TRANSIENT GAIN-VERSUS-ABSORPTION LASER PROBING OF SPIN-ORBIT STATES, KINETICS AND DYNAMICS

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ABSTRACT

A tunable F-center laser and a diode laser are used to probe the spin-orbit populations of excited \( ^2(\text{P}_3/2) \) and ground \( ^2(\text{P}_1/2) \) state Br and I atoms at 2714 nm and 1315 nm, respectively. The technique uses pulsed laser photolysis and time-resolved cw laser probing of the gain or absorption signals from the coupled pair of states in the halogen atoms. Transient laser gain-versus-absorption measurements provide highly accurate quantum yields of the spin-orbit states in the photodissociation of molecules such as Br\(_2\), IBr, CH\(_3\)I, ICN and CF\(_3\)I. In Br\(_2\), the continuum yields that result from absorption of vibrationally excited states are investigated as a function of temperature to determine the contributions to the absorption of individual upper excited states. The process of collisional dissociation upwards in energy, termed “collisional release”, is investigated with single vibronic state excitation. The high resolution of the probe lasers allows Doppler velocity effects to be studied, and differing reactivity of the spin-orbit excited and ground state atoms is explored. The high sensitivity and excellent time resolution of the transient gain vs. absorption technique provides a powerful way to study numerous kinetic phenomena with exceptional detail.

RÉSUMÉ

Un laser accordable a centre F et une diode laser sont utilisées pour sonder les populations des états spin-orbite excités \( ^2(\text{P}_3/2) \) et fondamental \( ^2(\text{P}_1/2) \) des atomes Br et I, respectivement à 2714 et 1315 nm. La technique utilise une photolyse laser pulsée et une détection temporelle, au moyen d’un laser continu, des signaux correspondant à un gain ou à une absorption entre les deux états de l’atome d’halogène. Les mesures du rapport entre le gain et l’absorption transitoires permettent de déterminer très précisément le rendement quantique de formation des états spin-orbite dans la photodissociation de molécules telles que Br\(_2\), IBr, CH\(_3\)I, ICN et CF\(_3\)I. Dans Br\(_2\), les rendements dans le continuum qui résulte de l’absorption d’états vibrationnellement excités sont étudiés en fonction de la température afin de déterminer les contributions de chaque état supérieur excité à l’absorption. Le processus de dissociation collisionnelle par accroissement d’énergie est étudié par excitation d’un état vibronique unique. La très haute résolution des lasers permet d’étudier l’effet Doppler et d’explorer la différence de réactivité entre l’état spin-orbite et le fondamental. La sensibilité élevée et l’excellente résolution temporelle de la technique de mesure des rapports gain-absorption, constituent un moyen très puissant d’étude de nombreux phénomènes cinétiques avec un détail d’information exceptionnel.

Introduction

The study of the halogen spin-orbit excited states has been the subject of numerous investigations for many years \(^{(1)}\). Various methods of detection have been used, including vacuum ultraviolet absorption and resonance fluorescence, infrared emission, molecular beam time-of-flight, and optoacoustic spectroscopy \(^{(2)}\). Recently, tunable laser, gain-versus-absorption techniques have been demonstrated as a powerful, general new method to study the kinetics and photodissociation dynamics of Br and I-atom spin-orbit states \(^{(3)}\). The technique of two-laser pulse and cw probing is a familiar one for the study of product state distributions in collisional dynamics \(^{(4)}\). However, the applicability of this method to make exceedingly accurate quantum yield measurements and its unique ability to extract kinetic information from both the gain signal as well as the transient absorption have not generally been considered for electronically excited species.

In this lecture, the method of tunable laser probing of Br and I atom spin-orbit states is considered in the study of a number of new kinetics and dynamics experiments. The Br atoms are probed by a tunable F-center laser at 2714 nm, and the I atoms are studied with a room temperature, tunable InGaAsP laser diode operating at 1315 nm.

