scope of photoselective chemistry and to the contagious enthusiasm of its practitioners.

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January 1981*

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PHOTOSELECTIVE CHEMISTRY

PART 2

ADVANCES IN CHEMICAL PHYSICS

VOLUME XLVII

Section 3

**ONE-PHOTON AND TWO-PHOTON
PHOTOSELECTIVE CHEMISTRY**

ENHANCEMENT OF CHEMICAL REACTIONS BY INFRARED LASERS

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I. INTRODUCTION

The detailed effect of reactant internal energy on chemical reactions has been a subject of considerable interest in chemical kinetics for many years. Classic work of Evans and Polanyi in the 1930s illustrated the importance of vibrational energy in reaction dynamics, and the intimate nature of the coupling of vibrational and translational energy with a reaction potential energy surface.^{1,2} Although a topic of central importance in reaction dynamics, explicit effects of reactant vibrational energy on a chemical reaction have been difficult to assess because of problems associated with preparing molecules in well-defined initial states by traditional chemical or thermal activation techniques. Even so, molecular beam³ and infrared chemiluminescence⁴ experiments have provided a great deal of experimental data on the role of internal energy in chemical reactions.

A powerful new tool that has been added recently to the experimentalist's arsenal is the infrared laser. The advent of tunable infrared lasers now makes possible population of well-defined initial internal energy states, and the concomitant ability to examine more closely the role of vibrational energy in chemical reactions. Several recent review articles discuss the use

of lasers in promoting chemical reactions and in probing reaction dynamics.⁵⁻⁸ In this chapter we shall be concerned only with the effects of laser excitation on enhancing chemical reactivity.

The ability of both pulsed and cw infrared lasers to induce chemical reactions is well known. CO₂ lasers are now common equipment in many laboratories. The infrared laser-induced process studied most extensively is multiphoton excitation of molecules (using megawatt CO₂ laser radiation) to high vibrational states from which reaction, usually dissociation, may occur. This field is the subject of intense effort by many research groups, and a number of excellent review articles have been written about multiphoton excitation.⁹ At lower laser intensities it is possible to prepare molecules in specific initial vibrational states below the dissociation threshold and to study their subsequent bimolecular and unimolecular (isomerization) reactions. In this chapter we shall restrict ourselves to considering only the results of low-level vibrational excitation on chemical reactions.

II. VIBRATIONAL ENHANCEMENT OF BIMOLECULAR REACTIONS

It was recognized early in the study of chemical kinetics (particularly with regard to unimolecular reactions) that increasing the energy of reactants increased reaction rates. This was usually accomplished by simply raising the reaction temperature. As experimental techniques were refined, it became possible to answer the question of whether vibrational or translational energy was more important in enhancing a bimolecular reaction. Evans and Polanyi presented the first qualitative description of how reactant initial energy is coupled to details of the potential energy surface.¹ Although strictly concerning three-atom reactions (1) the concepts are useful for more complex systems as well. For exothermic reactions, the



ability of vibrational or translation energy to enhance a reaction depends on whether the potential energy surface is attractive (late barrier) or repulsive (early barrier). For an attractive surface trajectory studies show that reactant vibrational energy is most effective at promoting reaction. Conversely, for a repulsive surface reactant translational energy enhances reaction. Molecular beam studies (generally for reactions of hydrogen halides) have confirmed these predictions.

Endothermic reactions may be considered as the reverse of the exothermic reactions just discussed. Considering both attractive and repul-

TABLE I
Bimolecular Reactions of Infrared Laser Excited Molecules

Reaction	Pump laser ^a	ΔH_{298}^{2b}	Comments ^c	Ref.
HCl($v=1$) + H → H ₂ + Cl	HCl	-1.2	No enhancement	34
HCl($v=1$) + K → KCl + H	HCl	1.5	$k_1/k_{th} = 100$	13
HCl($v=1$) + O → OH + Cl	HCl	0.7	$k_1/k_{th} = 300$	41
HCl($v=2$) + Br → HBr + Cl	HCl	15.5	$k_1/k_{th} = 10^{11}$	34, 42
HF($v=1$) + Ba → BaF(v) + H	HF	> -2.6	$k_1/k_{th} = 0.1-300^d$	11
HF($v=1$) + Ca → CaF + H	HF	9.2	$k_1/k_{th} > 10^4$	14
HF($v=1$) + Sr → SrF + H	HF	8.0	$k_1/k_{th} > 10^4$	14
DF($v=1$) + Ca → CaF + D	DF	9.2	No reaction	14
DF($v=1$) + Sr → SrF + D	DF	8.0	No reaction	14
HCl($v=6$) + D ₂ → HD + DCl	Visible dye	~0	No reaction	6
O ₃ (v) + NO → NO ₂ [*] + O ₂	CO ₂	-4.8	$k_1/k_{th} = 4$	15, 16, 18
→ NO ₂ [†] + O ₂	CO ₂	47.	$k_1/k_{th} = 17$	15, 16, 18
O ₃ (v) + O → 2O ₂	CO ₂	-94	No enhancement	33
O ₃ (v) + O ₂ → 2O ₂ + O	CO ₂	25.4	$k_1/k_{th} = 40$	15
O ₃ (v) + SO → SO ₂ + O ₂	CO ₂	-107	$k_1/k_{th} = 2$	32
O ₃ (v) + Ba → BaO + O ₂	CO ₂	-107	$k_1/k_{th} = 5-10$	43
O ₃ (v) + Pb → PbO + O ₂	CO ₂	-59	$k_1/k_{th} = 10-20$	44
NO($v=1$) + O ₃ → NO ₂ [*] + O ₂	CO	-4.8	$k_1/k_{th} = 6$	17
→ NO ₂ [†] + O ₂	CO	47.6	$k_1/k_{th} < 22$	17
OCS(v) + O → CO + SO	CO ₂	-51	No enhancement	45
C ₂ H ₄ (v) + O → CH ₃ + CHO	CO ₂	6.2	No enhancement	45
CH ₃ Br(v) + Cl → CH ₂ Br + HCl	CO ₂	NA	$k_1/k_{th} \sim 1.05$	19
CH ₃ F(v) + D → CH ₃ + DF	CO ₂	-26	No reaction	46
CH ₃ F(v) + O → CH ₂ F + OH	CO ₂	5	No enhancement	46
BH ₃ PF ₃ (v) + BH ₃ → B ₂ H ₆ + PF ₃	CO ₂	NA	Enhancement observed	20
BCl ₃ (v) + 3C ₂ Cl ₄ → C ₆ Cl ₆ + 3Cl ₂ + BCl ₃	CO ₂	NA	Laser promoted	21
B(CH ₃) ₃ (v) + HBr → B(CH ₃) ₂ Br + CH ₄	CO ₂	NA	Laser promoted	22
B(CH ₃) ₂ Br(v) + HBr → B(CH ₃)Br ₂ + CH ₄	CO ₂	NA	Laser promoted	22
B(CH ₃)Br(v) + HBr → BBr ₃ + CH ₄	CO ₂	NA	Laser promoted	22
SF ₆ (v) + e ⁻ → SF ₅ ⁻ + F	CO ₂	~4	$k_1/k_{th} \sim 3$	28
Fe(CO) ₄ (v) + CH ₄ → Fe(CO) ₄ CH ₄	CO	NA	Laser promoted, matrix isolation	25
Fe(CO) ₄ (v) + CO → Fe(CO) ₅	CO, SFRL ^e	NA	Laser promoted, matrix isolation	24
UF ₆ (v) + SiH ₄ → UF ₅ , UF ₄ , SiH ₃ F	16 μm diode ^f laser	NA	Laser promoted matrix isolation	26

