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T-Jump/time-of-flight mass spectrometry for time-resolved analysis of energetic materials

Lei Zhou, Nicholas Piekiel, Snehaunshu Chowdhury and Michael R. Zachariah*

Department of Mechanical Engineering and Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

We describe a new T-Jump/time-of-flight (TOF) mass spectrometer for the time-resolved analysis of rapid pyrolysis chemistry of solids and liquids, with a focus on energetic materials. The instrument employs a thin wire substrate which can be coated with the material of interest, and can be rapidly heated (10^5 K/s). The T-Jump probe is inserted within the extraction region of a linear TOF mass spectrometer, which enables multiple spectra to be obtained during a single reaction event. By monitoring the electrical characteristics of the heated wire, the temperature could also be obtained and correlated to the mass spectra. As examples, we present time-resolved spectra for the ignition of nitrocellulose and RDX. The fidelity of the instrument is demonstrated in the spectra presented which show the temporal formation and decay of several species in both systems. The simultaneous measurement of temperature enables us to extract the ignition temperature and the characteristic reaction time. The time-resolved mass spectra obtained show that these solid energetic material reactions, under a rapid heating rate, can occur on a time scale of milliseconds or less. While the data sampling rate of 10 000 Hz was used in the present experiments, the instrument is capable of a maximum scanning rate of up to ~30 kHz. The capability of high-speed time-resolved measurements offers an additional analytical tool for the characterization of the decomposition, ignition, and combustion of energetic materials. Copyright © 2008 John Wiley & Sons, Ltd.

We report on a new time-of-flight mass spectrometry (TOFMS) electron ionization (EI) source that can obtain time-resolved mass spectra during the ignition of energetic materials. The unique feature of this instrument is (1) implementation of TOFMS/EI with a Temperature Jump (T-Jump) technique to monitor highly reactive condensed-state samples at high heating and decomposition rates, and (2) measurement of the chemistry in a bimolecular gas-phase-free kinetic environment. Due to its low detection limits and fast time response, the instrument developed here allows for a time-resolved characterization of the decomposition, ignition, and combustion of solid energetic materials.

Quantitative measurement of condensed-phase reaction kinetics is usually performed using conventional thermal analysis techniques[1] such as TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry). However, those methods fail in the measurement of fast chemistry processes such as rapid thermal decomposition, ignition and combustion of energetic materials where high heating rates are involved. It is known that the high heating rates in those processes are critical and must be attained in order to study rapid condensed phase reactions.[2–4] In recent years, many experimental diagnostic methods have been developed to characterize rapid reaction

processes.[1,5–12] In particular, T-Jump/FTIR (Fourier transform infrared) spectroscopy was developed to study the reaction kinetics of condensed-phase propellants.[2,13] In T-Jump/FTIR spectroscopy the sample is placed on a Pt filament and rapidly heated to a chosen temperature, and the gaseous species are detected and quantified using FTIR spectroscopy. The thermal decomposition behavior of numerous energetic materials under isothermal conditions has been studied using this technique.[14–16] However, for rapid condensed-phase reactions, especially those associated with an ignition event, the relevant time scale can be of the order of milliseconds or less. The low scanning rate of the IR spectrometer greatly limits the application of T-Jump/FTIR spectroscopy in characterizing ignition, and combustion.

Mass spectrometry (MS) is widely used to study condensed-phase reactions.[11,17] For decades, MS alone or MS used in conjunction with other techniques has become a powerful tool for thermal analysis.[9,18–23] Blais and co-workers developed a TOFMS/EI apparatus capable of measuring the intermediates and products of chemical reactions from detonation of explosives.[9,24] The decomposition of thermite-based aluminum/iron(III) oxide energetic material was also studied using matrix-assisted laser desorption/ionization (MALDI)-TOFMS, and the products of laser-initiated thermite reactions were identified.[25,26] Time-resolved measurements for condensed-phase reactions have also been conducted using MS techniques. Dauerman and co-workers developed a scanning sector mass spectrometer, which directly attaches to a low-pressure strand burner, to study the thermal decomposition and combustion

Correspondence to: M. R. Zachariah, Department of Mechanical Engineering and Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA.
E-mail: mrz@umd.edu

of nitrocellulose.[8,21] The sample is heated by exposure to the radiation of an arc image furnace and the gaseous species as well as the surface temperature are continuously analyzed by a mass spectrometer and thermocouple as a function of time. Behrens developed a thermogravimetric modulated beam mass spectrometer that combines thermogravimetric analysis, differential thermal analysis, and modulated beam mass spectroscopy. This instrument is capable of quantitative measurement, and has been used to study the thermal decomposition mechanisms and kinetics of many compounds.[27–29] Korobeinichev and co-workers developed a pulse heated mass spectrometer to study the high-temperature decomposition of ammonium perchlorate.[30]

Common to all these methods has been that the studies were conducted at either slow heating rate, e.g. the thermal decomposition took place in minutes, or the mass spectrometer sampling rates were slow, e.g. ~0.1 s. Recently, confined thermolysis FTIR spectroscopy with a TOFMS system has allowed the study of the gaseous products from a high-pressure thermolysis chamber.[31] Although the time resolution of the mass spectra measurement can be ~1 ms, the system time response is limited by the slow sampling rate of the FTIR probe.

