

Color-center laser spectroscopy of transient species produced by excimer-laser flash photolysis

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Kinetic spectroscopy based on excimer-laser flash photolysis and color-center-laser (CCL) infrared probing is explored. In simple absorption, the achievable signal-to-noise ratio (S/N) is not satisfactory even though the signal itself (corresponding to >1% absorption) is fairly large. This is due to amplitude fluctuations of the CCL. By using a double-beam detection scheme to balance out these amplitude fluctuations the sensitivity can be improved to the extent that a 1% absorption gives a S/N ~ 100. In certain situations transient decreases in absorption of the precursor and transient increases in absorption due to final product formation can produce severe interfering signals even in simple systems. This problem is overcome without a major loss in sensitivity by a recently developed 45° magnetic rotation scheme. These points are illustrated with spectra of Br, OH, and NH₂.

INTRODUCTION

A powerful method for the detection of transient species is the UV flash photolysis of stable precursor gases and subsequent IR probing of the molecular fragments produced.^{1,2} Such experiments can provide three different kinds of information: (1) the absorption spectra of short-lived radicals often in electronically excited states as well as the ground state; (2) chemical kinetic data of the transient species produced; and (3) determination of the nascent distribution of the product states formed. The infrared is an especially interesting region of the spectrum because almost all substances exhibit absorptions in this region, thereby providing a nearly universal monitor of transient species. However, this has its drawbacks owing to interferences of the precursor molecules used.

The new generation of commercially available excimer lasers producing several hundred millijoules of output power per pulse at a repetition rate of 50 Hz and a pulse-to-pulse reproducibility of better than 90% provides an excellent UV radiation source for the flash photolysis. Recently excimer-laser flash-photolysis experiments using an IR diode laser or frequency-difference laser probe have been reported.³⁻⁵ In the work reported here, the use of a color-center laser (CCL) is explored.

The relatively high tunable output power of several milliwatts of the CCL makes it an attractive choice as an IR probe. However, this high-output power is accompanied by substantial amplitude fluctuation noise, produced predominantly by the ion pump laser. Several methods of overcoming source noise and achieving a good sensitivity for steady-state CCL spectroscopy have already been described. These include magnetic rotation,⁶ tone modulation,^{7,8} and velocity modulation.⁹ In this work we focus on sensitivity enhancement for transient spectroscopy and, in particular, on the advantages of a balanced double-detector scheme for transient-mag-

netic-rotation spectroscopy. This method can discriminate against disturbing precursor and final-product absorptions, an important advantage for those cases in which the precursor gas and/or final products exhibit an overlapping spectrum.

SENSITIVITY CALCULATIONS

The expected signal strength can be estimated, and thus the required sensitivity for the detection system can be determined. The transmission of an IR probe beam may be expressed as

$$I_{TR} = I_0 \exp(-\sigma NLn), \quad (1)$$

where I_0 is the incident intensity, I_{TR} the transmitted intensity, σ the IR-absorption cross section, N the number of absorbers per cubic centimeter, L the length of the absorption region, and n the number of IR beam passes. For simplicity we assume that

- (1) The pressure of the precursor gas is large enough so that all the incident UV-excimer radiation is absorbed;
- (2) The quantum yield for the formation of the radicals from the precursor gas is unity.

Then the number of absorbers per unit volume is

$$N = E/(h\nu_{exc}AL). \quad (2)$$

For small absorptions, it follows that

$$I_{abs}/I_0 = \sigma En/(h\nu_{exc}A), \quad (3)$$

where $I_{abs} = I_0 - I_{TR}$ is the absorbed intensity. Using a typical value of 100 mJ per excimer-laser pulse over an area of 1 cm² for a single traversal through the cell and a moderately weak absorption cross section of $\sigma = 10^{-19}$ cm²,^{10,11} one can calculate the ratio

$$I_{\text{abs}}/I_0 = 0.01, \quad (4)$$

i.e., a 1% absorption of the IR beam occurs, which must be measured within the lifetime of the molecules produced.

EXPERIMENTAL DETAILS

The experimental arrangement is shown in Fig. 1. The IR source used in this work was a computer-controlled single-mode CCL¹² (Burleigh FCL 20), pumped with the red lines of a Kr⁺ laser. The UV source was an excimer laser (Lambda Physik EMG-101), which was operated on the ArF transition at 193 nm. The maximum repetition rate was 50 Hz, the maximum output energy was 150 mJ per pulse, and the pulse-to-pulse reproducibility, which was monitored by a UV power meter (Gentec ED-200), was better than 90%.