^aHCl laser: 3.8 μm; HF laser: 2.8 μm; DF laser: 3.8 μm; CO₂ laser: 10.6 μm; CO laser: 5.6 μm.

^b ΔH_{298}° calculated from data in Ref. 47. Values are kcal/mole. NA indicates data not available.

^c k_1/k_{th} = ratio of rate constant with laser excitation to thermal rate constant.

^dValue of k_1/k_{th} depends on v' state of BaF.

^eSFRL = spin flip raman laser.

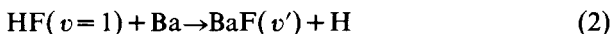
^fThis reaction also promoted by broadband IR excitation.

sive potential energy surfaces leads to the conclusion that for endothermic reactions the crest of the activation barrier lies in the reaction exit channel (i.e., a late barrier).¹⁰ The expectation, then, is that reactant vibrational energy will be most effective at enhancing an endothermic reaction. A second consideration for endothermic reactions is whether the vibrational excitation is sufficient to raise the system above the activation barrier. In those reactions where this is the case, substantial rate enhancement should be realized.

Tunable, narrow bandwidth lasers provide a very convenient method for obtaining selective vibrational excitation. A number of reactions of infrared laser-excited species have been studied to date, and are listed in Table I. Also included is the frequency of the pump laser, the ground-state heat of reaction, and the effect of vibrational excitation on reaction rate. Reactions in Table I are listed according to increasing molecular complexity.

A. Atom Plus Hydrogen Halide Reactions

The reactions of excited hydrogen halides are convenient to study because of the availability of hydrogen halide chemical lasers for excitation. The correlation between ground-state heats of reaction and vibrationally induced reaction rate enhancement is striking for these processes (Table I). As expected, reaction enhancement is observed for all reactions except for those that are exothermic. In the case of reaction (2) the reaction rate is



highly state specific.¹¹ In fact, as the reaction is made endothermic (higher v') substantial rate enhancements are observed.

In an elegant series of experiments, Brooks and co-workers explored reaction (3) as a function of both relative translational energy¹²



and HCl vibrational energy.¹³ While translational energy is capable of enhancing the reaction rate by up to one order of magnitude, HCl vibrational energy is found to enhance the reaction by two orders of magnitude. The preferential enhancement of reaction (3) by vibrational energy is evident.

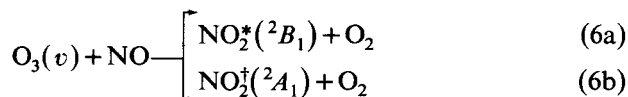
Reactions (4) and (5) are both examples of endothermic



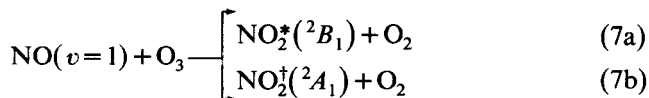
reactions, yet only the rate of reaction (4) is enhanced by reactant excitation.¹⁴ This is because one quanta of HF vibration (3600 cm^{-1}) is enough to surmount the activation barrier, while one quanta of DF vibration (2700 cm^{-1}) leaves the reactants below the activation barrier. The same situation is true if calcium is replaced by strontium.¹⁴

B. Polyatomic Bimolecular Reactions

While it is tempting to apply the concepts developed for atom plus diatomic reactions to polyatomic reactions in general, it becomes rapidly apparent that the situation is much more complex. One of the first reactions studied was the reaction of O_3 with NO, reaction (6).¹⁵ Two channels are available, one producing electronically excited NO_2 [exothermic, reaction



(6a)] and one producing vibrationally excited NO_2 [endothermic, reaction (6b)]. The rate for reaction (6a) is enhanced by a factor of 4, while the rate for reaction (6b) is enhanced by a factor of nearly 20. Because it is not known precisely what initial and final states are involved, and which O_3 vibrations are coupled to the reaction coordinate, it is not possible to correlate the observed rate enhancement with the reaction endo- or exothermicity. Initial studies indicated that reaction was dependent on intramolecular energy transfer from the O_3 ν_3 mode to the ν_2 mode. Subsequent studies show the O_3 ν_3 mode is involved in the reaction.¹⁶ As a further probe of this reaction, a CO laser was used to excite NO, reaction (7).¹⁷ Enhancement of reaction (7a) was comparable to enhancement in reaction (6a).