Despite the many efforts directed to characterizing condensed-phase reactions, time-resolved characterization of very rapid condensed-phase reactions, particularly those associated with ignition and combustion, has proved to be a formidable task. These processes where the heating rates are usually of the order of 10^3–10^6 K/s are beyond the limit of current thermal analysis techniques.[7,32]

One additional consideration is that for many of the MS and FTIR studies, experiments were conducted in an open tube condition, such that much of the chemistry occurred in the gas phase. However, to gain a mechanistic understanding one would like to separate the condensed- and the gas-phase contributions. Thus, in order to understand the decomposition mechanism or the combustion process of energetic materials, it is necessary to separate the primary and secondary processes, and to investigate the condensed-phase reaction under rapid heating conditions.

Our objective in developing the T-Jump/MS system was first to be able to characterize chemistry under high heating rate conditions (i.e. fast chemistry), and second to conduct the experiments under conditions where the secondary gas-phase chemistry can be minimized. In the former case high heating rates correspond more closely to the environment usually encountered by energetic materials but more profoundly one should expect reaction channels to increasingly favor the higher activation channels possessing the lowest entropy constraints. The latter emphasis on minimizing gas-phase chemistry eliminates the possibility of a bimolecular gas-phase reaction and probably much unimolecular decomposition. As a result the rapid pyrolysis of energetic materials in vacuum should be dominated by condensed-phase reactions, which should ultimately allow for a more direct probe of condensed-phase chemistry. The essence of the experiment is that the T-Jump probe is directly inserted into the electron ionization chamber of the mass spectrometer, and the species from T-Jump excitation are monitored by the TOF mass spectrometer continuously. The

time-resolved mass spectrometric capabilities of the instrument enable the characterization of rapid condensed-phase reactions, which should provide an insightful complement to conventional thermal analysis. The purpose of this initial paper is to describe the operation and capabilities of this new instrument.

EXPERIMENTAL

EI/TOF mass spectrometer
The EI/TOF mass spectrometer is comprised of a linear time-of-flight chamber, adapted from a previously developed single particle mass spectrometer,[11,33] and includes an electron gun for ionization, and the T-Jump probe with an electrical feedthrough, as shown in Fig. 1. The sample loading chamber is separated from the ionization chamber by a gate valve, which enables the T-Jump probe to be rapidly changed without the need to break vacuum in the TOF chamber. An electron gun (R. M. Jordan Co., Grass Valley, CA, USA) is mounted between the extraction plates of the TOF, and perpendicular to the orientation of the T-Jump probe. The electron beam is nominally operated at 70 eV, and 1 mA, with the background pressure in the TOF chamber at ~10^{-7} Torr.

T-Jump sample probe
For the T-Jump probe we have primarily used a 76 μm diameter platinum wire, with a total heated length of ~1 cm, which is replaced after each heating event. In each experiment, the wire is either coated with a thin layer of sample powder in the case of particulates, or solution-dipped to prepare organic coatings. Using an in-house built power source, the heating rate of the T-Jump probe can be varied by changing the pulse voltage or pulse width, at a rate of up to ~5×10^5 K/s for the present filament configuration.

Control and data acquisition system
The schematics of the control and data acquisition system for the T-Jump/TOF mass spectrometer are shown in Fig. 2. The
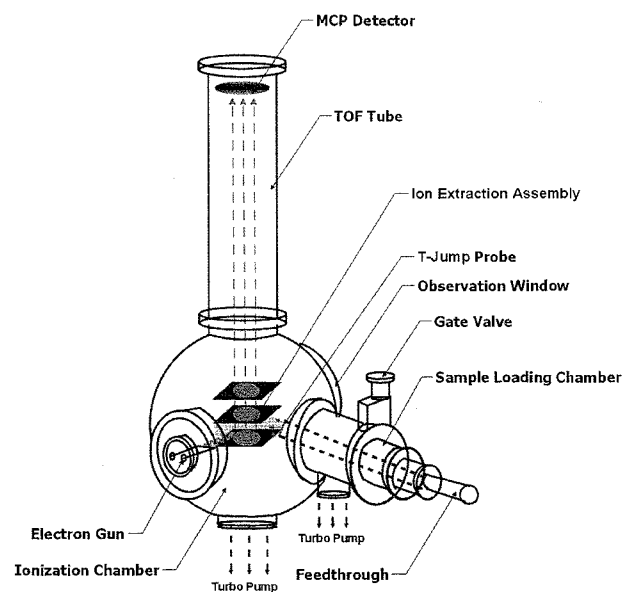
Figure 1. Schematic of the T-Jump/TOF mass spectrometer.
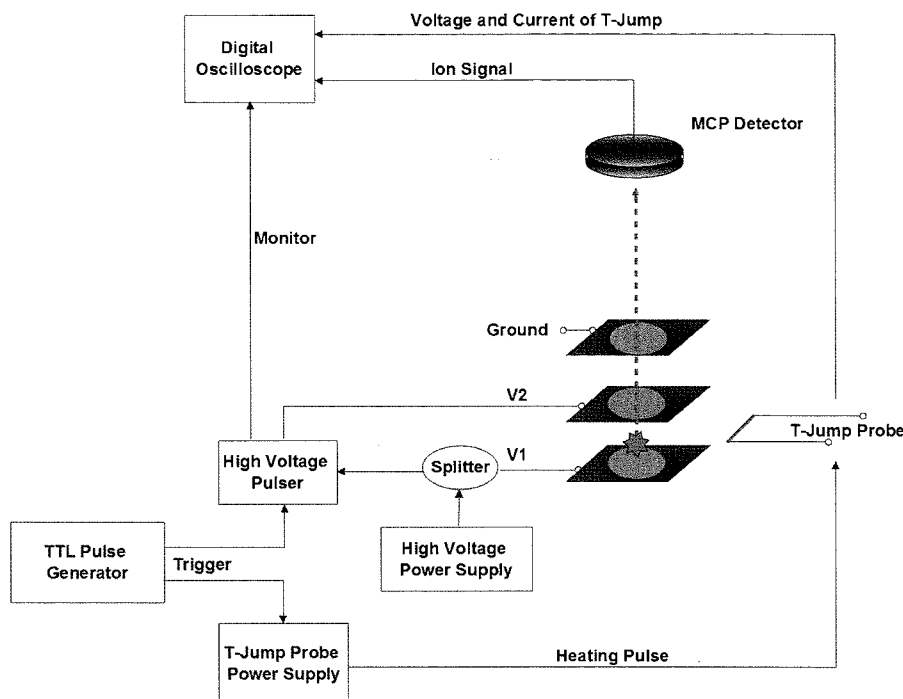
Figure 2. Schematic of the control and data acquisition system for the T-Jump/TOF mass spectrometer.