The use of the gain-versus-absorption method to obtain highly accurate quantum yields in photodissociation is discussed. The reasons for the cancellation of the important sources of error in the quantum yield determinations are elucidated. The method is used to study the photodissociation yields of a variety of Br- and I-containing compounds to learn about the electronically excited states that lead to dissociation. New information is obtained on the continuum dissociation yields in Br\(_2\) that arise from excitation of “hot” bands; this is achieved by exciting the continuum region between absorption lines with a high resolution pulsed laser and by using single isotopes of bromine, which relieves the spectral congestion. A combination of laser probing and infrared fluorescence is used to study the process called “collisional release”, in which molecules dissociate upwards in energy upon collision. The first results for collisional release using single vibronic level excitation in Br\(_2\) are presented. Finally, new effects such as the gain enhancement due to differential Doppler broadening of states produced by photodissociation and the transient kinetics determination of spin-orbit reactivity are presented.

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Experimental

The experimental apparatus has been fully described \(^{(1)}\). It consists of a two-laser, pulse and probe arrangement, in which the weak cw probe laser is tuned to the spin-orbit transition of the Br or I atom at 2714 or 1315 nm, respectively. A pulsed laser produces populations of excited and ground state atoms, usually by photodissociation, and these populations are subsequently probed for time-resolved gain or absorption by observing the transient signal on the cw probe laser beam. The signals are acquired by a transient digitizer and signal averaged by summing the results of multiple laser pulses to reduce the noise.

Of crucial importance to the understanding of the gain-versus-absorption technique is the recognition that the weak probe laser always "sees" the difference in population between the excited Br\(^{\text{IX}}\) (\(^{1}P_{3/2}\)) and ground \(^{1}P_{1/2}\) Br atoms. Thus the method is sensitive to the kinetics of the "coupled" pair of states. This gives rise to the important advantage of an internal normalization when a ratio is taken between signals from an early time and at some later time after all the atoms are quenched to their ground states.

The lasers used in this study are a pulsed Nd:YAG pumped dye laser and its frequency-doubled output, which provides the light for various excitations and photodissociation, a tunable cw F-center laser for probing of Br atoms, capable of 5-10 mW output in a single frequency with a 1 MHz linewidth, and a tunable, room temperature InGaAsP diode laser for probing I atoms, operated with a grating resonator to control the output to a nearly single frequency having a linewidth of about 100 MHz and several mW output power (Fig. 1). The initial tuning of the probe lasers to the atomic transitions is accomplished by monitoring absorption in a long path cell of heated Br or IBr to produce Br or I atoms, respectively. Figure 2 shows a scan of the diode laser absorption through the I atom hyperfine transitions and the corresponding hyperfine sublevel energy diagram. The Br-atom transitions are essentially identical, with the exception that the nuclear spin in Br is 3/2 rather than 5/2 as in iodine.

A high speed Ge:Au detector is used to monitor the transient signals of the Br/Br\(^{\text{IX}}\) atoms with the F-center laser, and a fast Ge photodiode is used to acquire the signals of the diode laser for the I/I\(^{1}\) atoms \(^{(2)}\). The only significant sources of noise in these experiments are the amplitude stability of the probe lasers and the noise introduced by thermal lensing effects or thermal changes in absorptions of the parent gases \(^{(3)}\). Transient absorption signals as small as a few tenths of a percent of the main probe power can be detected readily with the diode laser because of the small amplitude noise on this laser. Optical isolation is used to prevent large feedback instabilities that occur in the diode laser. For the F-center laser, the amplitude noise is a few percent; however, much of this noise is in the low frequency range. Thus if signals on a 1 usec timescale are of interest, an excellent detection limit is achievable after signal averaging just a few hundred pulses. The resultant signal-to-noise in all experiments is 20 or greater.

