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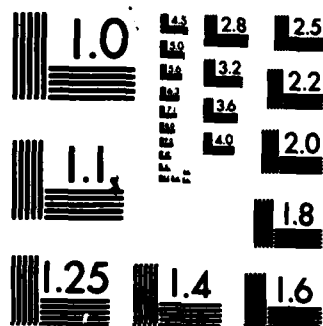
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A Laser Produced Plasma as a Pulsed Source of Continuum Infrared
Radiation for Time Resolved Absorption Spectroscopy

by

Arthur W. Adamson and Marc C. Cimolino

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**A Laser Produced Plasma as a Pulsed Source of Continuum Infrared
Radiation for Time Resolved Absorption Spectroscopy**

Arthur W. Adamson* and Marc C. Cimolino

**Department of Chemistry, University of Southern California, Los Angeles,
California, 90089-1062**

Abstract

The focussed beam from the 20 ns pulse of an amplified Nd glass laser produces a high temperature plasma in air or other media. Such plasmas, while well known as phenomena, seem not to have been investigated as a source of infrared radiation. We find the emission in the chemical infrared region, $2100\text{--}1700\text{ cm}^{-1}$, to be a continuum or white, and at least twenty five times more intense than that from a typical glow bar used in conventional infrared absorption spectroscopy. Emission from the plasma formed in air decays with a wavelength dependent lifetime, about 150 ns for the visible portion, and 2 μs for the infrared portion. When formed in argon, the plasma emission is more intense, and the decay time of the infrared emission rises to 4 μsec . Use of this source is demonstrated in a measurement of the carbonyl stretching absorption for W(CO)_6 and plans are to apply the method to the determination of infrared absorption spectra of thermally equilibrated excited states of organic molecules and of coordination compounds.

Introduction

It would be very desirable if ordinary infrared absorption spectra could be obtained for transient chemical species. As an example of interest to us, in both organic and inorganic photochemistry, the thermally equilibrated excited state is of major importance, particularly in solution systems. Such states, which we have called thexi states,¹ have all of the spectroscopic, thermodynamic, and kinetic types of properties that characterize ground state molecules. Knowledge of the structure and bonding of thexi states is of considerable potential importance to the understanding of their chemical and physical properties, yet virtually no direct information has been available. The traditional methods of infrared spectroscopy and of crystallography have not yet been applicable because of the short lifetimes involved, typically in the ns to short ms range. What bonding information that exists has been inferred from the vibrational structure of electronic absorption and emission bands.²⁻⁸ Also, excited state resonance Raman spectroscopy has provided useful although limited information.⁹

Excited state infrared (ESIR) spectroscopy seems not yet to have been reported, although infrared absorption spectra of photochemically produced ground state transient species have been obtained using a conventional glow bar source but with a fast detector;¹⁰ by means of rapid scan Fourier transform infrared spectroscopy;¹¹ and by means of an application of the stimulated electronic Raman scattering (SERS) effect.¹² What is needed for ESIR spectroscopy is a very bright (and therefore necessarily pulsed) source of continuum infrared radiation, and in the present paper we describe such a source and a first application of it.

The source is the plasma that is formed on focussing a pulsed laser beam. The plasma effect has been known for some time¹³⁻¹⁵ and has been

of interest to laser physicists in terms of the mechanism of its formation, the absorption properties of the plasma, and the nature of the emission in the visible and ultraviolet region. To the eye, a plasma appears (in air) as a blue-white spark or star of light; the temperature of a mature plasma has been estimated to be over 20,000 K.¹⁵

Plasmas have been proposed as continuum sources for ultraviolet and soft x-rays,^{16,17} and have been used for excited state absorption studies in the visible and near ultraviolet (Ref. 18, for example). There does not appear, however, to be any reports of measurements of the output of a laser produced plasma in the infrared region of chemical interest, 1300-2200 cm^{-1} , nor any exploration of the suitability as a possible continuum or white source for ESIR spectroscopy.