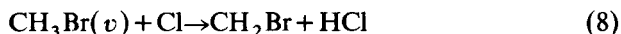


Only an upper bound was put on the rate for reaction (7b), indicating it could be comparable to reaction (6b) or much slower.

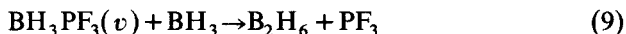
In related experiments¹⁸, SiF_4 was added to the O_3 -NO system. Irradiation with a CO_2 laser at the $9.6\mu\text{m}$ P(30) transition excites O_3 while the $9.6\mu\text{m}$ P(32) transition excites SiF_4 . Enhancement of reaction (6) is observed in both cases, either by direct O_3 excitation or by near resonant V-V transfer from SiF_4 to O_3 . In the latter case the $\text{O}_3(v)$ concentration is much

lower than when excited directly due to rapid redistribution of energy among SiF_4 vibrations not resonant with O_3 . This technique allows the enhancement of reaction (6) to be studied both directly and via a $V-V$ excitation step. While it is clear that vibrational energy enhances the reaction of O_3 with NO , the complexities of this reaction illustrate some of the difficulties in dealing with polyatomic systems.

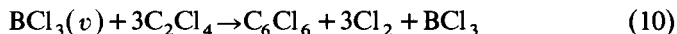
Enhanced reaction rates are seen for several more complex reactions. In isotope separation experiments, CH_3Br reacting with Cl [reaction (8)] shows



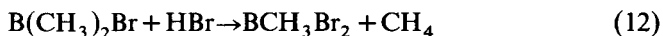
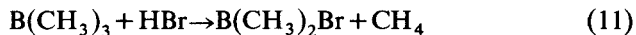
an enhanced reaction rate when pumped with a CO_2 laser.¹⁹ For process (9)



reaction of BH_3 with BH_3PF_3 has an activation energy of about 8 kcal/mole. Vibrational excitation of BH_3PF_3 is observed to enhance the reaction rate for reaction (9).²⁰ It is postulated that this reaction involves sequential absorption of two or three CO_2 laser photons for significant rate enhancement. In the reaction of BCl_3 and C_2Cl_4 , process (10),

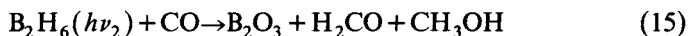
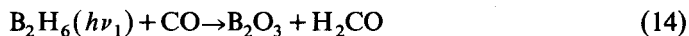


the products with lower activation energy are among those found for a thermal process.²¹ However, reaction (10) is found to be specific for BCl_3 ; use of either SF_6 or BBr_3 as sensitizer leads to reaction products characteristic of higher temperature processes, with little formation of C_6Cl_6 . Related experiments were carried out with brominated boron compounds, reactions (11)–(13).²² These are all known thermal reactions, with



reaction (11) characteristic in the 150–180°C range, reaction (12) at temperatures > 250°C, and reaction (13) at temperatures > 450°C. What is particularly interesting is that irradiating BCH_3Br_2 in a mixture of BCH_3Br_2 and $\text{B}(\text{CH}_3)_2\text{Br}$ produces only BBr_3 , and no loss of $\text{B}(\text{CH}_3)_2\text{Br}$. Laser excitation selectively heats one component of the mixture, while the bulk sample remains at a low temperature.

Diborane is an interesting molecule for studying laser-enhanced reactions because a CO₂ laser may be used to excite three distinct vibrational modes of the molecule. Reactions (14)–(16) are those found to



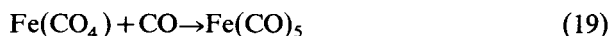
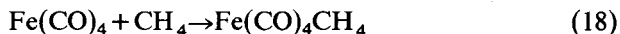
occur when a mixture of B₂H₆ and CO is irradiated with a CO₂ laser exciting the boron bridging mode, BH₂ scissors mode, and terminal BH stretching mode, respectively.²³ The only reaction resulting in products characteristic of the thermal process is reaction (16), where the terminal BH stretch is excited. Excitation at the other frequencies result in a proton stripping reaction. Thus the reaction is markedly influenced by which mode is excited.

Two experiments have dealt with the effect of higher levels of vibrational excitation on a bimolecular reaction. Overtone absorption from $v=0$ to $v=6$ can be induced in HCl using visible light from a dye laser. Due to the small cross-section associated with overtone transitions, the high laser intensities obtainable intracavity are needed. For reaction (17), the activation energy



is estimated to be 34 kcal/mole. No reaction could be observed with irradiation at room temperature.⁶ Since overtone excitation is expected to overcome the activation barrier, it is not clear why enhanced reaction is not observed in process (17). It may be that estimates of the activation energy are in error, and the four-center reaction requires more excitation than that available from HCl($v=6$).