A typical signal of transient gain and absorption for I atoms produced in the photodissociation of ICN at 266 nm is shown in Figure 3a. The signal exhibits two important pieces of amplitude information, as well as several types of time information. The initial abrupt rise of the signal to positive gain indicates that the photodissociation produces an excess number of excited I\(^{1}\) atoms, or in other words, a population inversion. The value of \(S_{0}\) on the figure is a measure of the initial

Fig. 1. — (a) Typical two-laser pulse and probe set-up for time-resolved gain-versus-absorption measurements. (b) Multimode pattern of diode laser output showing the reduction in modes achieved by tuning with grating feedback.

Fig. 2. — (a) Energy level diagram of the \(^{2}P_{1/2} - ^{2}P_{3/2}\) transition of I atoms showing the hyperfine structure. (b) A scan of the diode laser absorption through a long path cell of thermally dissociated IBr vapor showing the I atom transitions (scan not linear in wavelength).
determined that the ground state reactivity is substantially faster than the sum of quenching plus reactivity for Br with IBr.

Accurate Quantum Yields

Equation (1) shows the relationship of the signals $S_i$ and $S_r$ to obtain the desired quantum yield ($\phi = N(P_{i})/\left[ N(P_{i}) + N(P_{r}) \right]$) for compounds that dissociate to give only one $I^*$ or Br $^*$ atom ($^5P$):

$$S_i = \frac{2F^* + 1}{\sum(2F^* + 1)} \sigma_{r \rightarrow \pi} N(P_{i}) - \frac{2F + 1}{\sum(2F + 1)} \sigma_{r \rightarrow \pi} N(P_{r})$$

(1)

In this equation, the $(2F + 1)$’s are the degeneracies of the given hyperfine states being probed, the $\sigma$’s are the cross sections for stimulated emission or absorption for the transition being probed, and the N’s are the populations in the spin-orbit states. Because of the cancellation of all factors involving the degeneracies, the transition strengths, and the lineshapes and tuning of the probe laser, the measurement of $S_i$ and $S_r$ reduces to an extremely simple expression for the quantum yield:

$$\phi^* = \frac{1}{3} \left( \frac{S_r}{S_i} + 1 \right)$$

(2)

The amplitude of $S_i$ is defined as positive for gain and negative for absorption; $S_r$ is always taken to be positive. The limits on $S_i/S_r$ are −1 to 2. If only two states are produced and it is known that the quantum yield for dissociation is unity, then the relative results can be put on an absolute scale, and the results above directly give the yield. If more than one excited state is produced, then pairs of states can be probed to obtain the complete quantum yield information.

Because of the internal normalization inherent in the probing of the coupled pair of states, the measurement of the quantum yields by this method is independent of the composition and pressure of the photolysis gas, the probe laser power (which does not usually vary on the short $10^{-3}$ s timescale of the measurement), the photolysis laser power, and the tuning of the probe laser (provided the tuning and lineshape do not change during the $10^{-3}$ s timescale of the measurement). This gives an improvement in accuracy of a factor of ten or more over other quantum yield methods that involve measurements of different signals for each atomic state.

Initial work has considered the quantum yields of Br* produced in the photolysis of Br$_2$ and IBr in the visible continuum regions that lead directly to dissociation ($^1$). Figure 4 shows a “family” of time-resolved traces of gain-versus-absorption signals from IBr as a function of the wavelength of the tunable photodissociation laser. The signals readily show the changeover from early-time gain to early-time absorption, and the “titration” of the 33.3% point (neither gain nor absorption) at approximately 460 nm. In recent work, the quantum yield determinations are shown to be reproducible to better than 2%. The initial quantum yield results for Br$_2$ and IBr are tabulated in Ref. 4.

