**CURRENT PROBLEMS IN RESEARCH**

# Selective Laser Photocatalysis of Bromine Reactions

## Laser light excites gaseous bromine molecules to single bound quantum states near the dissociation continuum.

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We have used photocatalysis, induced by monochromatic laser light, to study the nature and dynamics of a gaseous chemical reaction. The experimental study of such dynamic processes is inherently more difficult than that of static properties because there are a number of simultaneously occurring processes in competition with one another. The laser permits simplification of the situation with selective excitation techniques. In particular, a specific type of molecule within a system can be excited initially to an individual quantum state. Its subsequent behavior can be studied more easily because the number of processes which can occur is restricted by the selective initiation. Careful choice of the method for this selective initiation permits the processes of most interest to be observed without interference from other possible processes.

In contrast to this, the activation energy for a chemical reaction is ordinarily furnished by thermal collisions of the participating molecules. Usually the required energy is much greater than can be obtained in a single collision. Thus, many such uncorrelated events are required, and during the course of these events information about the detailed behavior can be lost, and unwanted side effects may occur. Photochemical activation can be much more direct because the required energy can be delivered by a single photon (*1*). It can also be selective if the wavelength of the light source can be chosen to coincide with an absorption wavelength of a specific type of molecule in the system. Clearly, the laser provides a very highly efficient and selective method for chemical activation, because it concentrates a large amount of light energy into a very narrow spectral range (*2*).

The use of lasers to influence chemical reactions was first suggested at the time of their earliest development (*3*). Since that time, numerous photochemical experiments with lasers have been reported (*4*). However, none of the previous experiments truly exploited the monochromatic property of laser light. We now report on the usefulness of highly monochromatic laser light for selective photochemical activation.

A frequency-tuned ruby laser with a high repetition rate was designed and constructed; special techniques to obtain high monochromaticity were used. The laser was used as a light source for the selective photocatalysis of gas-phase reactions between bromine and certain unsaturated fluorocarbons. This was the first reported photochemical reaction of bromine with light in the 14,400 $\text{cm}^{-1}$ ($\sim$ 6940 Å) spectral region. The selective excitation technique provides new information, which can be used to determine both the mechanism of the reaction and the rates of molecular energy transfer which are not accessible by other methods.

### Absorption Spectrum of Bromine

In the 14,400 $\text{cm}^{-1}$ region of the ruby laser, bromine molecular absorption occurs in the individual lines belonging to the $^3\Pi_1 \leftarrow {}^1\Sigma_g{}^+$ band system (*5*). Because of the vibrational and rotational splitting of the electronic energy states, these lines are very closely spaced. An energy diagram for bromine (*6*), showing the lowest-lying molecular electronic and vibrational states, is given in Fig. 1. The specific upper levels for absorption at 14,400 $\text{cm}^{-1}$ are bound molecular states lying 500 to 800 $\text{cm}^{-1}$ below the level for dissociation into two ground state $^2P_{3/2}$ bromine atoms. The 300 $\text{cm}^{-1}$ uncertainty is due to the fact that a rotational analysis of the $^3\Pi_{1u}$ state has never been performed, and that lines arising from two different lower vibrational states occur in the same region.

A weak continuous absorption, indicative of direct dissociation into atoms, might occur in the same spectral region. If so, it would have to arise from more highly excited vibrational levels of the $^1\Sigma_g{}^+$ state, which are sparsely populated at room temperature. Attempts to establish the existence of a continuum at 14,400 $\text{cm}^{-1}$ by means of conventional spectroscopic techniques have been inconclusive.

Bromine was chosen for the investigation largely because of these features of its spectrum. If photochemical activity could be observed at 14,400 $\text{cm}^{-1}$, the use of a monochromatic tunable laser could establish the extent of its dependence upon the closely spaced individual lines, and upon the possible continuum, respectively. In addition, bromine has two isotopes, $^{79}$Br and $^{81}$Br, with almost equal abundance. These form three isotopic species of diatomic molecule, which exhibit isotope shifts in their absorption spectra (*7*). Under certain conditions, the selective excitation of an absorption line belonging to an individual isotopic species might lead to isotope effects in the reaction product (*8*). Indeed, it seemed initially that it might be possible to separate bromine isotopes if the bromine reaction could be initiated selectively enough.

