

MEGAWATT INFRARED LASER CHEMISTRY

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A good inductive model should have several attributes: It should be intentionally incomplete. The possible disproof of an inductive theory [is] not a flaw in the method, but... an essential and welcome part of the process of understanding. The model should be able to be refined.... It is poor inductive practice to foreclose the possibility of later insertion of new knowledge. Calibration [of the model] to experiment is essential.... It is the process of calibration and subsequent use that makes the heaviest demands on one's chemical judgment.

Don L. Bunker (1931–1977)

Preface

During the past two or three years we have found research in infrared laser chemistry engrossing, not only because of the practical aspects and prospects of this budding science, but also because the required theory reaches to the very foundations of chemical dynamics. This sentiment is shared by others, for research is in a stage of rapid growth and major chemical industries are thinking seriously about large scale applications.

The volume is intended as a greeting to new workers in the field, and as a primer to acquaint chemists in general with the salient features of the phenomenon. For this reason the contents have been limited largely to established facts, theories, and basic issues. The contents have also been limited largely to chemistry done with pulsed infrared lasers at megawatt per square centimeter power levels, which (it seems to us) is the most important branch of infrared laser chemistry about which a book that addresses itself to chemists can be written at this time. At gigawatt per square centimeter pulsed power levels where laser-isotope separation was first discovered, the chemistry still seems very complicated, being best described as molecular fission rather than as orderly decomposition. At the more modest power levels of continuous infrared lasers, controversy surrounding even characterization of the phenomenon is still too widespread.

Throughout the book we have carefully avoided riding theoretical hobby-horses, even those from our own stables. However, we have felt no similar compunction about drawing on published data from our own laboratories for illustrative examples.

It is a pleasure to acknowledge helpful discussions with many individuals, particularly with our students and collaborators C. Cheng, D. Garcia, G. A. Hill, C. M. Lonsetta, and K. J. Olszyna. E. G. expresses special thanks to H. J. Wetzstein for having aroused his interest in this subject and for steady counsel. D. F. D. acknowledges the help of L. Fountain,

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Philip M. Keehn

Waltham, Massachusetts
Macon, Georgia
May 1978

Glossary of Symbols

The units commonly used in this book are given in parentheses.

c	speed of light
CPF	conversion (of reactant) per flash (fractional, or %)
CW	continuous wave
D	dose (radiant energy per unit area); dose transmitted by sample; also called <i>energy fluence</i> (J/cm^2)
D_0	dose incident on sample (J/cm^2)
e_A	extinction coefficient by laser spectroscopy (cm torr^{-1}), Eq. 2-6
E_{abs}	energy absorbed per mole of substance (kcal)
E_{act}	Arrhenius activation energy (kcal)
E_0	amplitude of electric vector of coherent radiation
ϵ_A	extinction coefficient by conventional spectroscopy (cm torr^{-1}), Eq. 2-5
$\bar{\epsilon}$	rms-average energy exchanged with heat bath, per collision
f	spoil factor
f_k	mole fraction of molecular oscillators in k th level
GW	gigawatt, 10^9 watt
I	beam intensity (radiant power per unit area); intensity transmitted by sample (W/cm^2)
I_0	beam intensity incident on sample (W/cm^2)
J	rotational quantum number
K	collisional efficiency parameter, Eq. 3-7
l	path length
MW	megawatt, 10^6 watt
$ \mu $	electric dipole transition moment
N_0	Avogadro's number
ν	frequency; wavenumber (cm^{-1})
ω_R	Rabi frequency
p	probability
P	pressure (torr)

P_A	pressure of absorbing gas (torr)
P_{eff}	effective pressure of gas mixture (torr)
P_X	pressure of nonabsorbing gas in mixture (torr)
s	number of oscillators
TEA	transversely excited, atmospheric pressure
τ	effective pulse duration, Eq. 3-4
v	vibrational quantum number
\bar{v}	ensemble average of v for the given vibrational mode
Z	gas-kinetic collision number per second, under standard pressure conditions

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Chapter 1

Introduction

Infrared photons are relatively energy poor. For instance, a mole of photons at 1000 cm^{-1} carries only 2.86 kcal. It was therefore a pleasant surprise when it was discovered a few years ago that exposure of gases to high-power infrared laser beams could induce chemical reaction [1]. Previous to this, photolyses were done with visible, ultraviolet or even shorter wavelength radiation.