It is found that excellent agreement is achieved with the relative yields measured by Petersen and Smith for Br$_2$ and IBr ($^2$), and those results can be scaled for the absolute values obtained here. The yields obtained for Br$_2$ and IBr are also in good agreement with the accepted information on the molecular potentials ($^1$). However, for IBr, it is found that no consistent picture of the elec-
Brs Yields from Hot Band Absorptions

The availability of a method to make quantum yield determinations with high accuracy and reliability and which is also relatively easy and quick, allows several new kinds of investigations to be carried out. One example is the determination of the yields for dissociation of Brs when exciting the molecular B state at wavelengths longer than required for dissociation. Even for molecules at room temperature, such wavelengths of excitation result in substantial direct yields to the higher energy Br+ + Br limit due to the thermal population in excited vibrational states (hot bands). There is also significant collisional dissociation, which will be discussed below, due to excitation of the bound levels in the B state.

A wavelength-narrowed pulsed dye laser is used to excite the continuum regions of Brs in between the line transitions in the B electronic state. The laser has a bandwidth of 0.04 cm⁻¹. Even though the laser resolution is good, the congestion in the Brs spectrum is so great that clear regions of continuum can be best observed if a single isotope of Brs is used. Figure 5 shows a portion of a spectral scan of bromine in the visible, demonstrating the reduction in the congestion that is essential for these studies. The pulsed laser is tuned to selected regions of the continuum, and quantum yield determinations are made. For the studies of "collisional release" below, the pulsed laser is tuned to assignable single line features in the spectrum.

Table I displays the yields of directly dissociated molecules when exciting hot bands with the laser at various wavelengths well below the formal dissociation limit. The yield determinations are obtained at two temperatures, so that the results may be fit to extract information about the contributions of the A, B, and C electronic states. Only the B state is thought to contribute to the Brs yield. Figure 6 shows the positions of the excited bromine states relative to the ground state. As can be seen from the figure and the data in Table I, the fraction of the Franck-Condon excitation that samples the higher vibrational states and which concurrently overlaps with the B state changes dramatically with

tronically excited states can be assembled to explain all the continuum yields and other information available (1). The present results show that the ¹He⁺, state most likely dominates the first visible continuum dissociation; however, further work is needed to analyze the parallel and perpendicular components of the total absorption for the Brs yield in order to describe fully the electronic states in this region (1). The quantum yields of ¹⁺ have long been a subject of active investigation. Much of the existing work is built upon infrared fluorescence measurements and molecular beam time-of-flight determinations (2). In many cases, the yield for a molecule such as C₂F₂I has been taken to be a comparison standard with a value of unity, since a value of unity seems to be in agreement with most results reported in the literature. However, optoacoustic determinations have obtained significantly lower yields, casting doubt on this value (1). Because these yields are important for various photolysis lasers, an accurate check on the yield from several iodide compounds was the subject of a test investigation with our recently developed diode laser probe.

Measurements on C₂F₂I and CH₃I at 268 nm obtain yields of essentially 100 % and 75 %, respectively (1), in excellent agreement with accepted values. New measurements on ICN at 266 nm obtain a yield that is in excellent agreement with that reported previously (66 ± 2 % compared to 61 % reported by Pitts and Baronavski (1)) and 65 % reported by Nadler et al). However, at 280 nm, where the diode laser results show a clear initial gain, the results of Ref. 11 suggest that the yield is only 30 %. Since this value is below 33.3 %, it would require a corresponding early-time absorption. This comparison shows the remarkable capability for discrimination of the values of the quantum yields that is inherent in the diode probe laser method.

Fig. 4. — Family of curves for 1Br photolysis showing the change in initial gain at different wavelengths. CO₂ is used as the quenching gas with a large excess of Kr buffer.

Fig. 5. — Absorption scans in Br₂ taken with the 0.04 cm⁻¹ resolution pulsed dye laser (a) all isotopes ³Br₂, ¹²Br₂, and ⁷Br₂²Br₂. (b) Single isotope ⁷Br₂. 80 % ³Br₂.
TABLE I
Br$^*$ Quantum Yields for Br$_2$ (Br$^*$ + Br) at wavelengths longer than the formal dissociation limit (various $v'$ dissociation limits indicated)