High-resolution absorption spectra of samples of pure $^{79-79}\text{Br}_2$, pure $^{81-81}\text{Br}_2$ (*9*), and natural $\text{Br}_2$ were taken with a Jarrell-Ash 1.8-meter Ebert scanning spectrometer. The results in the ruby laser wavelength region are shown in Fig. 2. The wavelength scale for the three samples is the same. In spite of the extremely close spacing of the individual lines, it is possible to identify in the spectrum of natural $\text{Br}_2$ certain strong lines belonging to the pure isotopes. The laser could be tuned to coincide with one of these lines if desired.

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## Photochemistry of Bromine in Conventional Light

To complement the laser studies, photocatalysis experiments were first made with ordinary white light. One of the most widely studied types of bromine photochemical reactions is the addition of two bromine atoms to an organic molecule of the olefin structure, which has a double bond (*10*). The photochemical addition of bromine to ethylene, the simplest molecule of this type, produces the stable saturated molecule 1,2-dibromoethane. Reactions of this type consist of a complex set of consecutive steps initiated by dissociated bromine atoms, known as a free-radical chain. In previous cases it was possible to attribute the reactivity to direct dissociation by absorption of light in the continuum (*10*). Photochemical quantum yields as high as $10^5$ molecules per absorbed photon were obtained. The longest wavelength at which these reactions were observed, however, was 6800 Å.

In the present investigation, two fluorocarbons with the olefin structure were chosen, namely perfluorobutene and heptafluorochlorobutene. Reactions were first performed with light in the continuous absorption region of bromine. Results were substantially the same with either of the fluorocarbons. The reactions followed the free-radical chain mechanism, but were much slower than those observed with nonfluorinated olefins. The quantum yields obtained were on the order of only one molecule per absorbed photon. This slowness was desirable, because it provided the capability of observing slow competing processes during the laser photocatalysis experiments.

## Techniques and Apparatus

The details of the ruby laser design and construction have been described (*11*). The device could be pulsed repetitively at a rate of twice per second, and could be tuned over the approximate range 6934 to 6943 Å by changing the temperature of the ruby rod (*12*). The spectral width of the laser oscillation was controlled by replacing the output cavity mirror with a sapphire optical flat (*13*). The combined reflectivity from the two parallel faces of this flat depended strongly on wavelength, so that it provided positive feedback over less than 0.04 $cm^{-1}$ of the ruby fluorescence line width. In contrast to this, operation with an ordinary mirror resulted in an output line width of approximately 0.33 $cm^{-1}$. The sapphire flat was housed in a thermostat to stabilize the frequency of its maximum reflectance. This frequency could be tuned by changing the temperature of the thermostat. Stable operation with approximately 1 watt of average output power was achieved over durations of 25,000 consecutive pulses.

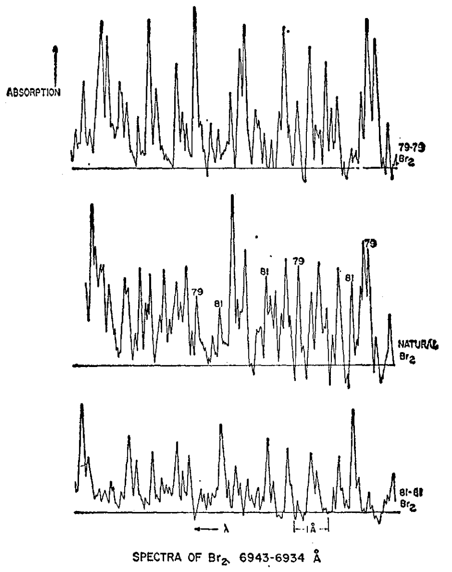

Fig. 2. High resolution absorption spectra of pure isotopic and natural $Br_2$ at the ruby laser wavelength. Numbered lines in natural $Br_2$ belong to the corresponding pure isotopic molecules.