present design is based on a previously developed single particle mass spectrometer which is configured for a standard laser ionization source.[11,34] To ensure a field-free region for electron ionization, one direct current (DC) high-voltage power supply is used with a 'T' splitter to bias both the repeller plate and the extraction plate (V1 and V2 shown in Fig. 2). In the presence of a field-free region, electrons are injected between the plates and ionization takes place. After a predetermined ionization period the voltage on the extraction plate is changed by a high-voltage pulser, to create the field for an ion extraction region between the plates. The extracted ions drift in the linear TOF tube, and are counted at the MCP (microchannel plate) detector. Following the ion extraction period, the voltage on the extraction plate is pulsed back, and a new ionization period begins. Serial pulses generated from a pulse generator (DG535; Stanford Research Systems Inc., Sunnyvale, CA, USA) are used to trigger the high-voltage pulser so that the ionization and extraction processes occur continuously. The pulse timing sequence of the high-voltage pulse is also traced from the monitor signal output of the high voltage pulser. Both the detector signal and the monitor signal are recorded with a 500 MHz digital oscilloscope and transferred to a PC for further analysis.

The heating of the T-Jump probe is also synchronized with the TOF measurement system by triggering the probe power supply from the pulse generator as shown in the timing sequence diagram. (There is ~2 μs delay between trigger and monitor signal; for illustration purposes, we show them as the same pulse in Fig. 3.) The temporal voltage and current of the T-Jump probe during the heating event are recorded, so that a resistivity measurement can be obtained, and related to the instantaneous temperature, which can be mapped against the mass spectra.

RESULT AND DISCUSSION

Before testing the T-Jump/TOF mass spectrometer, heating experiments were conducted by heating an uncoated wire to evaluate the performance of the T-Jump probe. The heating rate of the probe can be varied by changing the heating pulse width and the output pulse intensity. The pulse width can be varied from ~1 ms to ~100 ms, with a maximum output voltage of ~50 V. Figure 4(a) shows a typical current, voltage trace, while Fig. 4(b) shows the resulting temporal temperature of the platinum wire. Since the rise time of the heating pulse is in the range of 10 to ~100 μs, depending on the output pulse voltage, the resistance and the corresponding temperature are calculated after the rise time of the heating pulse. Thus the filament temperature is estimated to be ~400 K initially, and it reaches ~1800 K after 2.5 ms; i.e. a heating rate ~640 000 K/s.