The excimer beam traversed the sample cell (30 cm) in the opposite direction to the IR probe beam. The counterpropagating scheme avoids exposing the detector to the excimer-laser discharge. In this discharge, an IR emission is produced that cannot be easily blocked by filters, significantly increasing the effective noise. For the same reason the windows of the cell were tilted to avoid reflections of this IR emission toward the detector. Unfortunately, the presence of this emission limits the utility of any multipass experiment until a scheme for removing the IR from the UV beam is developed.

The signal intensity can be increased by reducing the UV-beam diameter [see Eq. (3)]. However it was found that all UV optics, especially the CaF₂ windows of the absorption cell, emitted an IR fluorescence and became damaged on exposure to the focused UV beam even for a short time.

Several detection schemes were tested, ranging from single-beam absorption with lock-in detection at the repetition frequency of the excimer laser to double-detection magnetic rotation using a transient digitizer. For double-detector experiments, the signals from detectors specially selected for equal sensitivity were input into a differential preamp. Figure 1 illustrates the various systems used. A particular experiment can be chosen by selecting the appropriate switch combination (S₁, S₂). A DEC LSI 11/23 minicomputer was used for data storage and further postdetection data processing.¹³ The optimum detection method for the species investigated depends on its lifetime, its magnetic properties, and the severity of precursor interference effects.

TRANSIENT ABSORPTION SPECTRA

The transient signal at a single wavelength can be examined by acquiring the detector signal as a function of time using the transient digitizer (S₁, S₂) = (C, E). Figure 2 illustrates the signal with the highest fractional absorption that we have observed so far. This trace was obtained by tuning the CCL to the center of the strongest hyperfine component of the Br atom fine-structure transition at 3685 cm⁻¹.^{14,15} The excimer laser was focused to one quarter of its normal area, and four passes through the sample were made. Under these conditions substantial IR interference from excimer window fluorescence and a spurious transient absorption are present but have been eliminated from the trace shown by subtracting the signal obtained when the probe laser is tuned off the Br line. For comparison a transient digitizer signal obtained by chopping the IR laser is also displayed. The initial spike

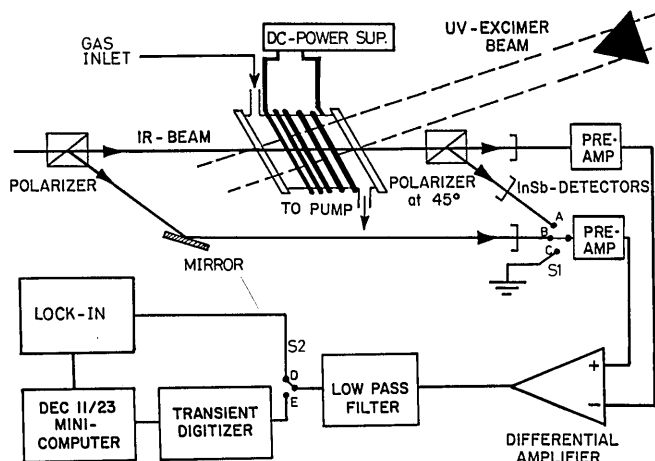


Fig. 1. Experimental setup of several detection schemes. A specific scheme can be chosen by selecting the appropriate switch combination (S₁, S₂).

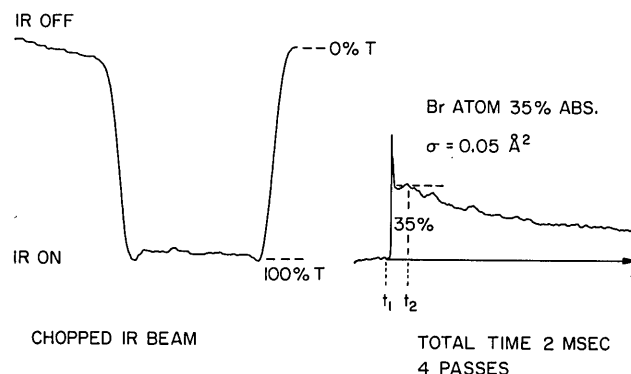


Fig. 2. Bromine transient absorption of the strongest hyperfine component at 3685 cm⁻¹ and comparison with a chopped beam trace (=100% absorption).

observed before the photolysis zone expands corresponds to about 60% absorption. Using the known distribution of Br atoms¹⁶ between the two fine-structure states, the absorption cross section of the line is calculated to be 5×10^{-18} cm². The value and Eq. (3) predict a somewhat larger absorption under these conditions. Note that noise, which arises from amplitude fluctuations of the CCL, is clearly visible in this trace. If a spectrum is obtained by acquiring signals at the time points marked t_1 and t_2 (Fig. 2) and taking their difference as a function of wavelength, the S/N to be expected for the strong peak is less than 50. Such a spectrum is shown in Fig. 3.