Infrared photochemistry is a new kind of photochemistry because reactions take place in the electronic ground state. It offers the potential of high specificity because the infrared laser radiation is monochromatic and can be tuned to a frequency which matches an absorption frequency of the molecules to be excited. Because the molecules can "climb up the vibrational ladder," absorption is not limited to one photon per molecule. Indeed, with commercially available pulsed lasers, it is easy to introduce 10 kcal/mole or more with each pulse when the laser is tuned to a strong absorption band.

From a practical point of view, it is convenient to divide laser chemistry into three subdivisions, depending on the power level used. When excitation takes place with continuous-wave (CW) lasers, the power is necessarily limited to a few kilowatts per square centimeter or less; continuous absorption at higher power levels would atomize the molecules. When excitation takes place with pulsed lasers, the outputs per pulse of commercial tunable lasers are typically 1 J/cm^2 , with pulse durations ranging from 0.2 to $1\text{ }\mu\text{s}$. This corresponds to average power levels of 1–5 MW/cm². The beams produced by such lasers have radii up to several

centimeters. This kind of radiation is therefore suitable for studies involving fairly large samples. Finally, when megawatt beams are concentrated by means of lenses, power levels of gigawatts (GW) per square centimeter are obtained near the focal point. Gigawatt power levels have been found useful for isotope separation work under "collision-free" conditions, mostly at pressures below 1 torr [2-4].

In this volume we consider almost exclusively megawatt laser chemistry, which we believe to be of special interest to chemists. First of all, pulsed megawatt irradiation is a convenient way to study high-temperature ($> 1000^\circ\text{K}$) reactions in what is essentially room-temperature apparatus. The effective temperature is readily changed over wide ranges by changing the infrared dose. This permits the detection and detailed study of reactions heretofore inaccessible because of their high activation energies.

Also, reactions observed in laser chemistry appear to be cleaner than their counterparts studied in classical thermal apparatus for several reasons: The reactant is exposed to high temperature conditions for only a short length of time. The initial "heating rate" is in the range of 10^6 - 10^{11} $^\circ\text{K/s}$; the subsequent "cooling rate" is in the range of 10^3 - 10^6 $^\circ\text{K/s}$. If the laser beam is smaller than the reaction cell cross-section, wall effects are practically absent. If the laser beam irradiates not only the gas but also the cell wall, reactions occurring on the cell wall are accentuated.

Because high-temperature reactions frequently have bond-breaking steps as primary processes, very high concentrations of free radicals (> 10 torr) can be generated in a matter of microseconds and studied by kinetic spectroscopy. Contrary to conventional free-radical chemistry where bimolecular reactions *among the free radicals* are stoichiometrically unimportant, the high concentrations of free radicals produced by laser flash lead to dominance of radical-radical reactions.

The primary steps of laser-induced reactions in most cases are decomposition reactions. However, examples are accumulating in which the original molecules are being isomerized, or in which larger molecules are being synthesized by bimolecular combination or displacement.

Chapter 2

Some Phenomenology

One of the perquisites of participating in the development of a new field is being able to observe one of its symptoms: theories come and go like the blooms on a rosebush. Infrared laser chemistry exhibits this symptom actively; therefore, until theories become more settled, this chemistry's claim to usefulness must be based on facts. In this chapter we consider some of the salient phenomena.

THE CO₂ LASER

At present the CO₂ laser is best suited in terms of energy, power, availability, and ease of use. It consumes only environmentally acceptable, commercially available supplies and is a clean and low-maintenance instrument operating in the 9.2–10.9 μ range. Bonds that absorb in this region include C—C, C—O, C—F, Si—F, S—F, P—O, W—O, and S—H. Other available lasers are the HF/DF laser (2.8–4.0 μ) and the CO laser (5.1–5.6 μ), but unlike the CO₂ laser, the gases they use (in necessarily large quantities) are either corrosive or lethal. These and other problems, involving monochromaticity or power, make their adoption for day-to-day use in the laboratory problematical at this time [5, 6].

Nirvana in this field, of course, is a laboratory with a laser beam continuously tunable to any wavelength desired with high power and high efficiency. Any infrared-active vibrational mode could be stimulated, including those modes that absorb strongly. Actually, this may be not far

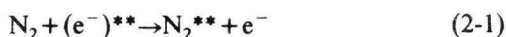
from reality because there is now under development a laser tunable from 10μ to 1000 \AA ; this covers the spectrum from the infrared stretch region to the vacuum ultraviolet [7]. To gain this high degree of tunability, a synchrotron is coupled to a low power laser; frequency selection is done by changing the energy of the electrons in the synchrotron. Present power levels are up to 10 kW and the investigators are discussing 0.1 MW as a reasonable goal for output for this instrument.

