

KINETIC SPECTROSCOPY WITH THE COLOR CENTER LASER*

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Abstract

Transient infrared absorption spectra of reactive chemical species produced by excimer laser flash photolysis are obtained by use of a color center laser probe providing a means of both observing new spectra and studying chemical kinetics.

Introduction

Kinetic spectroscopy was developed in the late 1940's by Norrish and Porter[1]. In this classic experiment, the absorption cell contains a precursor gas or mixture of gases which is flash photolysed by discharging a condenser through a rare gas flashlamp; after a time delay, the absorption spectrum of transient species produced by photolysis is photographed with a spectroscopic flash. By this means an absorption spectrum over a wide range of wavelengths is obtained at a single delay time in one experiment. Initially the time scale was a few milliseconds, but was rapidly improved to a few microseconds. This technique has proved to be a powerful means for obtaining the spectra of transient species and studying their chemical kinetics.

In the early 1960's serious efforts[2,3] were made, principally by Pimentel[2], to extend kinetic spectroscopy to the infrared. Such a development is highly desirable because almost all substances exhibit an infrared spectrum providing an almost universal monitor of transient species. Moreover, the spectra are never diffuse so that structural information is obtainable by resolving rotational structure. Photographic plates sensitive in the mid-infrared do not exist so that the experiment must be altered significantly. Sensitive, high speed detectors such as InSb and HgCdTe are available but are too expensive to multiplex into an array. Thus the approach used was to develop rapid-scanning monochromators in order to scan a significant portion of the spectrum after a single photolysis flash. Since the spectrographic flash is essentially a black body radiation source and mid-infrared wavelengths are well below the blackbody maximum, the intensity available for obtaining the absorption spectrum is poor. As a result resolution is low. Nevertheless, the infrared spectra of several transient species, most notably the methyl radical[4] were obtained in this manner.

With the development of infrared laser sources, interest in extending kinetic spectroscopy to the infrared has been rekindled. There are two basic approaches. One by Sorokin[5] is the laser analogue of the original experiment by Norrish and Porter. An infrared continuum is generated by stimulated Raman scattering of a broadband dye thus overcoming the source problem. The detector problem is overcome by upconverting the infrared to the visible by four wave mixing in an alkali metal vapor thereby allowing the use of relatively inexpensive array detectors (OMA or photographic plate). This is potentially a very powerful technique which will undoubtedly produce highly significant results. The other approach is to use a monochromatic infrared probe laser and to repeat the photolysis experiment many times. Several groups are exploring this approach using a variety of infrared probe lasers; so far all are using an UV excimer laser for photolysis. To our knowledge, the first work along these lines was done by Laguna and Baughcum[6] using a diode laser to observe the umbrella motion of the methyl radical. Moore and coworkers have used infrared obtained by frequency difference generation between a cw dye laser and an ion laser to study the CH stretching vibrations of singlet methylene[7]. Another group at the Institute for Molecular Science is developing the method using a diode laser for the infrared probe[8]. This work reports our efforts to develop kinetic spectroscopy in the infrared using a cw color center laser probe and ArF excimer laser flash photolysis.

Sensitivity Considerations

It is clear from the previously reported work that infrared kinetic spectroscopy must provide sufficient sensitivity to be useful. It is instructive to briefly consider some of the factors that determine and limit the sensitivity. Although a variety of experimental configurations are conceivable, the simplest for the purposes of exploring sensitivity is

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one in which the UV excimer beam and the infrared probe beam propagate colinearly through the sample. If the sample cell is made long enough and the precursor gas absorbing the UV is at high enough pressure, all of the excimer energy will be absorbed in the region probed. This results in a column density of infrared absorbers given by

$$N_c = Qn_p/A \quad (1)$$

where Q is the quantum yield of infrared absorbers per UV photon absorbed, n_p is the number of UV photons from the photolysis pulse, and A is the area of the excimer laser beam.¹⁷ For an ArF pulse energy of 0.1 J, an area of 1cm² and a quantum yield of unity, $N_c = n_p = 10^{17}$ cm⁻². The fractional absorption of infrared power may be expressed