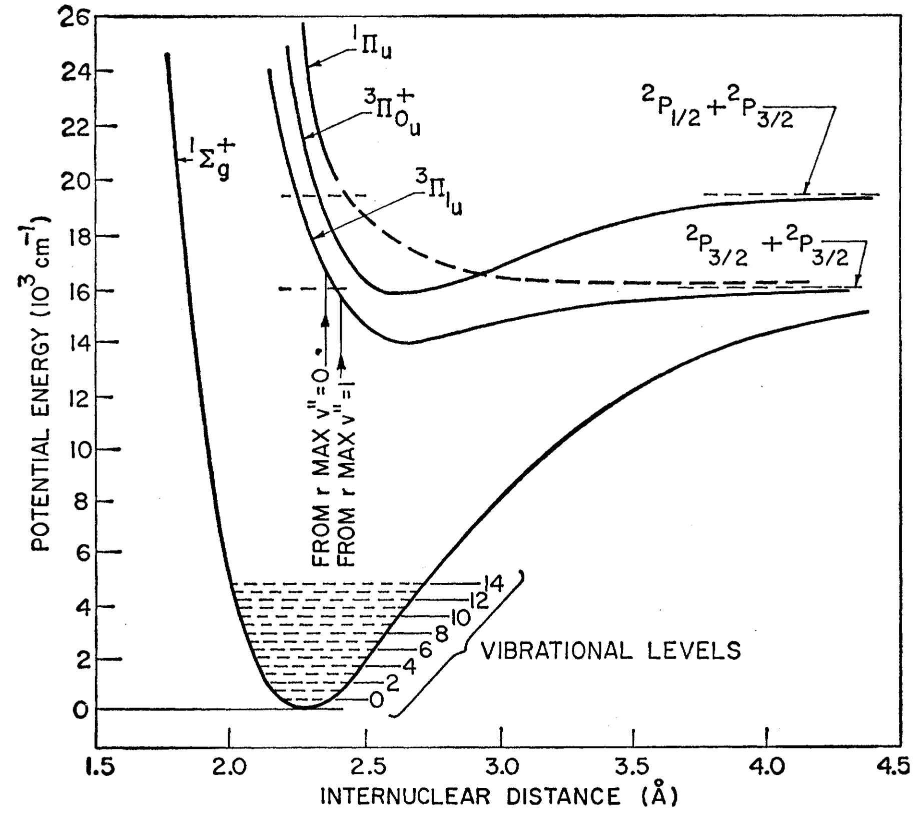

Fig. 1. Potential-energy diagram of the $Br_2$ molecule.

The laser wavelength was monitored by sampling the beam with a high-resolution scanning spectrometer. The spectrometer simultaneously scanned the absorption spectrum of a sample of bromine, upon which the laser pulses were superimposed at the appropriate wavelength. By this direct comparison, it could be ascertained that the laser wavelength coincided accurately with the desired absorption line of the bromine.

The fused-silica reaction cell had a volume of 2.5 ml and had plane walls on all sides. Two opposite faces were slightly wedged and were coated to reflect the laser beam internally. Thus many passes of the laser beam through the cell provided more efficient light absorption. The reaction rate was monitored optically by observing the disappearance of bromine molecules from the cell. This was accomplished by passing light from a weak source through optical filters and through the cell at right angles to the laser beam, and measuring the transmission by means of a photomultiplier tube. The monitoring wavelength was chosen in the blue so that it was absorbed only by bromine molecules in the cell, and so that the red ruby laser light could be filtered out. The intensity was low enough so that the monitoring light did not produce any measurable effect on the reaction.

