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A combined laser absorption and gas chromatography sampling diagnostic for speciation in a shock tube

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ABSTRACT

The first implementation of a combined laser absorption diagnostic/gas chromatography (GC) sampling system for the measurement of combustion-relevant species in a conventional shock tube configuration is reported, with ethylene pyrolysis as an example application. A heated, endwall sampling system is used to extract a post-shock sample for GC analysis. Analysis of the gas sample yields a measurement of the ultimate mole fraction values of multiple species (currently ethylene, acetylene, hydrogen, and methane) at the end of the reflected shock test time. A 10.532-μm laser absorption diagnostic is simultaneously used to measure time-resolved ethylene. A method to accurately model sampled speciation results using published kinetic models is discussed. A method for extending laser measurements into the expansion fan region for direct comparison with sampled GC results has also been developed. The combined optical and sampled-gas measurement techniques were used to study ethylene pyrolysis (1.0% mole fraction ethylene/argon) at approximately 5 atm, over a range of temperatures (1200–2000 K). The ethylene mole fraction measurements obtained using both techniques show close agreement.

1. Introduction

Modern chemical kinetic studies in shock tubes employ a variety of diagnostics to probe species concentrations in the high-temperature region behind reflected shock waves. Shock tube speciation techniques can broadly be divided into two categories: post-shock sampled and time-resolved *in situ* species measurements.

Common post-shock sample analysis methods include gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) [1–3]. In both techniques, a gas sample is extracted from the shock tube core after arrival of the expansion wave that quenches the reacting gases. GC analysis, which is of particular interest in the current work, allows for quantification of many different species relevant to combustion, including O_2, N_2, H_2, alkanes, alkenes, and aromatics like benzene and toluene, among others. Single-pulse, magic-hole style shock tubes, of the kind described by Hidaka et al. [1] and Lifshitz et al. [2], are typically preferred for sample-based diagnostics; the use of a dump tank weakens subsequent reflected shock and expansion wave events after the end of the test time, and can lead to higher quenching rates accompanying the arrival of the expansion wave.

Conventional shock tube configurations are often used in conjunction with time-resolved sampling methods or optical diagnostics to obtain species time-histories between the arrival of the reflected shock wave and the arrival of the expansion fan. Time-of-flight mass spectrometry (TOF-MS) is a particularly attractive speciation diagnostic, as it allows for time-dependent quantification of almost any stable species [4]. However, shock tube/TOF-MS test conditions are limited to near-atmospheric pressures due to the low-pressure requirement of the mass spectrometer ion source, and the measurements can suffer from limited temporal resolution and sensitivity. Optical diagnostics offer a non-intrusive, calibration-free alternative to sample-based species measurements. Laser absorption diagnostics, in particular, can be used to measure multiple hydrocarbon species at the same time, with superior time resolution, at a wide range of pressure and temperature conditions [5]. Absorption diagnostics are also particularly valuable because they can be used to measure time-histories of transient, radical species such as OH, CH, and CH_3, not just stable species. However, there is a limit to the number of species that can be measured simultaneously using optical diagnostics, and not all species relevant to combustion can be measured easily (e.g. H_2).

Due to the complementary nature of the data provided by the post-shock sampling and laser diagnostic speciation techniques, kineticists often use data obtained from multiple shock tubes with different diagnostic capabilities to gain greater insight into the pyrolysis or oxidation of a particular hydrocarbon fuel [6]. Less com-

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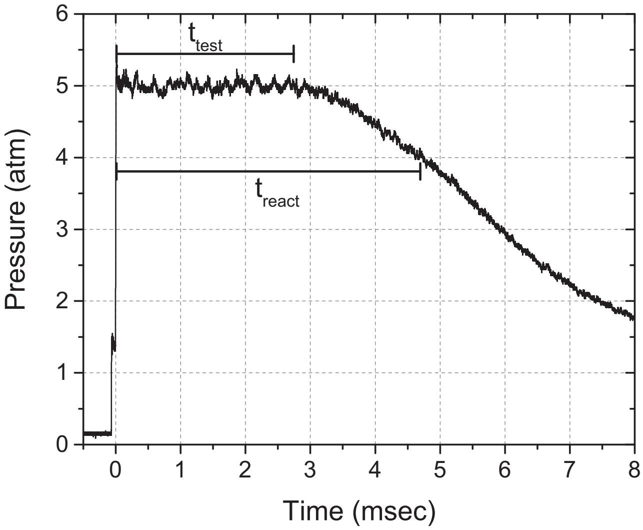

Fig. 1. A typical pressure trace, measured 2 cm from the shock tube endwall. Here, t_{test} is the duration of Region 5 (2.73 ms), and t_{react} is the effective reaction time (4.70 ms), as defined by Hidaka et al. [7]. Initial reflected shock conditions: 5.1 atm, 1602 K.

mon are experiments that combine both techniques. To the authors' knowledge, the first and perhaps only instance of a combined laser absorption/GC speciation experiment in a shock tube was conducted in 1985 by Hidaka et al. [1]. Even so, the experiments conducted by Hidaka et al. were distinctly different from those outlined here; the experiments were performed in a modified single-pulse shock tube with a piston, GC sample extraction was very delayed after the arrival of the expansion wave (20 s), and laser absorption measurements conducted at 3.39 µm only provided useful data for the first 300 µs of test time and were susceptible to interference absorbance. Modern laser diagnostics, such as the ethylene diagnostic described in this paper, are intentionally developed to isolate a single species and allow for its measurement, free from interference.

