

Frequency Modulated Laser Transient Absorption Technique Dramatically Improves Radical Detection Limit in Shock Tube Studies.

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Absorption spectroscopy is the method of choice for many applications due to its near universal applicability and simple, easily quantified, line shape functions. Replacing a discharge or filament lamp in a classical absorption spectrometer with a narrow line tunable laser can in principle yield a huge improvement in absorption sensitivity. Until the laser line becomes narrower than the absorption feature, the amount of light absorbed in the sample depends linearly on the source brightness at the molecular absorption frequency and signal strength becomes much larger than detector noise. The theoretically attainable sensitivity, which is governed by the statistics of the electrons corresponding to the signal current and known as quantum, or “shot”, noise is however often masked by instabilities in the power of the probe laser. Even for a relatively quiet laser source, the amplitude variations can easily be 0.1% of the power. Detection of molecular absorptions that are much smaller than this level is difficult in the absence of some

special measures to correct for or eliminate it.

In 1994, the Gas Phase Molecular Dynamics (GPMD) group at Brookhaven National Laboratory, in collaboration with Professor Robert Field (MIT), demonstrated a new variant of laser frequency modulation spectroscopy which is specifically tailored to the detection of weak absorptions due to chemically reactive, short-lived, molecular species. Such species are important in combustion chemistry, among other fields, and the technique has been applied successfully by the BNL group in subsequent studies. With guidance from members of the

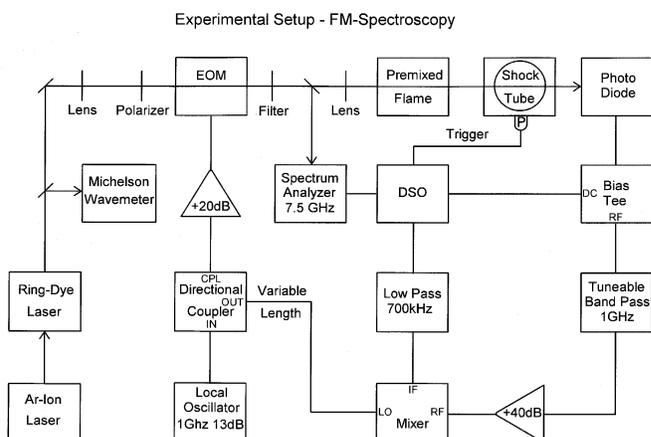


Figure 1 Block diagram of the FM absorption/shock tube apparatus at Göttingen. EOM=electro-optic modulator, DSO=digital storage oscilloscope. The premixed flame provides a steady state NH_2 absorption signal for wavelength calibration. (Reproduced by permission of Prof. H. Gg. Wagner)

GPMD group, other researchers around the world have begun to adopt the technique for their particular needs, and this report describes some exciting results obtained by Professor H. Gg. Wagner and his students at the University of Göttingen, Germany. The experiment at Göttingen uses a shock tube apparatus to measure the kinetics of chemical reactions at combustion temperatures. Figure 1 shows a block diagram of the experiment. NH_2 radicals were formed by the shock heating of hydrazine (NH_2NH_2) and their decay followed by FM laser transient absorption with a single pass (20 cm) of the probe laser beam through the heated mixture.

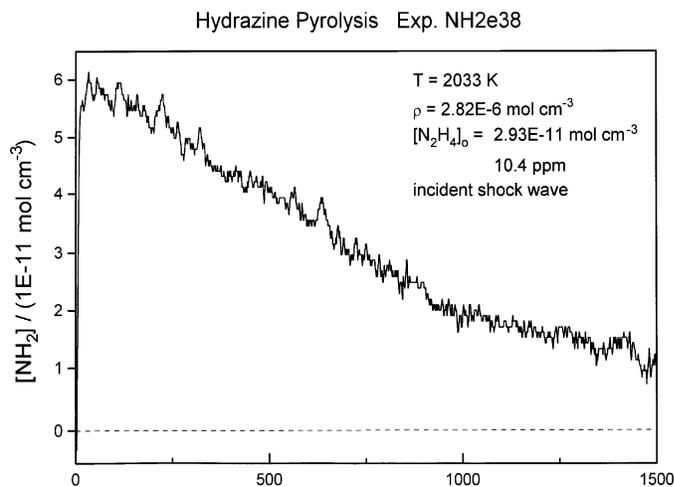


Figure 2 Experimentally measured decay of NH_2 radical concentration using the 597.375 nm NH_2 line and FM transient spectroscopy at 965 MHz. The horizontal scale is in μs . (Reproduced by permission of Prof. H. Gg. Wagner)

Figure 2 shows an example of the results at 2033 K. The initial concentration of NH_2 radicals was $3.5(3) \times 10^{13}$ molecules/cc. As Professor Wagner states “In summary, one can say that the detection limit for NH_2 is now one and a half orders of magnitude better than the reached detection limit with the normal difference method.” In addition, detection at high radio frequencies, in this case 965 MHz, results in a very stable measured base line for the experiments. Previously, acoustic noise and birefringence in the window materials resulting from the operation of the shock tube caused low frequency oscillations in the detected

signal at longer times, resulting in uncertainties in the decay measurements, and necessitating many more time-consuming experiments. Practically, the new results mean that more accurate measurements of the rates of reaction of NH_2 radicals at temperatures relevant to combustion systems will soon be available. In consequence, more reliable modeling of flame chemistry will be possible. Similar improvements are expected in the detection limit for CH_2 radicals at Göttingen, and the group at Stanford University lead by Professor Ronald K. Hanson is also working on the application of this method to shock tube measurements.

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