$$\Delta P/P_0 = 1 - \exp(-\sigma N_c n_T) \quad (2)$$

where σ is the infrared absorption cross-section and n_T is the number of traversals of the photolysis region by the infrared beam. The infrared absorption cross-section for a Doppler broadened line is given by

$$\sigma = \sqrt{\pi} |\mu|^2 S / (3\epsilon_0 huZ) \exp(-E_L/kT) \quad (3)$$

where μ is the molecule fixed dipole transition moment, S is the rotational line strength, ϵ_0 is the permittivity of the vacuum, u is the most probable molecular velocity, Z is the internal partition function, and E_L is the energy of the lower level in the transition. In this expression it has been assumed that the number of absorbers in the upper level of the infrared transition is negligible and that the absorber is at thermal equilibrium at some temperature (presumably ambient). Typical values of the molecular quantities in Eq. (3) are $|\mu| = 0.1 - 0.2$ debye, $S = 1 - 5$, $u = 300$ m/sec, $Z = 10 - 1000$ resulting in typical values of $\sigma = 10^{-17} - 10^{-19}$ cm². Substituting $N_c = 10^{17}$, $\sigma = 10^{-19}$ cm², and $n_T = 1$ in Eq. 2, we obtain $\Delta P/P_0 = 0.01$ (i.e. 1% absorption).

Furthermore suppose we wish to detect this transient absorption in 10 μ sec. Typical color center laser output powers are 3 mW in single mode operation corresponding to 4×10^{16} IR photons/sec or 4×10^{11} during the detection time. For 1% absorption, this corresponds to a signal of 4×10^4 photons. There are three sources of noise which could limit sensitivity: detector noise (corresponding to photomultiplier dark current or background thermal radiation), quantum noise (due to the quantal nature of the detection process) and noise due to laser amplitude fluctuations. Using an InSb detector with a $D^* = 10^{11}$ (cm $\sqrt{\text{Hz}}/\text{W}$), the number of photons equivalent to detector noise for a 1mm diameter detector in 10 μ sec is 4×10^4 . Assuming a quantum efficiency of an InSb detector of unity, the number of counts in the detection time is 4×10^{11} giving a standard deviation of 6×10^5 photons. Thus it appears that detector noise should be small in comparison with quantum noise, although care must be taken to consider the characteristics of the complete amplifier system. Amplitude fluctuations in the color center laser depend upon a variety of noise sources in the ion laser pumping the color center laser and upon the color center laser itself, and this noise source must be estimated experimentally. We find that a 1% transient absorption is barely discernable on a transient digitizer trace of 1000 points with a time scale of 50nsec per point and a detector rise time of 1 μ sec. As the signal-to-noise expected in the quantum noise limit is 10^4 , clearly sensitivity appears to be limited by noise arising from laser amplitude fluctuations. Fortunately, there are ways of reducing such source noise and we have obtained a $S/N \sim 100$ for 1% absorption.

Experimental

The color center laser used in this work was a Burleigh FCL-20 pumped with 1W of the red lines of a Kr⁺ laser. The laser is computer controlled by means of an 11/23 DEC computer and CAMAC crate through a stepping motor and high voltage amplifiers as has been described^[9] previously. A transient digitizer (LeCroy Model 2256AS) was added to the CAMAC crate in order to acquire time-resolved high resolution spectra. Appropriate software permits two new types of scans: scans in time at a single laser frequency, by acquiring a detector signal with the transient digitizer triggered by the excimer laser and storing it in the computer; and frequency scans in which up to four channels of the transient digitizer are stored at each laser frequency.

The excimer laser employed in this work is a Lambda-Physik EM-101 used on the ArF line at 193nm. This laser is rated at a maximum pulse energy of 0.2J on this line and a maximum repetition rate of 40Hz (with some degradation in pulse energy). A Gentec Model ED-200 pulse energy meter was used to monitor the pulse energy for repetition rates of less than 5Hz.