Experimental

The equipment block diagram is shown in Fig. 1. The exciting laser was a Q-switched doubly amplified Nd glass laser from Korad Co., which provides a 1060 nm, 20 ns pulse of 1-4 J in energy. To monitor either the pulse intensity or integrated energy, a portion was reflected by a glass plate onto a MgO surface viewed by a fast photodiode. The main portion of the pulse was focussed either in air or in a stream of argon, and gave a plasma about one cm long and somewhat oval shaped. An infrared mirror provided some focussing of the emission from the plasma onto the entrance slit of a Jarrell-Ash Monospec 18 1/8 m monochromator which has a grating suitable for the 2220-900 cm^{-1} region. The monochromator was argon flushed to avoid absorption effects due to water vapor. An infrared filter, of cut-off either at energies higher than 2500 cm^{-1} or 1700 cm^{-1} was used to take out radiation of overtone wavelength that might be passed by the monochromator. It was preceded by a Ge filter to cut out the visible and ultraviolet light from the plasma.

The (Hg,Cd)Te detector was selected for its rapid response and sensitivity in the chemical infrared region, and was a Judson Infrared model J15-D with a 4 mm square sensitive surface; it was supplied with an Irtran II window. Either of two pre-amplifiers were used: a model 000 of high impedance and high gain (signal/noise ratio of 2900), or a model 400 of low impedance and less gain (signal/noise ratio 1130). The detector was contained in a liquid nitrogen cooled model M-108 metal Dewar. Normally, both the output from the detector and from the photodiode were seen on a dual trace Tektronix model 7844 oscilloscope with 7A19 amplifiers, and a typical set of traces is shown in Fig. 2. In comparing results at different wavelengths, correction was made for the variation in detector sensitivity, using the manufacturers calibration. Successive points were also corrected for any variation in laser pulse energy from the photodiode reading.

A comparison of the intensity of the infrared output from the plasma was made with that from a standard glow bar source (from a Perkin Elmer Model 700 spectrophotometer), operated at 1500 K. The glow bar was mounted so as to be in the same position as the plasma, the rest of the detector train being the same. Since the glow bar is a continuous source, a Vincent Associates mechanical shutter was used to pass a 2 ms pulse. For these measurements, both the plasma and the glow bar intensities were measured using the high impedance amplifier, and a Tektronix storage oscilloscope.

The sample for the absorption measurements was a chloroform solution of W(CO)_6 (Strem Chemicals) contained in a 1.1 mm path length cell with NaCl windows. The comparison spectrum was obtained on a Perkin Elmer Model 281 instrument.

Observations and Conclusions

The intensity of the plasma emission decreased with decreasing wave-

number, as given in Table I. There did not appear to be any line emissions or singularities. The table also gives the corresponding intensities using the glow bar source and both sets of data show an intensity roughly proportional to the square of the frequency, as would be expected for black body emission. The peak intensities from the plasma were some twenty five times those from the glow bar source, however. This is probably a minimum ratio since the plasma source was not optimized. For example, a significantly higher intensity was obtained if the plasma were formed in argon rather than in air; other media were not tested. Also, an applied magnetic field could make important changes in the plasma characteristics.

Since the plasma is a complicated chemical and physical system, it was possible that the decay time of the output radiation would be wavelength dependent. This was indeed the case. The decay of visible light emission was measured by suitable positioning of the photodiode detector (with a filter to remove 1060 radiation), and was found to be essentially exponential over one or two half-lives, with a decay time of 155 ns. The output in the infrared region was again exponential in its decay, but now with the longer decay time of $2.2 \pm 0.2 \mu\text{s}$, with no significant variation over the $2200\text{-}1600 \text{ cm}^{-1}$ region. If the plasma was formed in argon, however, the decay time of the infrared emission increased to $3.8 \mu\text{s}$.

Finally, it was of interest to demonstrate that the plasma source could indeed be used to obtain an infrared absorption spectrum. Figure 3 shows the absorption in the carbonyl stretching region of W(CO)_6 as obtained in two separate point by point measurements using the plasma source, reported as absorbance, and with the maxima normalized. Our procedure was to measure at each wavelength the transmission of the sample cell and then that of the reference cell (solvent only). The two series of measurements

differed only in that in one case (open circles), the Ge filter was placed between the plasma and the sample cell, so that infrared radiation was passed, but not visible light. The sample was thus not subjected to possible photolysis by visible or ultraviolet light from the plasma. The peak absorbance is at $1990\text{--}1995\text{ cm}^{-1}$, as compared to the literature values of 1998 cm^{-1} in the vapor phase¹⁹ and 1986 cm^{-1} in *n*-hexane.²⁰ Our own spectrophotometric measurement in chloroform solution placed the peak at 1975 cm^{-1} ; this wavenumber is close to a grating change-over point, however, and there may have been a calibration error. A Perkin-Elmer polystyrene calibration standard correctly showed an absorption maximum at 1600 cm^{-1} both with the spectrophotometer and using the plasma source and associated monochromator (Fig. 1c).