Another important factor to consider in the design of the T-Jump/TOF mass spectrometer is the nature of the ion extraction in the presence of the T-Jump probe. The nominal configuration of the ion extraction electrode assembly ensures a uniform extraction field between the plates.[34] However, the presence of the probe and, in particular its location, were found experimentally to be sensitive to both signal sensitivity and resolution. One might reasonably expect that placing the probe too close to the extraction plates would distort the electric field, and result in a decrease in the mass spectrometer resolution. Placing the probe too far away from the ionization region would lower the concentration of reaction product species in the ionization region, and consequently decrease the sensitivity of the measurement. The effect of the T-Jump probe position was examined experimentally by inserting the probe at different distances from the plates, and monitoring the ion signal from the
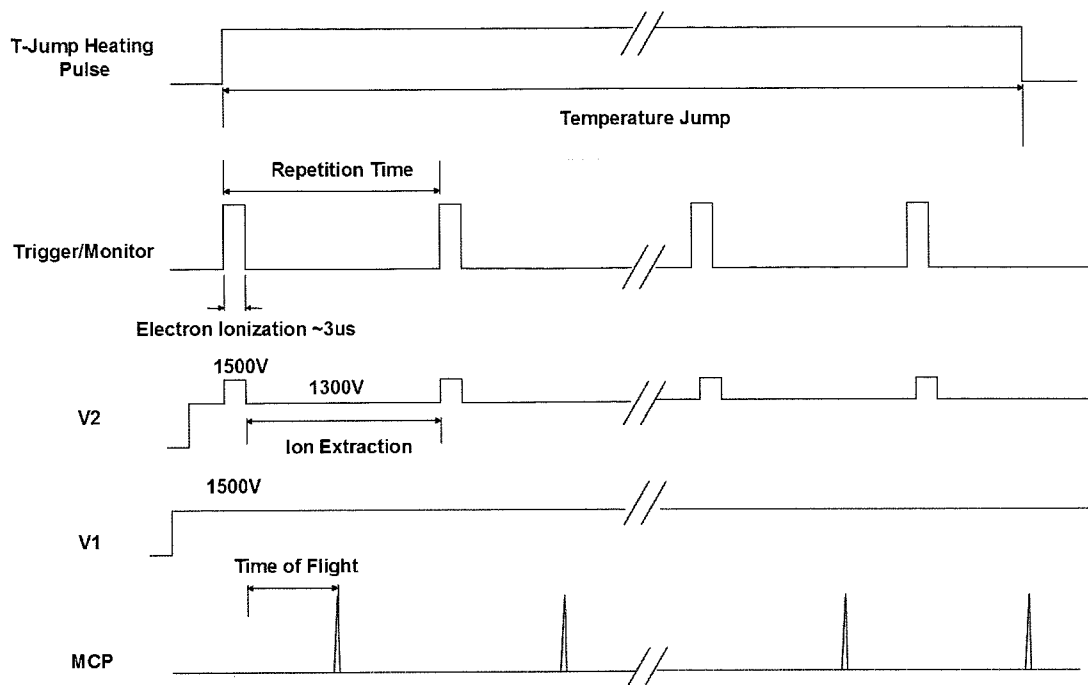
Figure 3. Pulse sequence used for electron ionization and ion extraction in the T-Jump/TOF mass spectrometer.

(a)

(b)
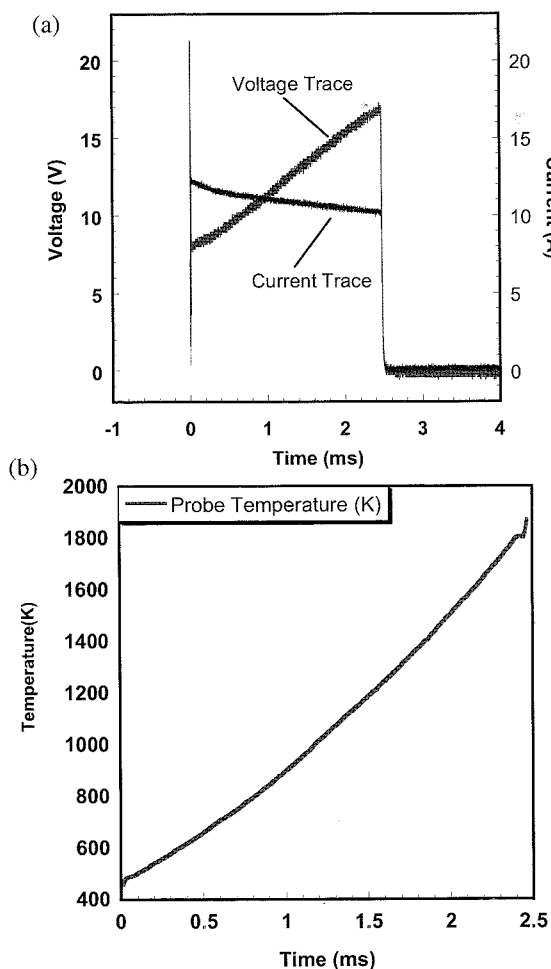
Figure 4. (a) Voltage and current across the T-Jump probe. (b) Estimated probe temperature from electrical resistance. This figure is available in color online at www.interscience.wiley.com/journal/rcm.

background gas. The relative water (H_2O) ion signal intensities are plotted in Fig. 5(a) as a function of probe position. Each experimental data point is an average of 40 mass spectrum measurements, and normalized by the ion intensity measured without the presence of the T-Jump probe. As a comparison with the experimental data, the effect of the T-Jump probe on the electric field and ion detection was also evaluated by conducting ion-trajectory simulations using Simion.[35] In the simulation, water ions with +1 charge were placed in the center plane of the ion extraction region with a uniform distribution, and their flight trajectories were calculated for the voltages used in the experiment. The relative ion abundance calculated from trajectory simulation is also plotted as the function of probe position in Fig. 5(a). Both the simulation and the experimental data show that the ion signal is significantly decreased when the probe is placed close to the extraction plates. As the probe moves away from the plates, the ion signal increases, and reaches a plateau at a distance of 1.3 cm, suggesting that the presence of the grounded probe significantly perturbs the electric potential in the ion source region. Figure 5(b) shows the calculated electric potential and ion trajectories for the T-Jump probe placed 1.3 cm from the ionization region. When compared with the no-probe case in Fig. 5(c), it is clear that the probe induces considerable distortion to the electric potential and ion trajectories in the region closest to the T-Jump probe, but very little change for the ion trajectories in the central region. As we move the probe further away from the ionization region, although the effect of the probe on the electric field is minimized, a slight decrease of the ion signal in the experimental data was observed. This implies that at larger distances sensitivity will be lost for material originating from the probe and that a distance 1.3 cm seems to be near optimal for this system.