A variety of cell arrangements and detection schemes were tested in the course of this work, ranging from a geometry in which the excimer laser propagates in a direction perpendicular to the infrared beam to one in which the two beams are exactly colinear. As

the absorption coefficients at 193nm of suitable precursor molecules cover a very wide range, the only geometry in which sample pressure can be varied without affecting the utilization of the excimer pulse is the strictly colinear one in a long cell. Fig. 1 shows the combination of the two beams using a UV reflecting, IR transmitting mirror with counterpropagating beams. Several detector arrangements were employed from the simple direct observation of absorption with a single detector with and without magnetic rotation sensitivity enhancement to two different schemes using differenced balanced detectors with and without magnetic rotation in order to reduce noise arising from laser amplitude fluctuations.

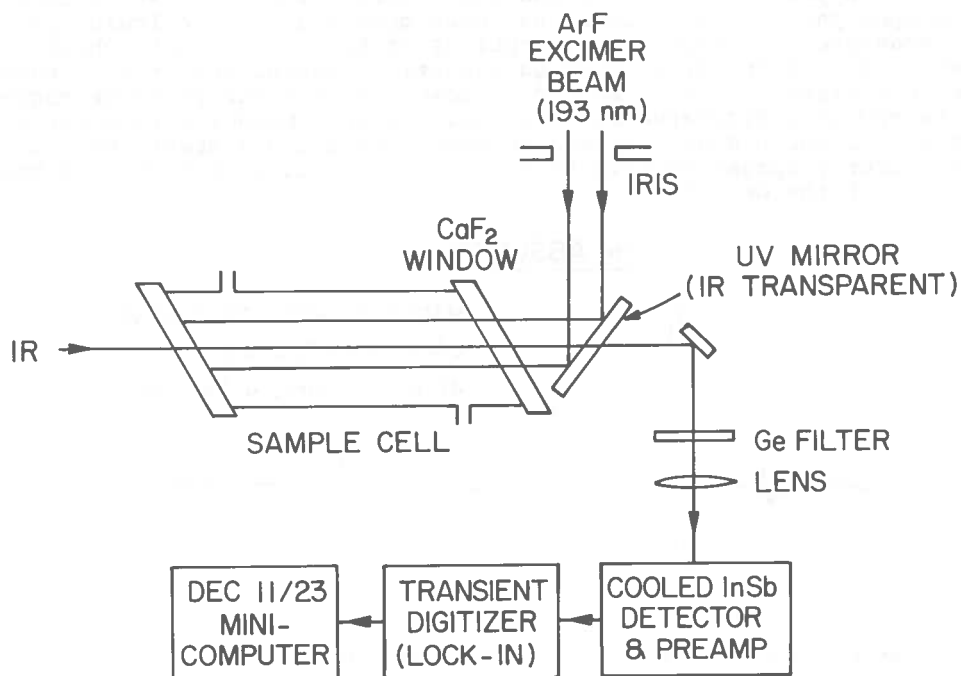


Fig. 1. Colinear cell geometry with counterpropagating beams using a UV reflecting IR transmitting mirror on a CaF_2 substrate. This geometry allows control of the sample pressure for a wide range of UV absorption cross-sections and avoids having the IR detector looking into the excimer laser discharge tube. However, only one IR pass is possible.

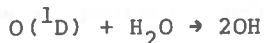
It might seem that special methods for reducing the noise arising from laser amplitude fluctuations might be rendered unnecessary by taking measures to increase the signal amplitude. Two variables might be manipulated to bring this about. Either the UV beam area could be reduced thus increasing the column density of absorbers or the number of traversals, n_m , of the infrared beam might be increased from near unity. Both approaches present problems. When the UV beam area is reduced, it is found that the optics used in the beam, CaF_2 windows (and in some arrangements UV mirrors), degrade rapidly in quality. In addition, it becomes more difficult to avoid thermal lensing effects. There are several problems which make it difficult to increase substantially the number of traversals. In particular, it is necessary to avoid having the IR detector look directly into the discharge tube of the excimer laser as there is IR emission from the excimer discharge which is not highly reproducible from shot-to-shot.