The use of matrix isolation techniques has led to several interesting infrared laser promoted reactions. The reactions of Fe(CO)₄ with CH₄ and CO, processes (18) and (19), have been observed when the Fe(CO)₄ is excited



by a CO laser.^{24–25} The mechanism for these reactions is unclear at this time. In similar experiments Catalano and Barletta have observed reactions of UF₆ and SiH₄ in matrices, to produce a variety of products, including UF₅, UF₄, and SiH₃F.²⁶ In the gas phase they estimate an

activation energy of 30 kcal/mole yet in the matrix experiments, the reaction is apparently induced by single-photon absorption by UF_6 (3 kcal/mole). In fact, the reactions can be promoted by use of a broadband infrared source (Nernst glower). It has been concluded that the drastic change in activation barrier is due to the fixing of reactant configurations in the matrix. Recent attempts to duplicate the infrared photochemical reaction of UF_6 with SiH_4 in a matrix have failed to reproduce the original data. There is some speculation that the reaction is induced instead by small amounts of UV light from the broadband infrared source used for either excitation or product analysis.²⁷

A somewhat different type of reaction for which vibrational enhancement of the reaction rate is observed is reaction (20).²⁸

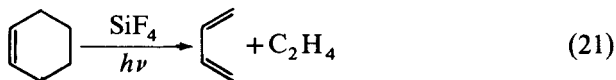


An estimate of the activation barrier for this reaction is 0.2 eV, comparable to the energy of a CO_2 laser photon. Excitation of the $10 \mu\text{m } \nu_3$ mode of SF_6 is seen to enhance the dissociative electron attachment process.

C. Laser-Enhanced Reactions at High Pressure

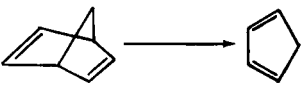

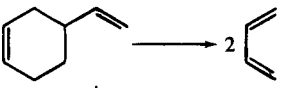
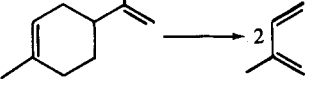
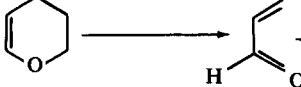
In order to maintain state-specific populations, low pressures are required. If pressures are raised to the point where collisions are frequent, then specific effects of laser excitation are lost and intermolecular energy transfer heats the entire sample. Reactions induced in this fashion then yield products characteristic of thermal processes. A particularly interesting aspect of this pyrolysis technique is the homogeneous nature of the reaction. Since heating is confined to the region near the laser beam, heterogeneous effects due to hot walls in a conventional pyrolysis reactor are avoided.

Table II lists a number of the high-pressure laser-induced reactions that have been studied. (References 29 to 30 contain more extensive tables of similar reactions not included here.) These reactions are carried out either directly or with a second component added as a sensitizer. Reaction (21)³¹ proceeds only in the presence of a sensitizer such as SiF_4 , since



cyclohexene is transparent to CO_2 laser radiation. SiF_4 absorbs light, heating the cyclohexene via intermolecular energy transfer. The reaction is particularly clean from the standpoint of not involving heterogeneous wall effects. A sensitizer is not needed if the reacting species absorbs the laser

TABLE II
High-Pressure Laser-Enhanced Reactions

Reaction	Pump laser	Pressure ^a	Ref.
	CO ₂ ^b	10–50	31
	CO ₂ ^b	10–50	31
	CO ₂ ^b	10–50	31
	CO ₂ ^b	10–50	31, 48
	CO ₂ ^b	10–50	31
CF ₂ ClCF ₂ Cl → C ₂ F ₄ + Cl ₂	CO ₂	200	49
CH ₃ CF ₂ Cl → CH ₂ CF ₂ + HCl	CO ₂	50–400	32
B ₂ H ₆ → B ₂ H ₉ , B ₅ H ₁₁ , B ₁₀ H ₁₄ , (BH) _n	CO ₂ ^c	50–500	50
CH ₃ F → C ₂ F ₄ , HF, C ₃ F ₆ , X ^d	CO ₂ ^c	50–100	30
CHClF ₂ → C ₂ F ₄ , HCl, C ₃ F ₆ , X ^d	CO ₂ ^c	50–100	30
c-C ₄ F ₈ → C ₂ F ₄ , C ₃ F ₆ , X ^d	CO ₂ ^c	50–100	30
CH ₄ → C ₂ H ₄ , C ₂ H ₆ , C ₂ H ₂	CO ₂ ^c	50–100	30
C ₂ H ₄ → CH ₄ , C ₂ H ₆ , C ₃ H ₆ , C ₃ H ₈ , C ₄ , C ₅ hydrocarbons	CO ₂	100–500	30, 51, 52
C–C ₃ H ₆ → C ₃ H ₆ , CH ₄ , C ₂ H ₄	CO ₂ ^c	50–100	30
C ₂ H ₆ → C ₂ H ₄ , CH ₄ , C ₂ H ₂	CO ₂ ^c	50–100	30
<i>trans</i> -2-butene → CH ₄ , C ₂ H ₄ , C ₃ H ₆ , <i>cis</i> -2-butene, C ₄ H ₆	CO ₂ ^c	50–100	30
<i>cis</i> -2-butene → CH ₄ , C ₂ H ₄ , C ₃ H ₆ , <i>trans</i> -2-butene, C ₄ H ₆	CO ₂ ^c	50–100	30
B ₂ H ₆ + O ₂ → boron oxides, X ^d	CO ₂ ^c	50–100	30
Fe(CO) ₅ + O ₂ → iron oxides, X ^d	CO ₂ ^c	50–100	30
Fe(CO) ₅ → Fe, CO, X ^d	CO ₂ ^c	50–100	30

^aUnits are torr.

^bSiF₄ added as sensitizer.

^cSF₆ added as sensitizer.