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$\lambda$ (nm)</th>
<th>$\delta^*$ (25°C)</th>
<th>$\delta^*$ (100°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>511.2</td>
<td>85.3</td>
<td>85.8</td>
</tr>
<tr>
<td>1</td>
<td>513.2</td>
<td>86.2</td>
<td>85.3</td>
</tr>
<tr>
<td>2</td>
<td>515.4</td>
<td>79.9</td>
<td>79.4</td>
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</tr>
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<td>522.2</td>
<td>71.7</td>
<td>71.7</td>
</tr>
<tr>
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<td>524.7</td>
<td>63.4</td>
<td>63.1</td>
</tr>
<tr>
<td>6</td>
<td>526.3</td>
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</tr>
<tr>
<td>7</td>
<td>527.1</td>
<td>46.7</td>
<td>46.7</td>
</tr>
<tr>
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<td>530.1</td>
<td>32.2</td>
<td>42.2</td>
</tr>
<tr>
<td>9</td>
<td>532.6</td>
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<td>35.1</td>
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<tr>
<td>12</td>
<td>540.0</td>
<td>15.3</td>
<td>29.2</td>
</tr>
</tbody>
</table>

Fig. 7. — Scan of a small portion of the $^9$Br$_2$ spectrum showing the single lines that can be assigned (designated as [v', J']).

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Total absorption

Normalized yield for collisional release.

The measurements here employ single isotopes of bromine and a narrow pulsed laser, so that single vibration-rotation states are excited and the continuum contribution may be assessed by tuning off line. The measurements also require determinations of the total quenching rates of the states and accurate calibration of the total absorption strengths by careful scans of the spectra with the narrow pulsed laser. Figure 7 shows one scan of a small piece of the bromine spectrum in the vicinity of 525 nm. This figure illustrates several of the points made above. From the assignments of the spectral transitions on the figure, it can be seen that a light source which is even a few cm$^{-1}$ wide will excite transitions to $v = 29, 30,$ and 37 simultaneously. The continuum contribution in this figure has been rescaled to zero, however it contributes an additional $\sim 20\%$ to the absorption in this region and thus produces Br and Br$^*$ atoms in addition to the collisional release process. Finally, in the figure, the fractional yield of collisional release is plotted on a normalized scale. It can be seen that lines which arise from higher $v$ states show almost unity probability for collisional release, while other transitions that sample energies of 400-500 cm$^{-1}$ below dissociation show only a 20-30\% efficiency for collisional release. Spontaneous predissociation under our conditions is minimal. However, the molecule is also strongly predissociated by collisions in this region, and thus molecules that do not dissociate upwards will predissociate to ground state atoms.

An important scientific question to consider in the study of collisional release is whether or not the energy of chemical reactivity available by forming weak van der Waals products is important in the dissociation process. By way of illustration, the collision of an excited Br$_2$ (B) molecule with another Br$_2$ might lead to the formation of a Br$_3$ species, and use the chemical energy of that process to produce Br$^*$ at energies below the energy thermally available. On the other hand, if the process of collisional release is strictly an energy transfer process, then it will follow a predictable model based on the total energy available in the collision ($^1$). Thus far the available evidence suggests that the role of chemical affinity is negligible ($^1$), however recent investigations conjecture that the formation of a Br$_3$ species may be important ($^1$). Until now, all of these studies have been done with broadband excitation and thus excite multiple states.

Collisional Release

The process of collisional release in iodine, bromine, and other molecules has been discussed for many years ($^{12-15}$). In Br$_2$ and I$_2$, the phenomenon involves the observation that molecules which are excited to bound levels in the B molecular state will dissociate upwards in energy upon collision with surprising efficiency ($^{16-18}$). Current studies in our laboratory using both infrared emission from Br$^*$ (sensitized through energy transfer to CO$_2$) and the F-center probe laser method are exploring the process of collisional release in Br$_2$, with single vibronic state excitation. All previous measurements involved broadband excitation, which simultaneously samples bound states covering a wide range of energies below dissociation as well as a substantial continuum contribution from hot band dissociation in the same region.