(a)

(b)

(c)
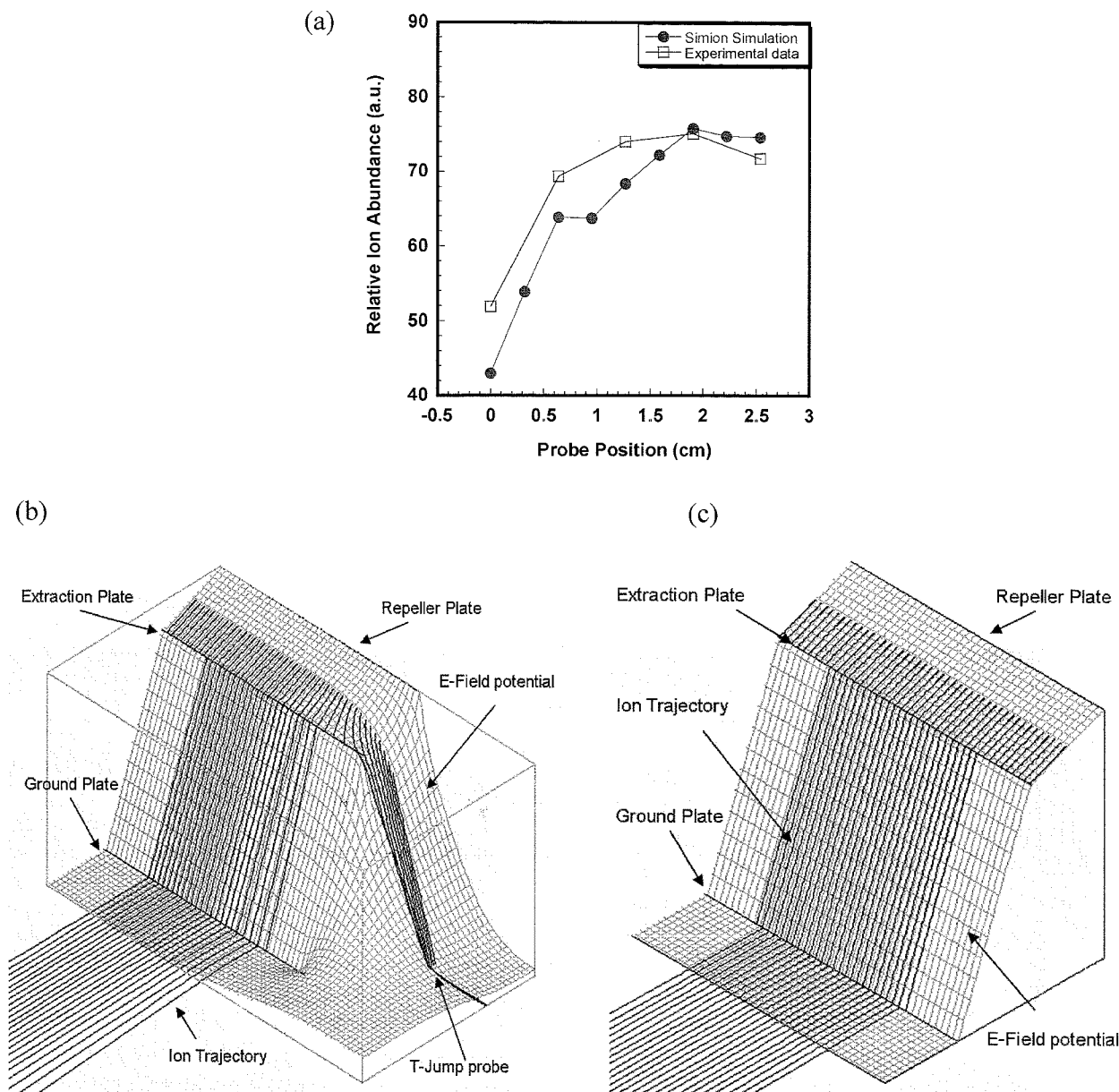
Figure 5. (a) Relative water ion abundance as a function of the probe filament position. (b) Ion trajectory and electric potential at ion source region with the presence of the T-Jump probe. (c) Ion trajectory and electric potential calculation at ion source region without the probe. This figure is available in color online at www.interscience.wiley.com/journal/rcm.

Nitrocellulose and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) samples were used to test the performance of the T-Jump/TOF mass spectrometer as examples of a slow and a fast 'burner'. In these experiments, nitrocellulose (Mallinckrodt Baker Inc., Phillipsburg, NJ, USA) or RDX was mixed with diethyl ether or acetone, and a small amount of solution (~7 mL) was coated on the T-Jump filament surface using a dropper. While the eventual goal of this instrument is to use the temporal mass spectra, and the temperature, to extract mechanistic information, the purpose of the present study is to focus on illustrating the capabilities of the instrument.