Results

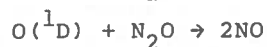
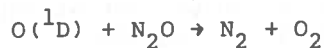
Two test systems were used to explore the method described above: the fine structure transition of the Br atom [10,11] at 3685cm^{-1} and the OH stretching fundamental of the OH radical [12]. Br atoms were produced by the photolysis of HBr at 193nm



OH was produced by the reaction scheme



This system also produces O₂ and NO by the reactions



The Br atom spectrum was used primarily to establish that estimates of the expected signal strengths were correct. The magnetic dipole transition moment may be calculated precisely for any hyperfine component and the distribution of Br atoms between the ²P_{3/2} and ²P_{1/2} levels upon photolysis at 193nm has been measured[13]. Allowing for experimental uncertainties, observed and expected absorptions of Br did, in fact, check. Fig. 2 shows the hyperfine structure of the Br atom using magnetic rotation sensitivity enhancement with nearly crossed polarizers. This should be compared with the previous magnetic rotation spectrum[11] obtained in a discharge-flow system. In this magnetic rotation experiment the sample cell in Fig. 1 was placed inside a solenoid providing a static magnetic field along the direction of laser propagation with nearly crossed polarizers in the IR beam before the sample and in front of the detector.

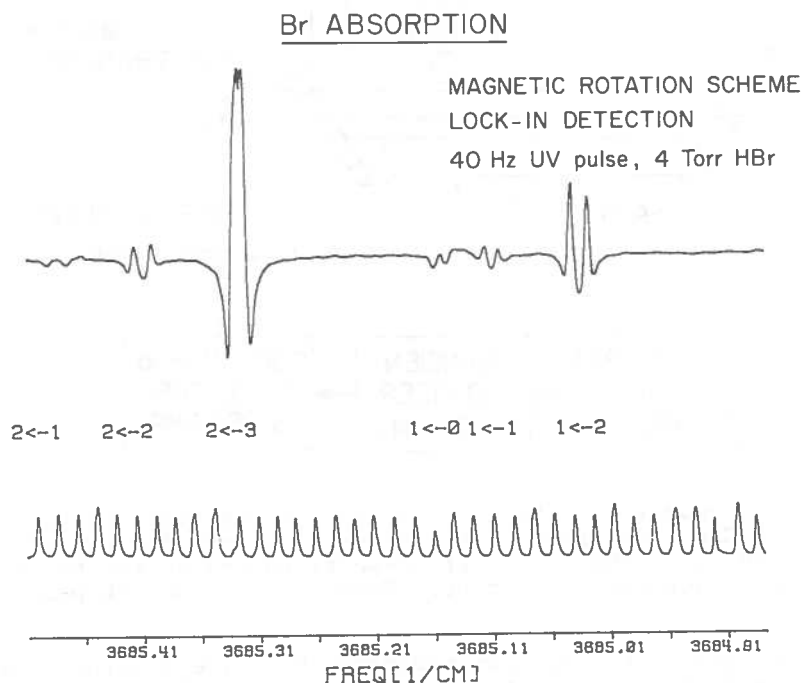


Fig. 2. Hyperfine structure of the Br atom obtained in magnetic rotation by the flash photolysis of HBr.

Br atoms are very long-lived, but OH provides an example of a shorter lived species (about 1msec in our system). To prepare OH, N₂O was bubbled through water cooled to about 5°C, and the resulting mixture then flowed through the photolysis cell. The operating pressure was typically about 20Torr because the absorption cross-section of N₂O at 193nm is small. With OH as the test system several sensitivity enhancement techniques were explored. The best sensitivity was obtained in direct absorption with balanced detectors amplifying the difference signal. Fig. 3 shows a S/N~100 for 1% absorption for the OH line. Also shown in the same trace are a much weaker line which is at the right frequency for a v 3-1 transition of NO and a strong transient absorption of unknown origin (the right frequency for a ground state H₂O line). This spectrum demonstrates the serious interferences associated with transient absorptions and decreased absorptions (arising from photolysis of absorbing precursors) intrinsic to mid-infrared kinetic spectroscopy.