## Laser Photocatalysis Results

Partial pressures of approximately 10 torr of bromine and 200 torr of the fluorocarbon were used for the laser-induced reactions. Absorption of the laser light by the bromine caused it to react with the fluorocarbon. When the laser frequency was tuned to coincide with individual absorption lines, the reaction rate was considerably enhanced. The residual reactivity between lines could be attributed to the overlapping wings of neighboring lines rather than to a true continuum. This showed that the primary photochemical process was the formation of stable excited bromine molecules with energies 500 to 800 cm$^{-1}$ below the dissociation level. All previous photochemical activity in bromine had been attributed to direct dissociation into atoms upon absorption of light in the continuum (*10*). Thus the use of monochromatic, tunable laser light provided the first evidence of a photochemical reaction of bromine in which excited molecules, not atoms, were formed in the primary process. However, when specific isotopes were selectively excited, no isotopic enrichment was detected in the product. The reaction kinetics, as well as inhibition by nitric oxide, gave evidence for a free-radical chain mechanism, which required dissociated atoms. The dependence of the reaction rate on laser light intensity was linear. The results are summarized in Fig. 3, which shows the fine structure of the bromine absorption on the same wavelength scale as the relative reaction rate.

The photochemical quantum yield was about 100 times less in laser light than in light of shorter wavelength that produced direct dissociation of bromine. The reaction products with both types of light were identified by gas chromatography and mass spectrometry, and were found to be the same.

## Interpretation of Results

The results (Fig. 3) indicate that the excitation process was indeed selective. On the other hand, many of the results, such as the kinetic behavior, the inhibition by nitric oxide, and the lack of isotope enrichment in spite of isotopically selective excitation, showed that the overall mechanism was not selective. These indicated that the reaction mechanism involved a free-radical chain, which required dissociated bromine atoms.

Calculations based on earlier work involving flash photolysis (*14*) and shock tube (*15*) experiments showed that the rate of collisional dissociation from the ${}^3\Pi_{1u}$ state was quite high, requiring slightly less than $10^{-7}$ second at the pressures used in our experiments (*16*). The gas-kinetic collision time was about $10^{-9}$ second. Equilibrium was overwhelmingly in the direction of dissociation, due to the entropy increase. Once the molecules were dissociated, the lack of isotope enrichment could be attributed to the isotopic exchange reaction

$$Br^* + Br_2 \rightarrow Br^*Br + Br.$$

From earlier work (*17*), this reaction was known to occur at a rate $10^5$ times as fast as the chain addition reaction. Thus the present result is consistent with the earlier data. In spite of the low quantum yield of the chain reaction and the short chain lengths which this implies, the exchange reaction was sufficient to produce the observed isotopic scrambling.

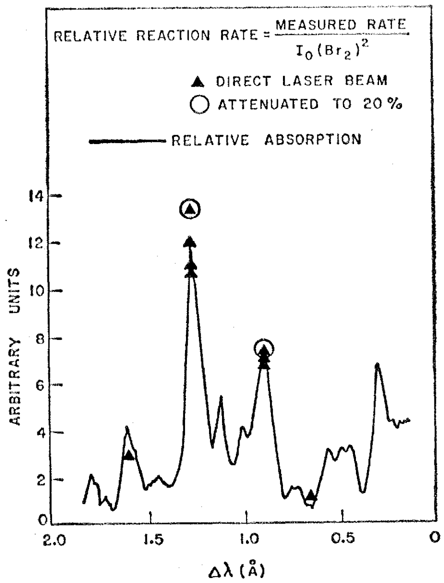

Fig. 3. Typical results of laser photocatalysis experiments, showing normalized relative reaction rate and relative absorption on the same wavelength scale.

Also, the possibility of a direct bimolecular addition reaction of the excited bromine molecules was eliminated. If it were to occur, a rapid bimolecular isotopic exchange of the type

$$Br_2^* + Br_2 \rightarrow 2Br^*Br$$

would be required to prevent isotope enrichment of the product. However, recent work by Noyes (*18*) indicated that this reaction should be at least $10^3$ times slower than the collisional dissociation process. Thus, bimolecular addition must also be at least several orders of magnitude slower than dissociation, and therefore is unimportant even under conditions in which highly excited molecules are being formed.