A challenge of particular interest to the shock tube community is how to best use experimental speciation data to guide development of, and validate results generated by, chemical kinetic models. Shock tube speciation measurements are typically compared to modeled results by supplying a mechanism solver with an initial temperature and pressure, specifying a constant-internal energy/constant-volume or constant-enthalpy/constant-pressure constraint, allowing the solver to step forward in time (iterating on solutions to energy conservation, mass conservation, and gas-phase chemical rate expressions), and finally extracting a species mole fraction value at a specified time. Comparison of laser-based, time-resolved diagnostics and kinetic model results is relatively straightforward. Typical laser measurements begin at "time zero" (arrival of reflected shock) and conclude at the end of Region 5 (the near-constant pressure region between time zero and the arrival of the expansion fan); this interval is commonly referred to as the "test time," t_{test}, of an experiment (see Fig. 1). The species time-histories obtained during the test time using laser diagnostics can be directly compared to the time-histories output by the model over the same time period. Sampling-based measurements, however, present a greater challenge.

Experiments utilizing GC sampling typically involve analysis of a sample that has been extracted from the shock tube after the test gas has been chemically frozen by the rapid cooling and expansion induced by the expansion fan. Experimentalists have long noted that this cooling occurs over a finite period of time, leading to the concern that reactions continue to take place during this quenching period [1,2,8]. However, it is thought that for reactions with sufficiently high activation energies (primarily reactions involving stable species), and experiments with sufficiently high quenching rates, the quenching period will have a negligible effect on the resulting stable species measurements obtained using the GC sampling technique [2,9]. To account for reactions that do continue to occur during the expansion fan, it is necessary to consider an effective reaction time, t_{react}, that extends beyond the experiment test time, into the expansion fan.

A common metric, originally proposed by Hidaka et al. [7], defines t_{react} as the time between the arrival of the reflected shock front and the point at which pressure has dropped to 80% of the reflected shock pressure, P_5 (see Fig. 1). Colket [10] was among the first to directly include quenching effects in chemical kinetic calculations by assuming an isentropic relationship between temperature and pressure and obtaining a temperature time-history from a recorded pressure trace. Tang and Brezinsky [9] employed a different approach, which requires use of a chemical thermometer to obtain an average temperature over the effective reaction time (as defined by Hidaka et al. [7]), and allows for the back-calculation of an initial T_5 temperature, $T_{5,\ init}$, and a time-resolved temperature time-history. A major constraint associated with using a chemical thermometer to back-calculate $T_{5,\ init}$ is the need for a highly dilute test gas mixture to ensure isothermal conditions for the duration of the test time. Additionally, if an average temperature is used to describe the effective reaction time, the quenching rate must be sufficiently high to ensure that the temperature time-history is dominated by the intended test conditions, not the quenching period. For highly dilute, single-pulse shock tube experiments, it has been found that satisfactory modeling of post-shock GC measurements can be achieved by assuming constant-temperature, constant-pressure conditions and extending the plateau values out to the time at which the pressure would have otherwise dropped to 80% of its maximum plateau value [9].

An inherent requirement of laser diagnostic measurements, however, is the need for sufficient fuel concentration to allow for detectable changes in light intensity due to absorbance. As a result, the typical method used for modeling iso-thermal, iso-baric, highly dilute shock tube experiments cannot be used, and a different methodology must be applied to model the experimental results obtained using the combined diagnostic.

Presented here is an accurate method for accounting for the quenching period in chemical kinetic simulations, one that utilizes a measured pressure trace to obtain a model-derived temperature time-history to more accurately simulate the time-evolving thermodynamic conditions experienced by the test gas. Additionally, despite widespread usage of the "80% of P_5" effective reaction time metric, it will be shown that a universal, pressure-based metric for determination of effective reaction time is not appropriate for all chemical kinetic studies, particularly those involving test gas mixtures that are not highly dilute and those performed in conventional, non-single-pulse shock tubes.

Despite the wealth of literature containing comparisons of GC speciation measurements to chemical kinetic model results and the associated methods for doing so, there is a relative dearth of literature on how best to compare GC speciation measurements to time-resolved speciation results obtained using diagnostics typically employed before the arrival of the expansion fan.

The purpose of this paper is therefore twofold: (1) to present a novel speciation diagnostic that combines GC sampling with a time-resolved, laser-based ethylene measurement in a single conventional shock tube experiment; and (2), to outline a methodology for accurately comparing GC speciation measurements to kinetic model results, as well as a methodology for accurately comparing GC speciation measurements to laser measurements in non-highly dilute experiments. The subsequent sections of this paper

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