The mass spectra obtained for rapid pyrolysis of nitrocellulose are shown in Fig. 6. The heating duration is about 9 ms with a heating rate of $\sim 1.3 \times 10^5$ K/s, with a total of 95 spectra sampled with a temporal resolution of 100 μs

per spectrum (10 000 Hz). Of the 95 spectra obtained in the experiment, we plot 17 of them in Fig. 6, along with a more detailed view of a spectrum at t = 2.5 ms. Since the heating pulse is synchronized with the first EI duration, the mass spectrum at t = 0 ms is actually the background in the ion source region, which consists of water (m/z 18), N_2 (m/z 28), N (m/z 14), OH (m/z 17), O_2 (m/z 32), and H (m/z 1). We sampled up to m/z ~300 for each spectrum, but no high-mass ions were observed, and major ions are only seen for m/z <100. At t = 1.7 ms, the estimated temperature of the probe is ~575 K, and a new ion of m/z 31 appears which suggests the start of the reaction. At t = 1.8 ms, which corresponds to a probe temperature ~590 K, the ion signal intensity of m/z 31 increases along with that of the ions at m/z 15, 27, 29, 45 and 59. As the reaction time advances to t = 1.9 ms (T ~ 600 K), the ion at m/z 31 achieves its maximum intensity, and now ions at
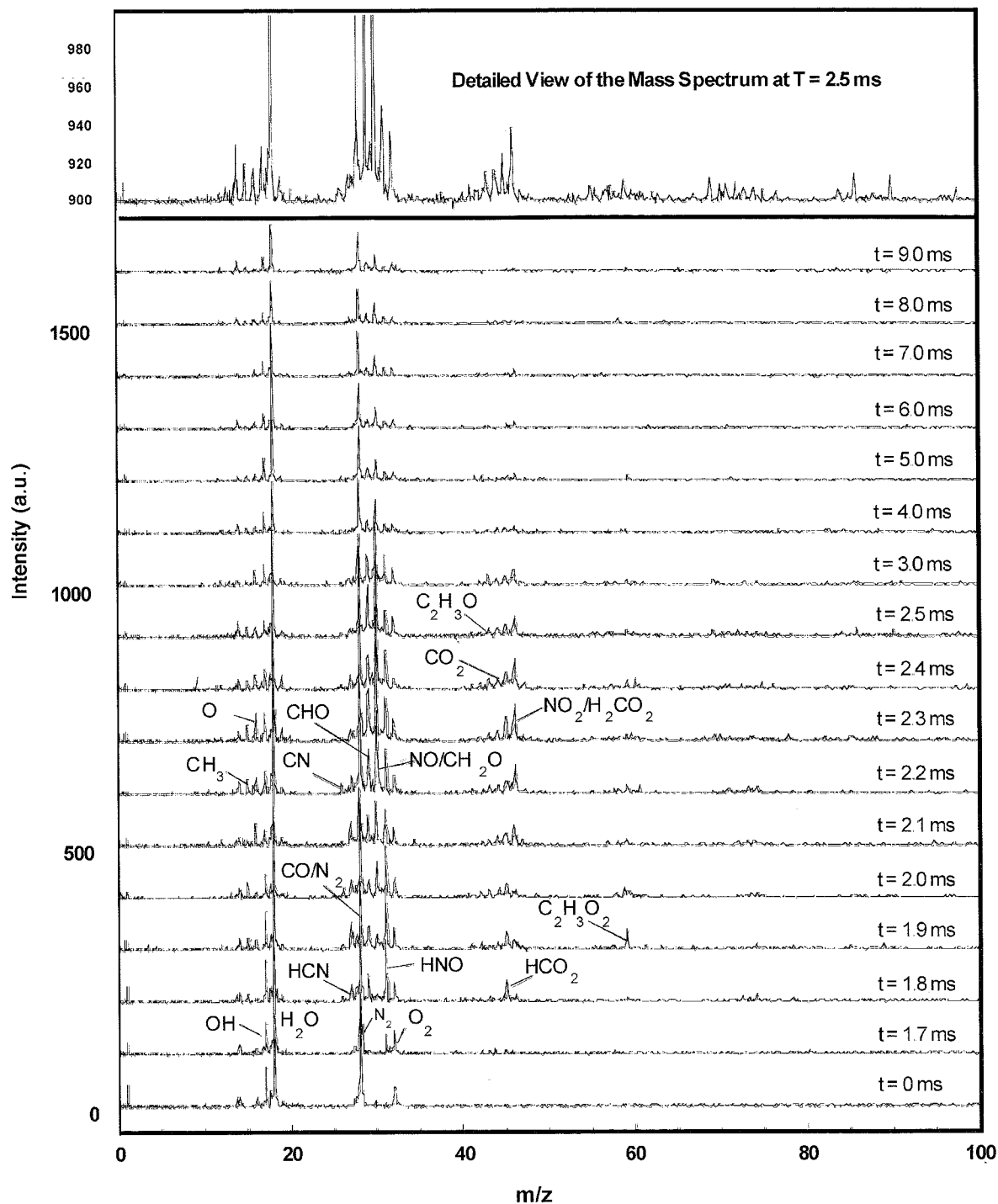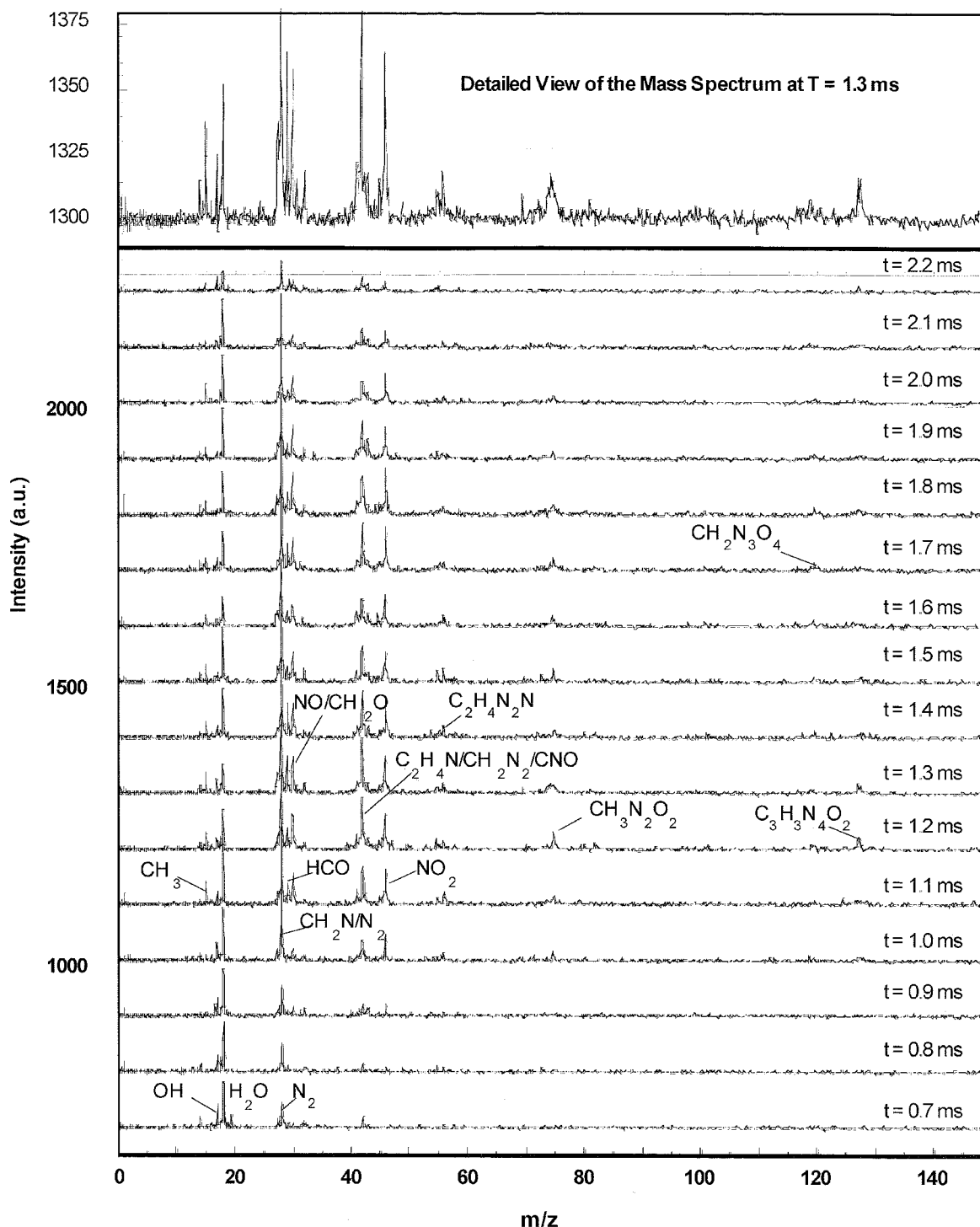
Figure 6. Time-resolved mass spectrum from rapid heating of nitrocellulose. Heating rate $\sim 1.3 \times 10^5$ K/s.