Color-center-laser amplitude fluctuations can be canceled by using a double-detector differential amplifier arrangement (S₁, S₂) = (B, E) as shown in Fig. 1. Figure 4 shows a frequency scan over the (1 ← 0)R(3.5)F1 transition of OH (Ref. 17) in which the peak absorption is only 1%, yet the S/N is ~100. This suggests that this method is potentially very sensitive for the detection of a variety of transient species.

TRANSIENT-MAGNETIC-ROTATION DETECTION

Figure 5 illustrates the complexity of the transient absorption spectrum when the precursor molecule also absorbs in the region of interest. In this experiment HNC0 was photolyzed

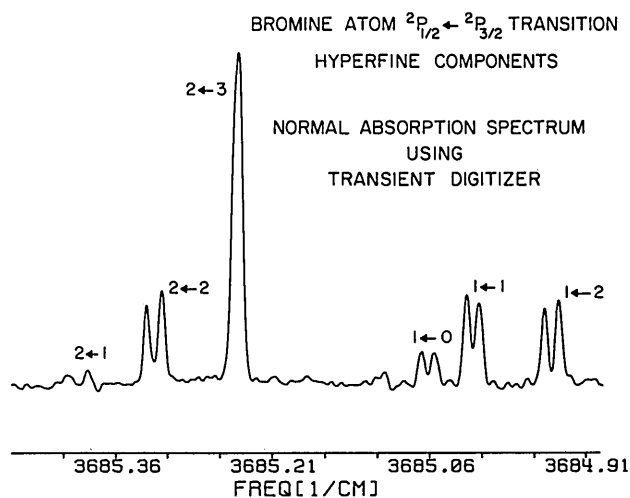


Fig. 3. Normal absorption spectrum of the bromine-atom hyperfine structure at 3685 cm^{-1} obtained by taking at each frequency step the difference between the intensity measured at time t_1 and t_2 (see Fig. 2).

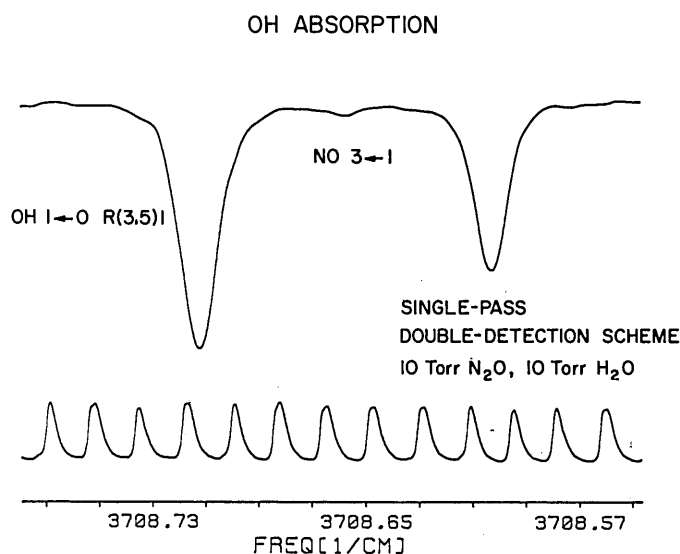


Fig. 4. Normal absorption spectrum of the OH ($1 \leftarrow 0$)R(3.5)F1 transition using balanced detectors. The OH radical was produced by photolyzing a ($\text{N}_2\text{O} + \text{H}_2\text{O}$) mixture: $\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}(^1D)$ followed by $\text{H}_2\text{O} + \text{O}(^1D) \rightarrow 2\text{OH}$.

in order to observe the $\text{NH } ^1\Delta$ transient in absorption (S_1, S_2) = (B, E). As can be seen, a complex spectrum is observed in which features corresponding to both increased absorption and decreased absorption can be matched with features of the normal absorption spectrum, indicating that the transient features originate from the HNCO and its final decomposition products. Even for this relatively simple system it is apparent that the detection of transient signals among those due to the precursor and products is difficult. (It should be mentioned that we have recently observed the $\text{NH } ^1\Delta$ fundamental using HN_3 as the precursor without interference problems.¹⁸)