Our results allow the following conclusions. A laser produced plasma is indeed a strong infrared emitter, the emission being essentially that of a black body continuum. The plasma source can be used to obtain absorption spectra on the long ns to μs time scale, and time resolved spectra could be obtained in this domain by suitable gating.

We plan to set up a detector array so as to be able to obtain complete spectra in a single pulse, and to proceed to investigate ESIR absorptions. For such, the laser pulse would be split, a portion being used to form the plasma and the remainder, to produce the excited state of interest. A first study might be with carbonyl complexes such as $\text{W}(\text{CO})_5\text{L}$, $\text{L} =$ 4-cyano pyridine, for which the thexi state lifetime ranges from 500 ns in solution to about $1.5\text{ }\mu\text{s}$ in the solid phase, at room temperature.²¹ Another candidate system would be $\text{Ru}(\text{bipy})_3^{2+}$ in solution or as a solid salt, for comparison with the reported excited state resonance Raman spectrum.⁹

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Table I

Intensity Measurements

Source	Wavenumber, cm^{-1}						
	2200	2100	2000	1900	1800	1700	1600
	Intensity, mV						
Plasma ^a	920(40)	860(10)	730(30)	680(30)	630(10)	505(10)	370(15)
Glow bar ^b	35	34	32	30	26	22	21

(a) Peak intensities for a plasma formed in air. Numbers in parentheses give the average deviation of duplicate or triplicate measurements. (b) Plateau intensity during the 2 ms open period of the mechanical shutter.

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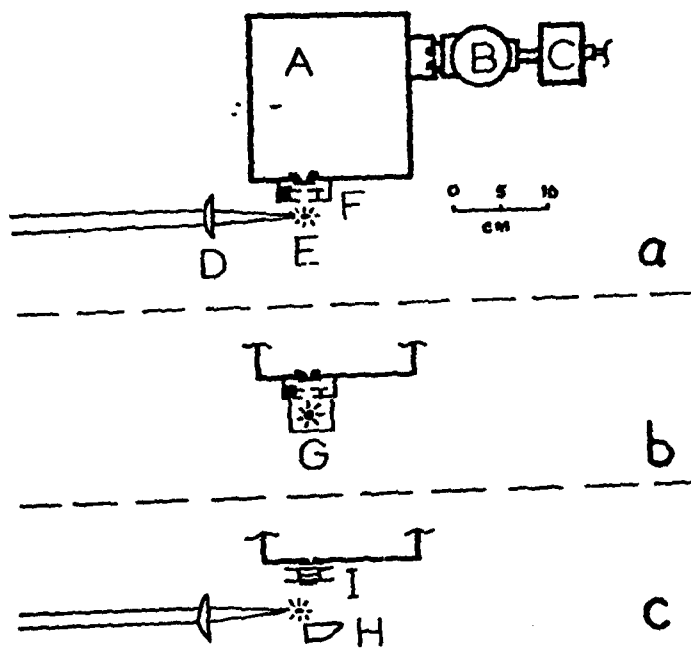
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Legends for the Figures

Figure 1. Apparatus block diagram. (a) A: monochromator; B: detector; C: pre-amplifier; D: focussing lens for the laser beam; E: plasma; F: mechanical shutter (kept open with the plasma source, but used with the glow bar source). (b) G: glow bar source in place of plasma source. (c) Arrangement for absorption spectroscopy. H: infrared reflector; I: sample cell.

Figure 2. Typical set of traces using the low impedance pre-amplifier. The sharp peak is the photodiode pulse (the points of zero time do not exactly correlate because of the nature of the triggering system).

Figure 3. Absorbance in the region of the carbonyl stretching frequency of W(CO)_6 in chloroform solution. Two separate runs.