m/z 30 and 46 appear, along with those at m/z 16, 43 and 44. These species last for the whole duration of the heating pulse ($\sim$9 ms), and some species are still present well after the end of the wire heating pulse due to the self-burning of nitrocellulose. The time-resolved feature of the spectra allows us to extract the characteristic time of the reaction. As the highest ion intensities for most of major ions were achieved at $t = 2.3$ ms, following which the ion signals gradually decrease with no noticeable changes after 4 ms, it is suggested that the most aggressive reaction (ignition) happens within $\sim$4 ms, and that the whole reaction lasts

$\sim$9 ms. We compare our results for nitrocellulose thermal decomposition with experiments done at lower heating rates. Chen and co-workers used a SMATCH (Simultaneous MAss and Temperature Change)/FTIR system to examine decomposition products of a nitrocellulose film heated at a rate of up to 320°C/s. The reaction products are noted as NO, CO, CH_2O, CO_2, HCOOH and NO_2,[36] which we also see, although we are unable to distinguish HCOOH from NO_2. It should also be noted that although m/z 28 is part of our background signal of N_2, there is a significant increase for this ion during the heating event, which can probably be

Figure 7. Time-resolved mass spectrum from rapid heating of RDX. Heating rate $\sim 1.5 \times 10^5$ K/s.

attributed to the presence of CO. We can also compare our results with the work of Dauerman and co-workers who used a mass spectrometer paired with a low-pressure strand burner to examine nitrocellulose combustion.[21] Their work shows multiple spectra at different times during heating, which include significant ions that are consistent with our work. The major ions cited are m/z 14, 15, 16, 17, 18, 27, 28, 29, 30, 31, 43, 44, 45 and 46, which are all seen in our experiment except for m/z 14, 17 and 18. We are currently continuing our studies in developing a mechanism and its comparison with theoretical work by Melius and colleagues which suggests

possible condensed-phase initial reaction steps in nitrate ester decomposition.[37] The reaction pathway shows consistencies with our findings, and will be more fully addressed in a future publication.