Most transient intermediates of interest are paramagnetic free radicals so that the well-known magnetic rotation method⁶ based on Zeeman splitting produced by a magnetic field can be used to discriminate against absorptions of non-magnetic precursors and final products while still providing good sensitivity. An example is shown in Fig. 6, where the

same portion of the Br spectrum as in Fig. 3 was observed but now in magnetic rotation. Because of the relatively long lifetime of the bromine atoms (~ 5 msec) lock-in detection was possible (S_1, S_2) = (C, D). The achieved S/N is comparable with a previous magnetic-rotation spectrum¹⁵ obtained in a discharge-flow system.

A segment of the OH spectrum (Fig. 7) taken using the magnetic-rotation method illustrates some of the drawbacks of the kinetic spectroscopy scheme when applied to short-lived species. The low-frequency absorption arises from a non-magnetic species, for it can be greatly reduced (for comparison see Fig. 4) with the 90° magnetic-rotation method. Nevertheless, a small interference still remains because a significant uncrossing of the two polarizers is necessary for optimum sensitivity.

To overcome this problem a modification¹⁹ of the normal magnetic-rotation scheme was adapted to this field of kinetic spectroscopy. In this setup the polarizer behind the absorption cell is set at 45° with respect to the first polarizer

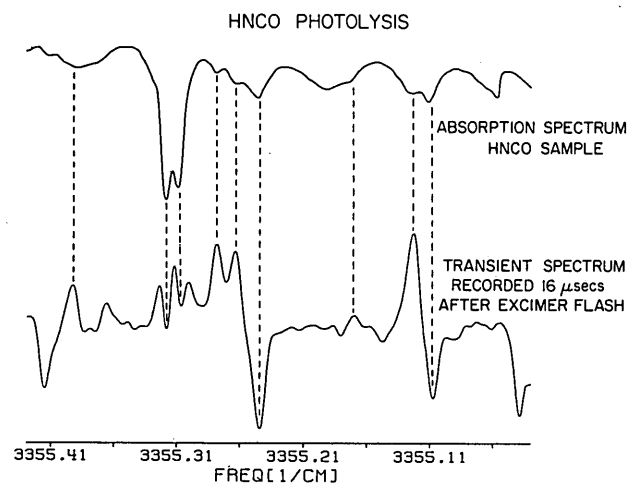


Fig. 5. Transient absorption spectrum of photolyzed HNCO compared with the normal absorption spectrum. The HNCO sample contained impurities that also appear to be final photolysis products.

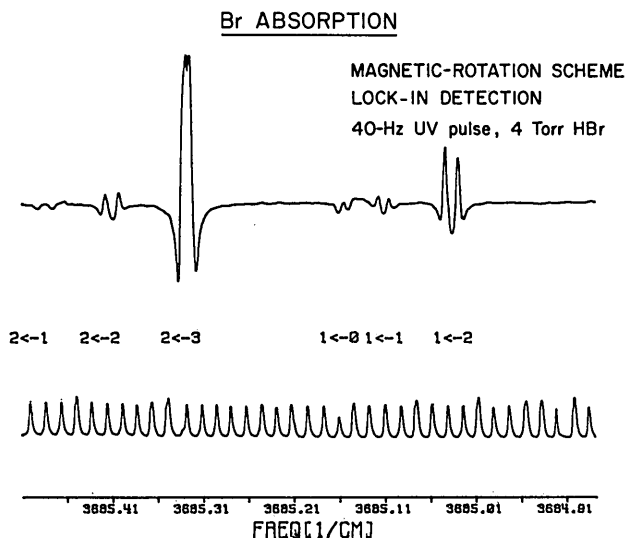


Fig. 6. Magnetic-rotation spectrum of the bromine-atom hyperfine structure using lock-in detection and the nearly crossed polarizer method (90° method). The dc magnetic field was about 300 G.