Emission Mechanism

The instrument used by the authors in their studies is a TEA (transversely excited, atmospheric pressure) tunable pulsed CO_2 laser with average power output between 0.1 and 2 MW/cm². Up to 10 J can be delivered in pulse times between 250 and 800 ns; the time between pulses is adjustable between 0.5 and 5 s. Beam areas are on the order of 8 cm² and doses* are reproducible to 2% in successive pulses. Its power supply and associated electronics are powered by 110 V AC, and it consumes gases at a rate of 5 ft³/h. The physical arrangement for the laser consists of gas flowing through an 8 ft glass tube fitted with internal electrodes across which electrical energy stored in capacitors can be discharged. Optics appropriate to laser behavior are mounted at the ends of the tube. Photographs are shown in Figs. 2-1 and 2-2.

The dominant processes that occur in the CO_2 TEA laser are (1) molecules are excited to the upper vibrational laser level by collision with electrons from the discharge, (2) the molecules emit laser radiation, falling to the lower laser level, and (3) they then return to the ground state where they can start the cycle again [5]. In order to effect this cycle with high efficiency, N_2 and He are added to the CO_2 ; the N_2 assists in the first step, He in the last. The process can be expressed by a series of equations:

1. Excitation by electric discharge



*Laser physicists sometimes use the term *energy fluence* for dose and *energy flux* for intensity.

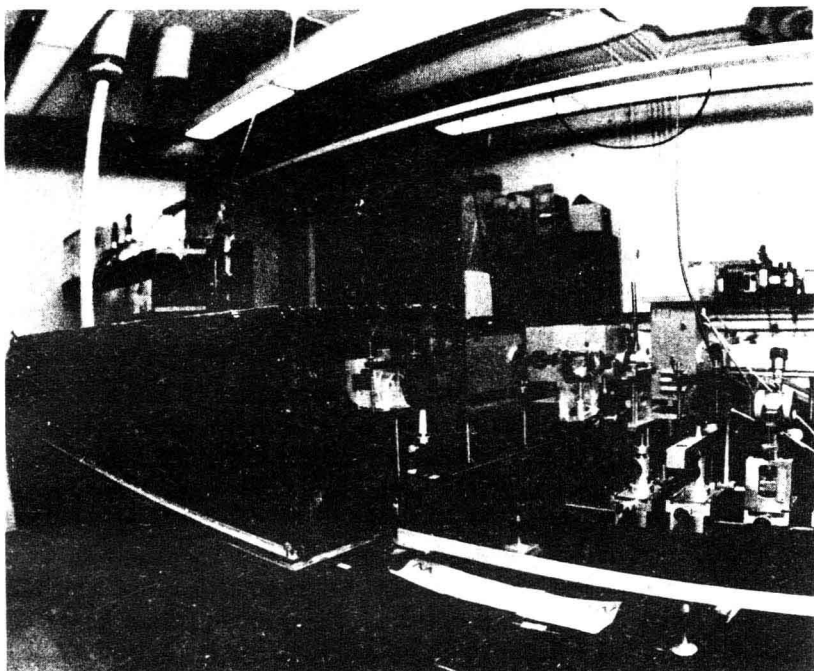


Fig. 2-1 View of the authors' infrared laser laboratory. The pulsed CO_2 laser is set up inside the Faraday cage (on the left) in order to contain electromagnetic noise. Wide-angle lens photograph by John Galano (1977). Courtesy Brandeis University.

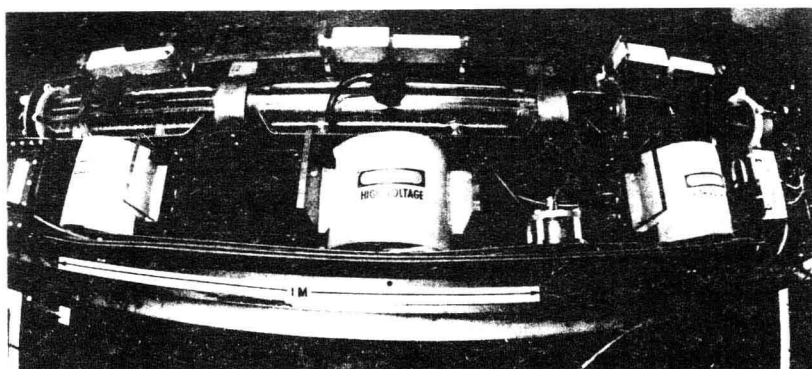
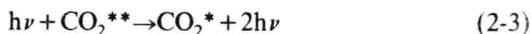


Fig. 2-2 Inside view of the CO_2 laser. Excitation and stimulated emission take place in the long glass tube that is mounted alongside the high-voltage condensers. There is some optical distortion owing to wide-angle lens photography. Photograph by John Galano (1977). Courtesy Brandeis University.