RDX was used as a second example to test the T-Jump/ TOF mass spectrometer. RDX decomposition has been the subject of investigation under different conditions. Behrens and co-workers have studied RDX decomposition using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS).[27,38,39] The STMBMS results provide detailed information about both the mechanisms and

rates of reaction of RDX decomposition at a low heating rate ($\sim$1 K/min). The combustion-like decomposition of RDX has been studied using a T-Jump/FTIR method[2–4,13,16,40] with a heating rate at $\sim$10^3 K/s. In our experiments, a heating rate of $\sim$10^5 K/s was used to study the ignition and combustion of RDX. Similar to the nitrocellulose experiment, we use a sampling rate of 100 μs per spectrum (10 000 Hz) to capture the progress of the reaction. The heating pulse is about 8 ms at a heating rate of $\sim$1.5 $\times$ 10^5 K/s, and 95 spectra are obtained. Figure 7 shows that species, other than background species (water/N_2/O_2), only appear from 0.7 ms to 2.6 ms, which corresponds to a wire temperature of 370K to 670K. These results clearly show, as expected, that RDX is more reactive than nitrocellulose, and occurs over an interval of only $\sim$2 ms. Although a mass range up to m/z 400 was recorded for each spectrum, no ions were observed above m/z 150. The major ions from RDX decomposition observed are m/z 15, 28, 29, 30, 42, 46, 56, 75 and 127. Less abundant ions of m/z 14, 16, 41, 43, 81 and 120 are also found in some spectra. The RDX mass spectra in terms of the m/z values of the ions observed and their most likely structures are listed in Table 1. Similar to what is found with the T-Jump/FTIR method,[2–4,13,16,40] NO_2, CH_2O, NO, CO and HNCO are also observed by our T-Jump/TOF mass spectrometer. Using gas-phase CO_2 laser photolysis of RDX, which provided extremely high heating rates, Zhao et al. observed ions at m/z 42, 56, 75, 81, 120 and 127, which we also see in our experiments.[41] However, HONO, HCN and N_2O which are reported in both the T-Jump/FTIR and the gas-phase infrared multiphoton dissociation experiments were not detected under our conditions. The differences point to the complex nature that heating rate and ambient environment may play in probing the decomposition pathways. For example, it is believed that two global reactions are responsible for the decomposition of RDX under flash heating condition.[13,40] The reaction channel which leads to the formation of N_2O is dominant at lower temperatures, while the reaction channel to NO_2 is favored at higher temperatures. Our heating rate is much higher than that employed in the T-Jump/FTIR experiments ($\sim$10^5 K/s vs. $\sim$10^3 K/s) so it is possible that the chemistry is dominated by the NO_2 channel and that N_2O formation is not favored under these conditions. Moreover, as one of the motivations in developing this T-Jump mass spectrometer was to minimize or eliminate the gas-phase chemistry, the failure to detect species such as HCN and HONO and possibly N_2O suggests these may be formed primarily in the gas phase.

Since the purpose of this paper is to demonstrate of the operation and capabilities of the instrument, we defer further analysis of the rates of reactions and mechanisms to the future. Based on the experimental results presented above, it is clear that the characteristic reaction time for decomposition/combustion of energetic materials is of the order of milliseconds or even less. We note that while a time resolution of 100 μs was used to test and demonstrate the instrument, the T-Jump/TOF mass spectrometer can be operated with a scanning rate up to $\sim$30 kHz. The experimental results suggest that the time-resolved spectra obtained using the T-Jump/TOF mass spectrometer should have sufficient sensitivity and time resolution to probe the reaction dynamics of extremely fast condensed-state reactions at high heating rates.

CONCLUSIONS

A new time-of-flight mass spectrometer combined with a temperature jump technique is described. The instrument allows for the time-resolved characterization of the decomposition, ignition, and combustion of solid energetic materials, or other highly reactive condensed-state reactions. Using heating rates of up to 10^5 K/s, samples of nitrocellulose and RDX were ignited, and time-resolved mass spectra were obtained. By monitoring the electrical characteristics of the heated wire, the temperature could also be obtained and correlated to the mass spectra. When combined with the time-dependent temperature information, the results indicate that the instrument can capture the signature of rapid condensed-phase reactions in a time-resolved manner.

Table 1. Ions observed from mass spectra of RDX pyrolysis and their possible assignments

m/z	Species
14	N[#]
15*	CH_3, NH
16	O
17	OH[#]
18*	H_2O[#]
28*	N_2[#], CH_2N, CO
29*	HCO
30*	NO, CH_2O
32	O_2[#]
41	CHN_2
42*	C_2H_4N, CH_2N_2, CNO
43	HCNO
46*	NO_2
56*	$C_2H_4N_2$
75*	$CH_3N_2O_2$
81	$C_3H_3N_3$ (1,3,5-triazine)
120	$CH_2N_3O_4$
127*	$C_3H_3N_4O_2$

*Major ions.
[#]species also observed in background mass spectra.

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