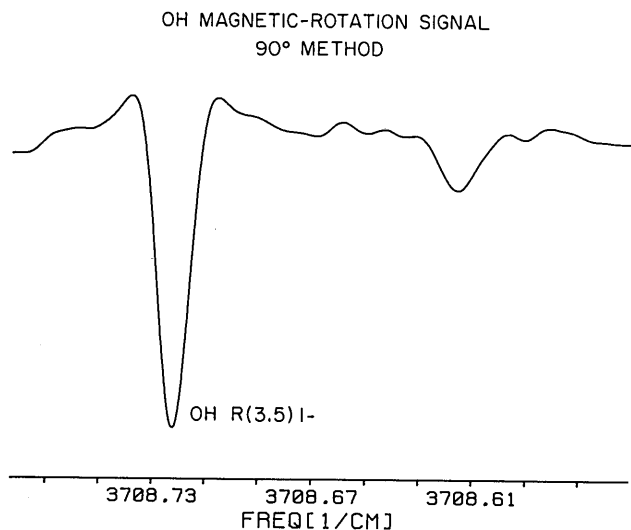
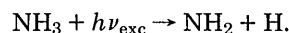


Fig. 7. Magnetic-rotation spectrum of the OH(1 ← O)R(3.5)F1 transition using the 90° method.



In this case a precursor (NH₃) transition has almost the same frequency as a NH₂ absorption line²¹ [Fig. 8(A)]. Figures 8(B) and 8(C) show that when using the 90° method it is not possible to suppress the NH₃ signal completely, whereas in the 45° spectrum it is eliminated.

CONCLUSION

The use of a CCL probe for kinetic spectroscopy with excimer-laser flash photolysis has been explored. As is usually the case in CCL spectroscopy, sensitivity is limited by amplitude fluctuations of the CCL. Several sensitivity-enhancement schemes for transient absorptions were examined, and the spectra of several transient species were observed using these methods. A S/N of 100 for a 1% absorption was achieved, sufficient for the study of a number of interesting transient species. For the observation of radicals, it was demonstrated that interfering signals arising from decreased precursor absorption can be removed without substantially sacrificing sensitivity using differential detection magnetic rotation (45° method).

ACKNOWLEDGMENTS

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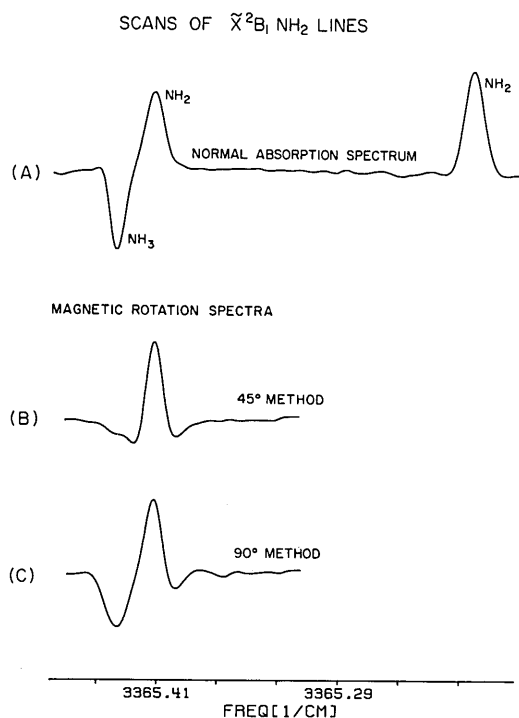


Fig. 8. (A) Transient absorption spectrum of NH₂ produced by photolyzing NH₃. (B) and (C) Comparison of the 45° with the 90° magnetic-rotation method. The 45° method allows almost total discrimination against precursor absorptions.

instead of nearly crossed. The two resulting beams are detected with balanced detectors, and the difference signal is amplified (S1, S2) = (A, E). Magnetic rotation increases the intensity of one beam while decreasing the other one. Normal absorption causes the intensity of both beams to decrease, giving no difference signal. The main advantage of the 45° method is that any nonmagnetic absorptions or power fluctuations (noise) of the CCL occur on both channels in the same way so that they cancel at the differential amplifier.

The ability of this method to cancel nonmagnetic absorption completely is demonstrated by spectra of the NH₂ radical produced by photolyzing NH₃ (Ref. 20):

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Horst Adams received the physics diploma from the University of Bonn, Bonn, Federal Republic of Germany, in 1982. In his thesis he described a new differential detection scheme for magnetic rotation spectroscopy. In 1983, he was awarded a stipend by the Fulbright Organization, which enabled him to spend 8 months as a research associate at the Departments of Chemistry and Electrical Engineering and Rice Quantum Institute of the Rice University, Houston, Texas. During this time he performed research in excimer-laser flash photolysis, time-resolved spectroscopy of molecular reactions, and frequency sideband spectroscopy. He is currently with the Institute of Applied Physics, Bonn, Germany. His present research activities are in the fields of color-center lasers and development of new spectroscopic techniques.