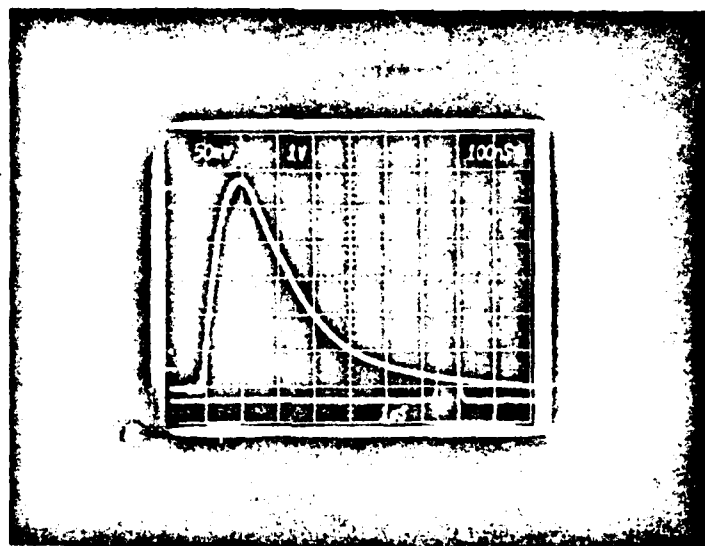
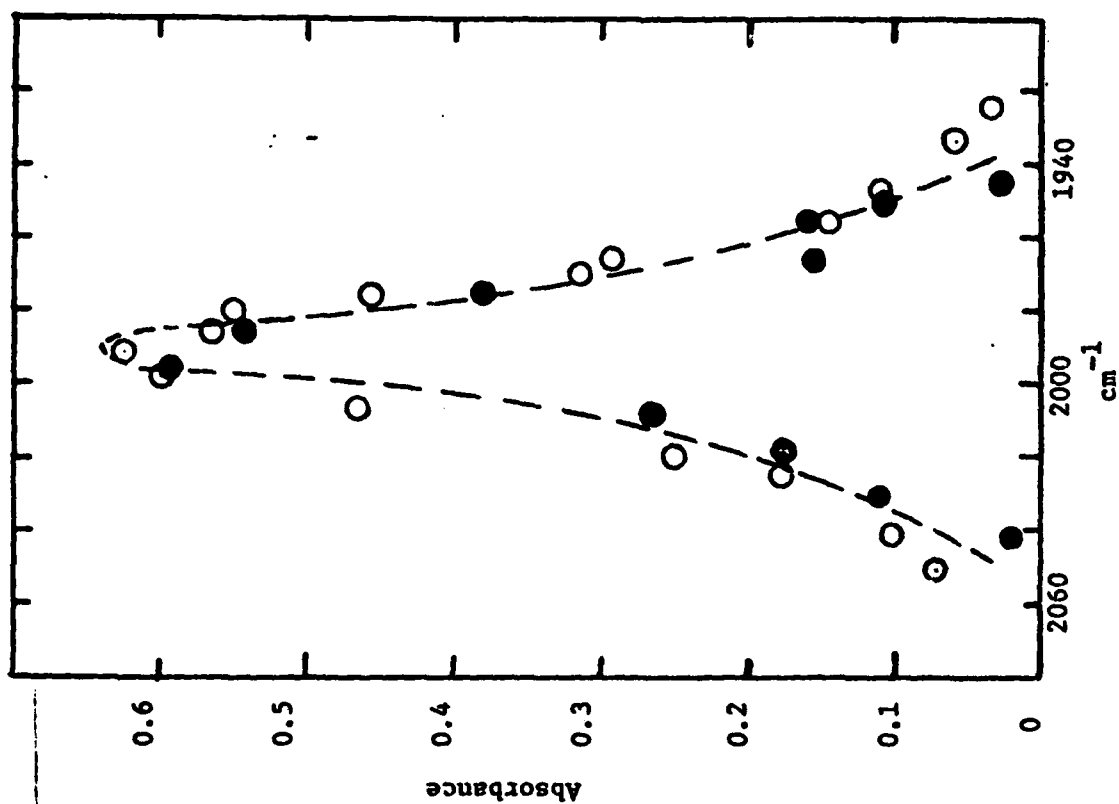


Fig 2

Fig 3



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