^dX indicates unidentified products.

radiation. This is the case for reaction (22)³². The products are



characteristic of the thermal pyrolysis, with excitation as a result of infrared absorption by $\text{CH}_3\text{CF}_2\text{Cl}$.

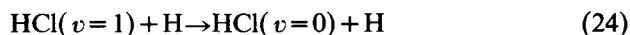
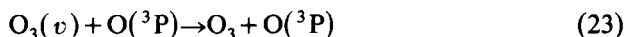
The reactions of various hydrocarbons listed in Table II are noteworthy in that they yield dehydrogenated products in amounts differing from those obtained by conventional heterogeneous pyrolysis techniques. For all hydrocarbon reactions listed in Table II, SF_6 was added as a sensitizer. An additional example, listed in Table II, of a novel type of reaction by laser pyrolysis is the production of metal particulates. This type of reaction, if selective for only one component of the starting material, could lead to production of very pure products.

The reactions listed in Table II illustrate the utility that this technique may have in conventional pyrolysis reactions. The homogeneous nature of the laser-induced reaction minimizes undesirable secondary products and results in cleaner processes with higher yields. Laser-induced pyrolysis may prove to be a useful synthetic technique.

D. Collisional Deactivation of Vibrationally Excited Species

It is appropriate here to point out that, in addition to the reactive collisions discussed so far, the possibility of inelastic nonreactive collisions is also present. In many instances the nonreactive channel may be dominant.

In the case of atom plus molecule reactions, the atom may very efficiently deactivate the excited molecule. Reactions (23)³³ and (24)³⁴



are examples of rapid deactivation by reactive atomic species. The ability of a reactive atom to form a long-lived complex with the molecule allows the atom to remove energy efficiently when the complex decomposes. In looking at enhancement of reaction rates by laser excitation it is necessary to observe both decay of the excited species and also product formation to distinguish correctly between reactive and nonreactive pathways.

Vibrational deactivation by polyatomic species takes place predominantly by V-V relaxation rather than V-T relaxation.^{35,36} The facility of one molecule for deactivating another molecule depends on many factors, for example, the energy mismatch between vibrational frequencies of the two species. When a near-resonance exists, the collisional deactivation

process may be rapid, requiring 10–100 collisions.³⁶ For reactions of molecules with only one quantum of vibrational excitation, collisions that remove 2–5 kcal/mole are particularly effective at canceling any rate enhancement, since the amount of energy removed is roughly the same as the amount of energy absorbed by the molecule from the laser. These nonreactive collisions may be more efficient than reactive encounters and need to be considered if an experiment is done under collisional conditions.

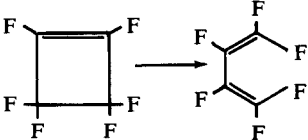
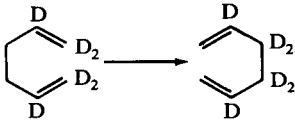
III. VIBRATIONAL ENHANCEMENT OF ISOMERIZATION REACTIONS

Isomerization reactions induced by vibrational excitation are listed in Table III. Probably the first infrared photochemical reaction to be observed was the isomerization of nitrous acid in a nitrogen matrix, reaction (25).³⁷



The excitation source was a filtered Nernst glower. At the power levels

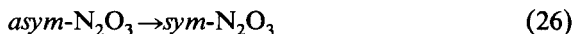
TABLE III
Isomerization Reactions of Infrared Laser-Excited Molecules

Reaction	Pump laser	Comments	Ref.
<i>cis</i> -HONO → <i>trans</i> -HONO	Broadband ^a 3000–4000 cm ⁻¹	Infrared promoted, matrix isolation	37
<i>asym</i> -N ₂ O ₃ → <i>sym</i> -N ₂ O ₃	Broadband near-IR	Infrared promoted, matrix isolation	38
Fe(CO) ₄ $\xrightarrow[\text{exchange}]{\text{ligand}}$ Fe(CO) ₄	CO, SFRL ^b	Infrared induced, matrix isolation	24, 39
	CO ₂	Gas phase	53
	CO ₂	Gas phase	54
<i>trans</i> -2-butene → <i>cis</i> -2-butene	CO ₂	Gas phase	30, 55
<i>trans</i> -C ₂ H ₂ Cl ₂ → <i>cis</i> -C ₂ H ₂ Cl ₂	CO ₂	Gas phase	56

^aRadiation from infrared spectrometer source.

^bSFRL = spin flip Raman laser.

involved, only single-photon processes can occur. It was postulated that rapid intramolecular energy transfer into the torsional mode led to isomerization. In a similar reaction using near-infrared radiation from a broadband source, isomerization of N_2O_3 was observed in a matrix, reaction (26).³⁸



Recent experiments have been carried out on isomerization of $Fe(CO)_4$ in an Ar matrix. By using labeled CO groups, it is possible to distinguish between the various isomers.^{24,39} It was found that, by tuning either a CO laser or spin flip Raman laser to a particular ligand absorption, isomerization could be induced. In addition, it was possible to distinguish between $Fe(CO)_4$ molecules in different orientations within the matrix, and to selectively excite those molecules in a particular orientation. Experiments with polarized light indicate that the observed isomerization is not due to simple heating of the matrix.²⁴

Gas-phase isomerization reactions have also been induced with infrared lasers. Examples of these are included in Table III. In general, these reactions require more than one photon to overcome the isomerization barrier, but less photons than required for a dissociation process. The gas-phase isomerization reactions are unique in that the product species has enough internal energy to react back to starting material. The ratio of reactants to products will thus depend on the relative isomerization rates and the rates of deactivation of excited molecules.