The 100-fold decrease in quantum yield in laser light, as compared with light of shorter wavelength, showed that most of the excited molecules were not being dissociated. Radiative decay cannot explain this, as the transition ${}^3\Pi_{1u} \rightarrow {}^1\Sigma_g^+$ is spin-forbidden, with an estimated lifetime of the order of $10^{-4}$ second (*6*). Thus, the only process which can account for the reduced quantum yield is collisional electronic relaxation of the molecules to the ground state, which must therefore occur 100 times faster than dissociation. This rate was slightly greater than $10^{-9}$ sec$^{-1}$ under our experimental conditions. Hence it was somewhat faster than the gas kinetic collision rate. Knowledge of electronic energy transfer rates in gas collisions is in general fragmentary (*19*). The rate for ${}^3\Pi_1$ bromine molecules was previously not known, but it was believed to be high because of the failure to observe fluorescence. The present result provides the first quantitative estimate of this rate, which in turn is comparable with known rates for other molecules (*20*).

The reduced quantum yield could not be attributed to more rapid termination of the chain reaction under the pulsed laser conditions. This could have come about because of an increase in the rate of second-order recombination of bromine atoms. However, that would have led to a very nonlinear dependence of the reaction rate on light intensity, in contrast to the observed linearity.

The results (Fig. 3) also allow a new upper limit to be placed on the amount of continuous absorption in bromine at 14,400 cm$^{-1}$. The residual reactivity observed between individual lines was no greater than 10 percent of the value obtained when the laser was tuned to the strongest line. If this residual reactivity were due to true continuous absorption, the resulting direct dissociation would be 100 times as efficient photochemically as excitation at a line. The observed reactivity, therefore, implies that the continuous absorption at 14,400 $cm^{-1}$ is at least $10^3$ times weaker than the strong individual lines in the same spectral region, at pressures of about 200 torr.

## Conclusions

The results have shown that selective excitation obtained with a tunable monochromatic laser is a useful technique for studying photochemical and energy transfer processes. A new phenomenon in the photochemistry of bromine was observed, in which bound excited molecules, and not atoms, were formed in the primary process. The mechanism of the subsequent reaction consists of collisional dissociation of the excited molecules into atoms, which then initiated free-radical chains. A quantitative estimate of the collisional electronic relaxation rate for excited bromine molecules was obtained, and a new upper limit to the continuous absorption strength at 14,400 $cm^{-1}$ was determined.

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**NEWS AND COMMENT**

# The Administration of Federal Aid: A Monstrosity Has Been Created

The administrative system for providing federal support for academic research and higher education has become a monstrosity.

That is the conclusion that emerges from a *Science* survey that drew detailed responses from 81 colleges and universities throughout the nation. These schools receive at least 65 percent of all federal expenditures in institutions of higher learning. The respondents, in most instances the chief campus officer for government relations or research administration, generally observed that administrative problems have always accompanied federal assistance. With few exceptions, however—and it must be emphasized that there were exceptions—they agreed that the difficulties have never been worse and have become, in fact, enormously burdensome, expensive, and disruptive. Specifically, the respondents were asked to describe "any significant changes" that have recently taken place in regulations governing the use of federal funds and in the paperwork requirements that accompany these funds. Representative excerpts from their replies follow.

G. W. Hazard, associate provost at Washington University, St. Louis, stated that, because of federal record-keeping requirements, "We estimate that a given transaction involving federal money costs twice as much to carry out as one involving endowment income."

Sidney G. Roth, director of the office of research services at New York University, stated, "The paperwork requirements have grown unconscionably," but he optimistically added, "self-correcting factors do appear with time."

More than half of the respondents singled out for strong criticism the "cost sharing" regulations on federally supported research. Hugh Clark, associate dean at the University of Connecticut, wrote, "The cost-sharing legislation is an absurdity and an abomination." Anson Burlingame, director of the office of projects and grants at Columbia University, stated that the cost-sharing "standards that are being applied vary not only from one government agency to another, but among different parts of the same agency."

Eugene H. Man, dean of research coordination, at the University of Miami, Coral Gables, wrote: "Paperwork, paperwork, paperwork—and with it all, the growing tendency for the feds to give more administrative responsibility (i.e., paperwork) to the University. One of the nightmares of all time is the protocol and procedure required by the PHS for research involving human subjects. Down the pike we see the same for animals, conflict of interest and who knows what. . . . I find it impossible to believe that the universities will not eventually find their administrative machine clogged by the administrative requirements of federal support on campus—unless by some miracle the Highest Authority decrees that all agencies follow the same format in disbursing and control of funds. It