Magnetic rotation provides a powerful means of eliminating this interference problem as it should be sensitive only to paramagnetic species. In fact, minor interference remains when magnetic rotation is used with nearly crossed polarizers because significant uncrossing is required for optimum sensitivity. This defect can be overcome by using a new magnetic rotation technique recently developed at Bonn[14]. The experimental arrangement is shown in Fig. 4. In this scheme, the Rochon prism analyzing polarizer is set at 45° to

the initial polarization, and the two resulting beams are detected with balanced detectors with the difference signal being amplified. Magnetic rotation causes the intensity of one beam to increase and the other beam to decrease while simple absorption causes the intensity of each beam to decrease giving no difference signal.

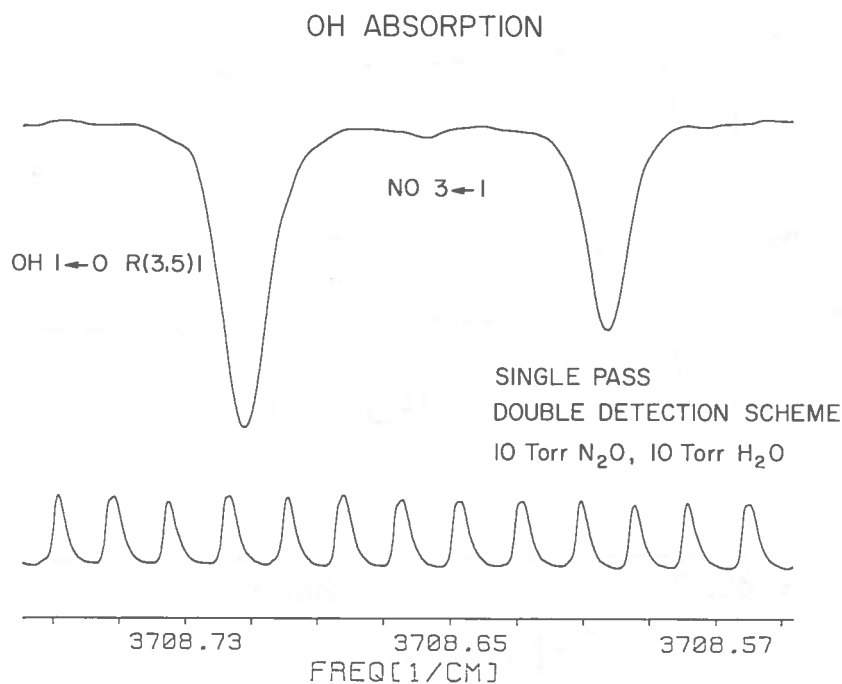


Fig. 3. Transient absorption spectrum of OH produced by the reaction of $O(^1D)$ with H_2O recorded with balanced detectors. The OH absorption peak represents about 1% absorption. A weak absorption believed to be due to NO and an as yet unidentified transient absorption which may be due to H_2O can also be seen.