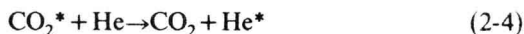
2. Collisional transfer to upper laser state



3. Laser emission, falling to lower laser state



4. Return to ground state



An energy schematic with each of the above steps labeled is shown in Fig. 2-3. It will be noted that there are two lower laser levels, one at 1388 cm^{-1} and one at 1286 cm^{-1} . These help to give rise to the wide selection of laser emission lines available to the researcher. The latter lines are indicated in the bottom part of the figure.

One of the tube-end optics mentioned above is a grating with which the laser can be tuned to any one of the emission maxima. This high degree of choice arises from the fact that the upper and lower laser levels

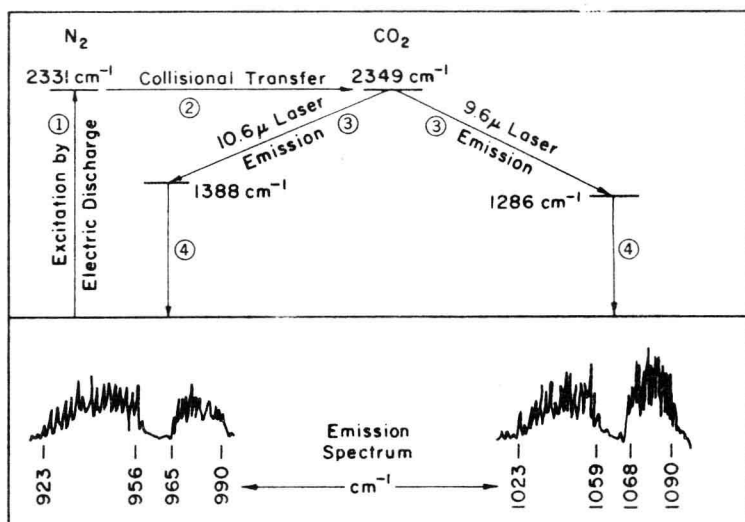


Fig. 2-3 CO_2 TEA laser excitation scheme. Circled numbers refer to step-sequence discussed in text. Emission spectrum shown below laser transitions indicates tuning range of laser.

each have rotational levels (not shown in the figure), about 40 of which have substantial population densities [5]. It is between pairs of these levels (selection rules permitting) that transitions take place. Tuning the laser to resonate on any one of these lines gives the operator control of the laser emission frequency.

ABSORPTION AND REACTION

For effective absorption of radiant energy, it is desirable that the laser be tuned so that its output frequency falls into the range of a strong absorption band of the substance to be excited. By "strong" we mean that the extinction coefficient, ϵ_A , of the absorbing species [defined in (2-5) and measured by ordinary nonlaser spectrophotometry] must be at least of the order of $0.001 \text{ cm}^{-1}/\text{torr}$ at the band maximum.

$$\log_{10}\left(\frac{I_0}{I}\right) = \epsilon_A l P_A \quad (2-5)$$

Multiphoton absorption from megawatt laser sources is a complex phenomenon and does not in general follow the Beer-Lambert law [8,9]. Nevertheless, it is useful to introduce a quasi-extinction coefficient, e_A , by way of (2-6), in which D_0 and D denote the incident and transmitted dose, respectively; that is, $D_0 - D$ is the amount of radiant energy absorbed by the gas per square centimeter.

$$\log_{10}\left(\frac{D_0}{D}\right) = e_A l P_A \quad (2-6)$$

Because the real extinction coefficient, ϵ_A , is only an imperfect model for e_A , the frequency at which e_A is a maximum may be different from that of the spectroscopic band maximum; the frequency at which e_A is at a maximum may also vary with dose. An approximate rule may be stated as follows [2]: Let ν_0 be the fundamental absorption frequency of the mode to be excited, and ν_1 be that of the first overtone. Owing to the anharmonicity of molecular oscillators, ν_1 is probably somewhat smaller than $2\nu_0$, a typical value for $(2\nu_0 - \nu_1)$ being approximately 10 cm^{-1} . The rule then states that e_A will be at a maximum when the laser frequency is $\nu_1 - \nu_0$.