IV. CONCLUSION

From Tables I–III it can be seen that there is a great deal of interest in a variety of infrared laser-enhanced reactions. At the same time there are many questions that remain to be answered. The basic concepts put forth in the 1930s by Evans and Polanyi are seen to be qualitatively valid for laser-excited hydrogen halide plus atom reactions. The influence of vibrational energy on reactions of complex polyatomic molecules is much less clear, especially in those cases where the initial and final molecular states are not well known. Tunable, narrow bandwidth lasers have proven to be valuable as tools in probing the reaction dynamics of vibrationally excited molecules. Their value will continue to increase as new laser sources are discovered that cover the infrared spectrum more fully. Combining these new laser sources with molecular beam techniques should allow the effects of vibrational vs translational energy to be sorted out for complex reactions, much as in the case of reaction (3). It will also be possible to explore the effects of exciting a molecule at various different frequencies. As

intramolecular energy relaxation is thought to be slow at low levels of excitation, it may be that some of the current questions regarding energy localization in polyatomic molecules⁴⁰ will be answered by bimolecular reactions of vibrationally excited species. It is clear that much work remains to be done and will provide new insights into reaction dynamics in the years to come.

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TWO-PHOTON EXCITATION AS A KINETIC TOOL: APPLICATION TO NITRIC OXIDE FLUORESCENCE QUENCHING

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I. MULTIPHOTON VERSUS ONE-PHOTON SPECTROSCOPY

The polarization \mathbf{P} of an atom or a molecule can be expressed as a power series in the field intensity \mathbf{E}

$$\mathbf{P} = \alpha \mathbf{E} + \alpha' \mathbf{E}^2 + \alpha'' \mathbf{E}^3 + \dots \quad (1)$$

One-photon spectroscopy is due to the linear term, whereas the nonlinear terms lead to the simultaneous absorption of two or more photons. Although the theory was worked out almost 50 years ago,¹ observation of multiphoton absorption was made feasible only after the development of lasers. This chapter deals with the application of two-photon excitation (TPE) to kinetic studies in low-pressure gas-phase samples. For a systematic, extensive discussion of spectroscopic applications, one of the excellent reviews available should be consulted.^{2,3}

The two-photon transition rate, W_{gf} , defined as the probability for absorption of a photon per molecule may be written as^{2,3}

$$W_{gf} = \delta_{gf} I(\omega_1) I(\omega_2) \quad (2)$$

Here $I(\omega_i)$ is a laser intensity (photons $\text{s}^{-1} \text{cm}^{-2}$) at frequency ω_i and δ_{gf} is the two-photon absorption cross-section ($\text{cm}^4 \text{s photon}^{-1} \text{molecule}^{-1}$) for transition from state g (at energy E_g) to state f (at energy E_f). The resonance condition is

$$\hbar(\omega_1 + \omega_2) = E_f - E_g \quad (3)$$

In the special case of two photons of the same frequency, ω , the final state is populated at a rate

$$\frac{dN_f}{dt} = (1/2)W_{gf}N_g = (1/2)N_g\delta_{gf}I(\omega)^2 \quad (4)$$

with N_g and N_f the number densities (molecules cm^{-3}) of the initial and final state, respectively. δ_{gf} is the analog of the one-photon absorption cross-section, and may be written as

$$\delta_{gf} = 128\pi^3 \cdot \alpha^2 \cdot \omega^2 \cdot S_{gf} \cdot g(2\omega) \quad (5)$$

Here α is the fine-structure constant ($\sim 1/137$), $g(2\omega)$ the line shape function, and S_{gf} the two-photon transition probability tensor, which is the counterpart of the transition vector in one-photon spectroscopy. For electric dipole transitions, by far the most important ones, S_{gf} may be written as

$$S_{gf} = \sum_k \frac{(\mathbf{e} \langle g | \mathbf{r} | k \rangle)(\langle k | \mathbf{r} | f \rangle \cdot \mathbf{e})}{\omega_{kg} - \omega} \quad (6)$$

where \mathbf{r} is the displacement vector operator and \mathbf{e} is a complex polarization vector of unit length ($\mathbf{e} \cdot \mathbf{e}^* = 1$).³ $|k\rangle$ are intermediate states such that

$\hbar\omega_{kg} = E_k - E_g$, summation must be extended over all k states. By (3) the transition is also subject to an overall resonance condition $E_f - E_g = 2\hbar\omega$.

The operator governing δ is thus not a transition vector, but rather a transition tensor, which may be represented by a 3×3 matrix. Matrix elements are of the form

$$\delta_{gf}^{xy} = \sum_K \frac{\langle g|x|k\rangle\langle k|y|f\rangle}{\omega_{kg} - \omega} + \frac{\langle g|y|k\rangle\langle k|x|f\rangle}{\omega_{kg} - \omega} \quad (7)$$

From (2)–(7) one can deduce the properties of two-photon spectroscopy. First and foremost is the fact that selection rules are different from those pertaining to one-photon absorption. For instance, in centrosymmetric molecules the selection rules are $g \leftrightarrow g$, $u \leftrightarrow u$ and $g \leftrightarrow u$, that is, the opposite of the one-photon selection rules. Thus, two-photon spectroscopy in this case is complementary to one-photon spectroscopy much in the same way as infrared and Raman spectroscopy are in the domain of molecular vibrations. Another property is the fact that δ depends on the polarization of the radiation even in fluid samples, that is, for complete orientation randomization. The form of δ for all point groups at various polarization combinations of the two photons has been derived and tabulated.³ Consequently, polarization studies may be used to obtain structural information. Another unique feature of two-photon absorption is the possibility to observe spectra free of Doppler broadening by using two counter propagating beams.^{4, 5}