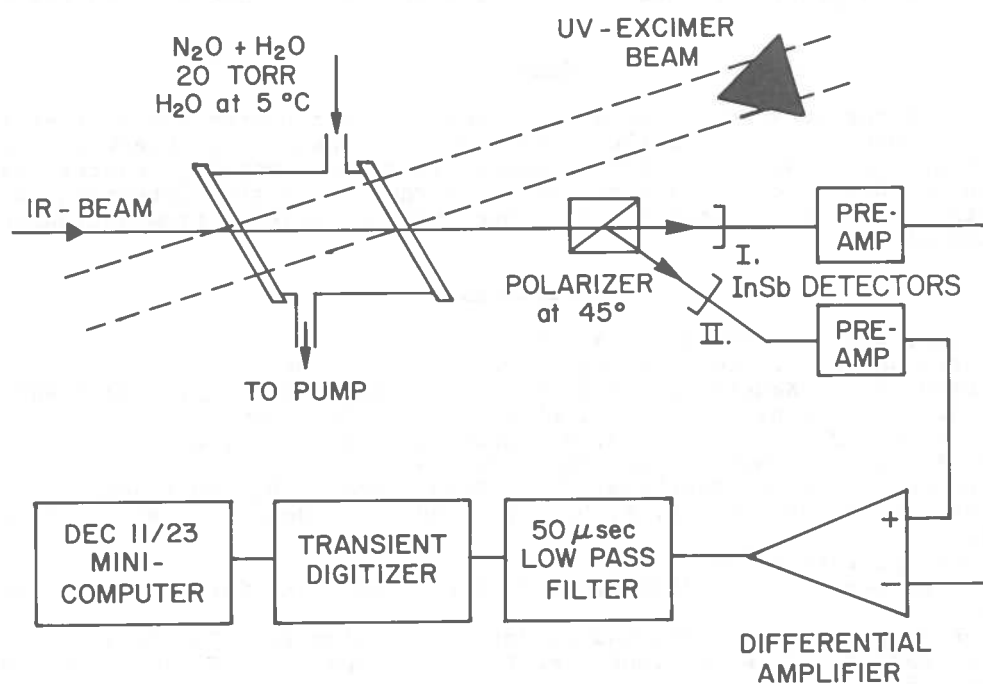


Fig. 4. The apparatus used in 45° magnetic rotation. The sample cell is placed inside a solenoid and subjected to a DC magnetic field giving rise to rotation of the plane of polarization by paramagnetic species.

Fig. 5 shows a comparison of the two magnetic rotation schemes for the same set of lines depicted in Fig. 3. Clearly the low frequency transient absorption arises from a non-magnetic species. It is almost completely eliminated with nearly crossed polarizer magnetic rotation (90° method) and is completely eliminated with the two detector magnetic rotation (45°) method.

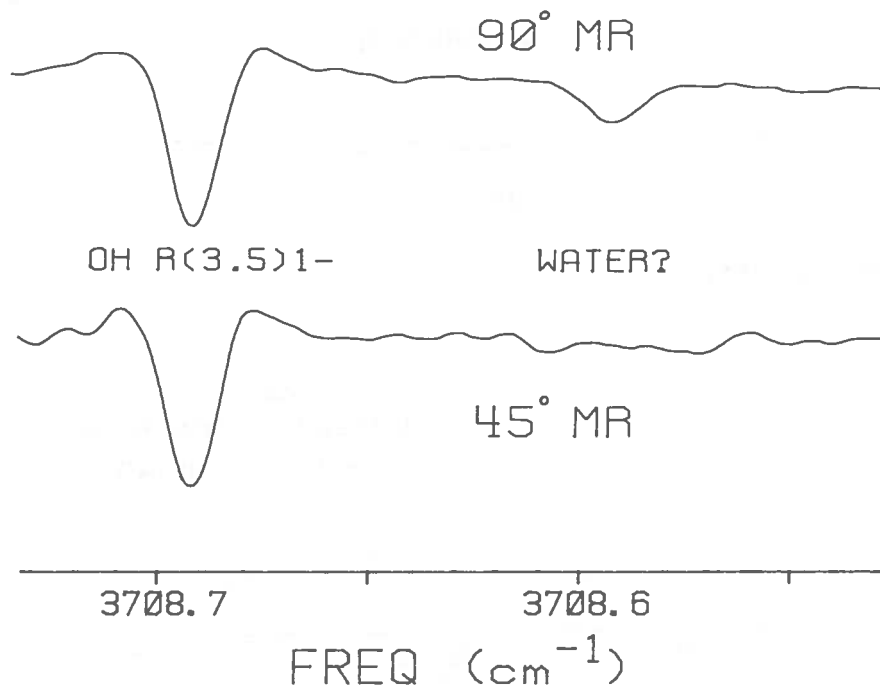


Fig. 5. Transient absorption spectrum of OH with the same preparation conditions as Fig. 3 recorded with magnetic rotation spectroscopy. In one trace the 90° magnetic rotation method was employed and in the other the 45° method. Note that the unidentified transient absorption of Fig. 3 is greatly reduced in relative intensity especially in the 45° method trace.

Summary

Infrared kinetic spectroscopy using a color center laser source and excimer laser flash photolysis has been demonstrated and should be a powerful means for observing a variety of free radical transient species. Expected absorptions are generally greater than 1% and a $S/N \sim 100$ has been demonstrated for 1% absorption. Magnetic rotation detection using the 45° method eliminates the major problem of interference arising from decreased precursor absorption on photolysis.

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