temperature. Our preliminary analysis indicates that the contributions of the A and B states are nearly equal at 526 nm. Further investigations will attempt to reveal the location of the wavelength maximum in the A state for room temperature molecules, thus defining the locations of the repulsive curves of all three states that contribute to the total absorption.
Table II shows the result of our preliminary measurements carried out on the collisional release process for several singly-excited states at different energies below the dissociation limit and with several collision partners, Br₂, Xe, and Ar. The differences in the rare gas polarizabilities and the very different chemical nature of Br₂ vs. Ar and Xe might be expected to show a difference in the collisional release probability with energy if chemical effects are important. As can be seen from the results in the table, there are no major differences in the probabilities of collisional release for the several collision partners, at least in the range of energies studied thus far. Thus it would appear that an energy transfer mechanism is primarily responsible for the magnitude of the collisional release process and not a reactive process. Further work is in progress to extend the measurements to a range of rotational states to look for effects of rotation on the dissociation.

Spin-Orbit Reactivity

The ability to derive time-dependent signals that are characteristic of both the excited state and the ground state of the atoms allows new measurements to be carried out on the different reactivities of spin-orbit states. This exciting field has been reviewed in detail (4). In our work on the photodissociation yields of IBr, we were able to make accurate determinations of the individual rates of reaction of Br and Br* with IBr (2). This case is unusual, because the spin-orbit excited state is considerably less reactive than the ground state (see references to earlier work in ref. 5). The reason is that the symmetry correlations from products to reactants hold strictly in this case, and the correlation from the excited atom leads to a high energy state which then involves a barrier to the reaction.

Figure 8 shows the interesting effect that is observed in the gain-versus-absorption signals if the quenching gas is left out of the IBr photolysis experiment entirely. The gain signal first has the expected abrupt rise, indicating a population inversion, but then the gain actually increases in time, reaching a maximum limit in which essentially all of the atoms remaining are in the excited state. The only explanation for such a signal is that the increase is due to the reactive loss of ground state atoms. In fact, our measurements confirm that the ground state reactivity is 40 times more efficient than the sum of reaction plus quenching for the excited Br* with IBr (2). These results also have important implications for the IBr photolysis laser and for other chemical lasers, in which selective spin-orbit reactivity might be considered as a means to eliminate the population in the lower laser level. In essence, for the IBr laser, the parent gas itself has the automatic feature of generating a complete population inversion of Br* by selective reaction of Br with IBr, no matter what the photodissociation yield is that is achieved initially.

Doppler Velocity Effects

A final consideration of these gain-versus-absorption experiments, which is also relevant to new kinds of photodissociation laser devices, is the fact that the initial Doppler velocities of the atoms produced in the photodissociation event are significantly different for Br
and Br\. Thus the spectral density of states will be greater for the slower-moving upper spin-orbit states than for the faster-velocity ground states. If there are no collisions with a buffer gas between the time of dissociation and the time of probing, an enhancement in the early time gain can be observed, which is a measure of this difference. Figure 9 shows a family of gain/absorption curves for IBr taken at a wavelength where the initial dissociation produces approximately 33\% of the excited atoms. Under these conditions the enhancement due to the spectral linewidths is most noticeable. As can be seen from the figure, when the buffer gas is reduced and finally removed (bottom to top), there is a gain enhancement due solely to the Doppler velocity difference between the excited and ground state atoms. Further work will exploit these effects and begin to probe the differences in both reactivity and collisional energy transfer as a function of velocity.

Conclusion

The time-resolved laser gain-vs.-absorption method is shown to be a powerful new means of obtaining highly accurate quantum yields as well as information on reactive dynamics and collisional energy transfer. The technique is applicable to probing a selected number of states in atoms or molecules with excellent time resolution and accurate population detail. Combining the probe method with a high resolution pulsed laser, a variety of new selective kinetic effects are measured. Work in progress will investigate the differences in recombination rates of spin-orbit states and other detailed studies of dissociation dynamics.

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