II. EXPERIMENTAL METHODS

A. The Need for High-Power Lasers

Power requirements for experimental observation of two-photon absorption may be estimated by rewriting (2) as (deleting subscripts from δ_{gf} for brevity):

$$\frac{\Delta I}{I} = \delta N_g I \quad (8)$$

ΔI is the intensity decrease on traversing unit distance in a sample with ground-state population density of N_g . A typical value of δ is $10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ and at 1 torr pressure N_g is about $10^{16} \text{ molecules cm}^{-3}$. In this case a relative attenuation $\Delta I/I$ of 10^{-6} is obtained at $I = 10^{28} \text{ photons cm}^{-2} \text{ s}^{-1}$, i.e., about $10^9 \text{ watt cm}^{-2} \text{ s}^{-1}$ for visible radiation. Powers of these orders of magnitude, at narrow frequency bandwidths, are practical only with laser sources. For TPE applications, lasers are often (not always) operated in a pulsed mode, allowing easy

attainment of high peak powers while avoiding optical damage to cell windows and associated optics by keeping average power as low as possible. In kinetic studies laser-pumped dye lasers offer both spectral tunability and resolution on the one hand, and good time resolution on the other hand. With typical available dye laser systems (pumped by a nitrogen or a Nd-YAG laser) pulse duration and energy are 10^{-8} s and 10^{-3} J, respectively. Using the data of the above example, about 10^{10} photons are absorbed per laser pulse, creating 5×10^9 excited molecules. Detection of such small changes in either laser intensity or excited molecule population is a considerable experimental challenge. In the following section we briefly describe some of the methods currently used to monitor TPE.

B. Monitoring Two-Photon Absorption

1. *Direct Attenuation of the Laser Beam*

This is conceptually the most straightforward technique. In view of the small relative change in laser intensity, it is mainly used in cases where two different laser beams are crossed in the sample. Often one of the lasers is a high-power, fixed-frequency device; attenuation is measured on the second, weaker laser appropriately termed the probe, or monitor, laser.⁶ The method was used in early days of two-photon absorption spectroscopy and applied mostly to high-density and liquid samples. Its obvious drawback is poor sensitivity, as the desired quantity is obtained as a small difference between two large numbers.

2. *Detection by Thermal Effects*

Rather than measuring the relative change in laser intensity, one can monitor the absolute of energy deposited in the sample. This energy may be reemitted as fluorescence (see below) or degraded into heat. This in turn can be detected by thermal lensing methods⁷ or by optoacoustic techniques.⁸ In the first method, a low-power laser collinear with the pump beam is used to monitor changes in the refraction index of the substrate (or the solvent) due to heating. In the second, a microphone picks up the acoustic wave created by the sudden heat change. We are not aware of a report using this technique for TPE applications, but it should be sensitive enough for many cases.

A major disadvantage of thermal methods for kinetic applications is their poor time resolution—determined by the rate of gas density changes. This usually limits the resolution to 10^{-3} – 10^{-6} s, washing out many interesting temporal effects.

3. *Detection by Fluorescence Excitation*

As noted above, fluorescence emission often follows two-photon absorption. This one-photon process occurs at a higher frequency than that of the exciting laser. Usually the spectral separation between the frequencies is large, minimizing scattered light problems. The method is highly sensitive, as shown below, and has been used in many TPE applications.⁹ Offering excellent time resolution (better than 10^{-9} s), it has so far been the only one used in kinetic studies.

The method's sensitivity can be estimated by following up the previous example. Assuming a fluorescence quantum yield of 0.1 and a spatial collection efficiency of 10^{-3} , a population of 5×10^9 excited molecules leads to 5×10^5 photons reaching the detector per pulse. Single-photon counting techniques easily allow the observation of 0.1–1 photon per pulse. Evidently fluorescence methods can easily be used to probe submillitorr samples.

4. *Detection by Ionization*

Being promoted to an electronically excited state, a molecule (atom) may be further energized by absorption of more photons. The process often leads eventually to ionization, making it easily observable.¹⁰ If the rate-determining step of the overall process is the initial coherent two-photon absorption rate, multiphoton ionization spectra are dominated by two-photon resonances. The method is highly sensitive, as demonstrated by recent molecular beam studies.¹¹ It has obvious kinetic applications, mostly in determining branching ratios and appearance rates of ionic fragments.

5. *Other Nonlinear Techniques*

Four-wave mixing has been used to generate VUV laser radiation.¹² In some cases (such as NO) two-photon resonances are decisive factors in overall yield, and laser output may be related to the two-photon absorption cross-section. A similar technique involves mixing of two dye laser frequencies ω_1 and ω_2 to yield ω_3 by $\omega_3 = 2\omega_1 - \omega_2$. This process is resonance enhanced when $2\omega_1$ coincides with a molecular transition.^{13,14} Keeping ω_2 constant and scanning ω_1 , one obtains the spectrum of ω_3 . This spectrum is strongly enhanced in two-photon resonances and may be used to derive the two-photon cross-section of the medium. The technique does not depend on subsequent processes, such as fluorescence or ionization, for detection. Its sensitivity, however, is limited by the ever-present nonresonant third-order nonlinear susceptibility $\chi^{(3)}$,¹⁵ limiting its use at present to condense phases and relatively high-pressure gases.

6. *Chemical Methods*

In some favorable cases TPE was efficient enough to form measurable amounts of photodecomposition products. Examples are the dissociation of iodoform by a ruby laser¹⁶ and of water by a doubled dye laser.¹⁷ In the first, the reaction was followed by titrating the liberated iodine, while in the second, OH radicals were monitored by laser-induced fluorescence, using the same laser frequency for both two-photon dissociation of H₂O and one-photon fluorescence excitation of OH.

7. *Null Methods*

Two-photon absorption can lead to changes in the polarization of the exciting beam. The changes can be described, in the case of elliptically polarized light, as rotation of the polarization ellipse. One can detect this rotation, by placing a two-photon absorption cell between two linear polarizer–quarterwave retarder combinations. In the absence of a sample, the combination is set so that the retardation caused by the first quarter-wave plate is exactly canceled by the second so that no light can pass through the crossed polarizers. With a sample in the cell, any slight change in the polarization ellipse destroys the exact match, and some light passes on through the second polarizer onto a detector. The method was termed ELLIPSA (elliptical polarization state alteration)¹⁸ and should prove to be of general applicability, being potentially quite sensitive.

The fate of two-photon excited neutral molecules and atoms is most easily followed in real time by fluorescence monitoring. In the next sections we show that in spite of the small two-photon absorption cross-section, the method can be used for quantitative kinetic measurements. For some applications, it is more straightforward and leads to less ambiguous interpretation than one-photon excitation.

III. KINETIC STUDIES

A. *Motivation*

Thus far, the use of TPE for kinetic studies was limited to relatively few cases [see, e.g., (19)–(23)]. This is hardly surprising in view of the smallness of δ and the difficulties encountered in even detecting TPE. It turns out, however, that the small absorption cross-section can actually be of advantage in some instances, as discussed below. Furthermore, present dye laser technology (using doubling crystals) provides tunable, narrowband radiation in the range from about 200 nm to about 1000 nm. The time resolution is 10^{-8} s with most pump lasers currently used (*Q*-switched Nd–YAG, excimer, or nitrogen laser) but can be readily extended to 10^{-11}

s using mode-locked lasers.²⁴ TPE extends the wavelength range to 100 nm, without using expensive vacuum UV optics, being supplemental to frequency doubling and summing techniques that are not universally available. These properties, coupled with the different selection rules, make TPE a tool for populating a range of excited states not readily accessible by one-photon excitation.

In quantitative photokinetic studies one must control the spatial and temporal population of the initially excited species. The discussion in Section IV centers on the special case of fluorescence quenching. Energy transfer to an acceptor (quencher) results in changes in fluorescence lifetime and intensity. Typically these changes are monitored as a function of quencher pressure, keeping the donor pressure constant. It is attempted to keep the initial conditions (concentration and spatial distribution of excited donor molecules) constant as well. Difficulties arise when donor and acceptor absorption spectra overlap: inner filter effects decrease initial excited donor concentration, resulting in lower emission intensity. The same problem is encountered in the determination of self-quenching rate constants, which must be known for correct analysis. Taking NO as an example, it was found necessary to use ternary mixtures²⁵ to extract self-quenching rate constant. Cases of considerable photochemical interest were not studied, apparently because of overlapping donor and acceptor absorption. Examples pertinent to NO photochemistry are NO-SO₂, NO-CH₃NO₂, and NO-organic amines mixtures. Complications due to acceptor's absorption are avoided when optically thin conditions hold, namely, when the absorbed fraction ΔI_0 is much smaller than the incident light intensity I_0 . In that case (optically thin conditions) Beer's law leads to the relation

$$\Delta I_0 = I_0 \alpha P l \quad (9)$$

with α the absorption coefficient and p the absorber pressure. For several absorbing species

$$\Delta I_0 = I_0 l \sum_i \alpha_i P_i = \sum \Delta I_i \quad (10)$$

i.e., light attenuation is additive. Excited state population of the donor per unit length, n_D^* , is given by

$$n_D^* = I_0 \alpha_D P_D \quad (11)$$

being proportional to the incident intensity and the donor pressure P_D , even in the presence of other absorbing species. In the case of two-photon

absorption, we get

$$n_D^* = (1/2)I_0^2 \delta_D P_D \quad (12)$$

the small value of δ ensuring optically thin conditions at practically any pressure of donor and acceptor(s). Thus, quenching cross-sections can be extracted for donor-acceptor pairs whose one-photon absorption spectra strongly overlap. The method is of special interest in the energy range above $45,000 \text{ cm}^{-1}$, where many molecular absorption spectra are very intense, and where tunable, pulsed laser sources are not readily available.

B. Excited States of Nitric Oxide

A partial energy level diagram of NO is shown in Fig. 1. The ground state, $X^2\Pi$, has the configuration

$$KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p) \quad (13)$$

One can thus roughly consider the molecule as consisting of a core, composed of 14 electrons in closed shells and a lone electron orbiting outside. Transitions of the lone electron to states with principal quantum numbers exceeding 2 lead to Rydberg series, converging to the ionization potential. Examples of Rydberg states are $A^2\Sigma^+$, $C^2\Pi$, $D^2\Sigma^+$.

Transitions of core electrons into the antibonding π^* orbital are called valence transitions. Examples of valence excited states are $a^4\Pi$, $b^4\Sigma^-$, $B^2\Pi$. It is noted that excitation into Rydberg states moves the antibonding electron away from the nuclei, while in valence state transition a bonding electron is moved to an antibonding orbital. Therefore, one expects the internuclear distance to decrease for Rydberg excitation and increase for valence state excitation. These expectations are borne out by experiment (cf. Fig. 1).

C. Quenching Kinetics

For states below the dissociation limit of the molecule, the decay rate constant in the presence of a quencher Q may be written as

$$k_{\text{TOT}} = k_f + k_{\text{SQ}}P + k_QQ \quad (14)$$

with $k_f = \tau_f^{-1}$ the radiative rate constant, k_Q and k_{SQ} the quenching rate constants by Q and NO, respectively, and P and Q the pressures of NO and the quencher, respectively.