T-JUMP/TIME-OF-FLIGHT MASS SPECTROMETRY FOR TIME RESOLVED ANALYSIS OF ULTRA-FAST SOLID STATE REACTIONS

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ABSTRACT

We describe a new T-jump/time-of-flight mass spectrometer for time-resolved analysis of solid state reactions, 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 with the extraction region of a linear-TOF, 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 example, 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. A 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 10000 Hz were 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 characterization of the decomposition, ignition, and combustion of solid energetic materials

KEYWORDS

Temperature-jump, time of flight mass spectrometry, energetic material

INTRODUCTION

Here we report on a new Time-of-Flight mass spectrometer (TOFMS) electron impact (EI) ionization source that can obtain time resolved mass-spectra during the ignition of energetic materials. The unique feature of this apparatus is a) implementation of TOFMS/EI with a Temperature Jump (T-Jump) technique to monitor highly reactive solid state-samples at high heating and decomposition rates, and 2) measurement of the chemistry in a bi-molecular 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 the condensed phase reaction kinetics are usually performed using conventional thermal analysis techniques[1] such as TGA and DSC. 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 well established 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/FT-IR spectroscopy was developed for studying reaction kinetics of condensed-phase propellants[2, 13]. In the T-Jump/FT-IR 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 have been studied using this technique[14-16]. However, for rapid solid state reactions especially those associated with an ignition event, the relevant time scale can be on the order of milliseconds or less. The nominally low IR spectra scanning rate greatly limits the application of the T-Jump/FT-IR spectroscopy in characterizing ignition, and combustion.

Our objective in developing the T-Jump-MS system was first 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 increasing favor the higher activation channels possessing the lowest entropy constraints. The later emphasis is that minimizing gas-phase chemistry allows a more direct probe of what is happening in the condensed state. The essence of the experiment is that the T-Jump probe is directly inserted into the Electron Impact (EI) 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 solid state 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 SECTION

a. 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 (SPMS)[11, 17] and includes an electron gun for ionization, and the T-Jump probe with an electrical feedthrough, as shown in figure 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 Company) 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.

b. T-Jump Sample Probe.

For the T-Jump 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 coated with a thin layer of either sample powder as 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.

c. Control and Data Acquisition System.

The present design is based on a previously developed Single Particle Mass Spectrometer (SPMS) which is configured for a standard laser ionization source[11, 18]. To ensure a field-free region for EI ionization, one DC high voltage power supply is used with a "T" splitter to bias both the repeller plate, and the extraction plate. 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 ion extraction region between the plates. The extracted ions drift in the linear TOF tube, and are counted at the MCP 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 TTL pulse generator 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 time-of-flight measurement system by triggering the probe power supply from the TTL pulse generator. The temporal voltage and current of the T-Jump probe during the heating event is 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, T-Jump probe heating experiments were conducted by heating an un-coated wire to evaluate the performance of 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 2 shows the resulting temporal temperature of the platinum wire from the voltage and current trace. Since the rise time of the heating pulse is in the range of 10 to ~100 us depending on the output pulse voltage, the resistance and the corresponding temperature is calculated after the rise time of the heating pulse. Thus the filament temperature is estimated to be ~400 K initially, and reaches ~1800 K after the 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[18]. However the presence of the probe and in particular its location was found experimentally to be a sensitive parameter 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's 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 background gas. The relative water (H_2O^+) peak intensity are plotted in figure 3 as a function of probe position. Each experimental data point is an average of 40 mass spectrum measurements, and normalized by the peak intensity measured without the presence of the T-Jump probe. As a comparison to 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[19]. 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 figure 3. Both simulation and 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. Extraction of the probe further out results in a slight decrease of the ion signal in the experimental data, even though the effect of the probe on the electric field is minimized. This implies that at larger distances sensitivity will be lost for material originating from the probe, and that a distance 1.3 cm would seem to be a near optimal for this system.

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 fast “burners”. In these experiments, Nitrocellulose sample (Mallinckrodt Baker Inc.) or RDX was mixed with diethyl ether or acetone, and a small amount of solution is 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 temperature, to extract mechanistic information, the purpose of the present paper is to illustrate the capabilities of the instrument, and we defer any detailed analysis to the future.

The mass spectra obtained for rapid pyrolysis of nitrocellulose are shown in figure 4. The heating duration is about 9 ms with a heating rate of ~1.3 $\times 10^5$ K/s, with a total of 95 spectra sampled with a temporal resolution of 100 μs per spectrum (10000Hz). Out of the 95 spectra obtained in the experiment, we plot 17 of them in figure 4, along with a more detailed view of a spectrum at t = 2.5 ms. Since the heating pulse is synchronized with the first EI ionization duration, the mass spectrum at t = 0 ms is actually the background in the ion source region, and is primarily water (m/z +18), N_2 (m/z +28) and O_2 (m/z +32). We sampled up to m/z ~ 300 for each spectrum, but no heavy ions were observed, and major peaks are only seen for m/z <100. At t =1.7 ms, the estimated temperature of the probe is ~575 K, and a new peak of m/z 31 (HNO^+) appears which suggest the start of the reaction. At t = 1.8 ms which corresponds to a probe temperature ~590K, the ion signal intensity of m/z 31 increases along with peaks at m/z +27 ($C_2H_3^+$), m/z +29 (COH^+), m/z +45 (HCO_2^+) and m/z +59 (2-oxoethanolate, $C_2H_3O_2^+$).. As the reaction time advances to t = 1.9 ms (T~ 600K), peak m/z 31 achieves its maximum intensity, and now peaks at m/z +30 (CH_2O^+/NO^+) and m/z +46 (NO_2^+) appear, along with m/z +16 (O^+), m/z +43 ($C_2H_3O^+$), m/z +44 (CO_2^+). There is significant increase for m/z +28 during the heating event, which can be attributed to the release of CO from nitrocellulose combustion. The species identified in this experiment are similar to those reported previously at slower heating[20, 21]. These species last for the whole duration of the heating pulse (~9ms), and some species are still present well after the end of the wire heating 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 peak intensity for most of major peaks were achieved at t = 2.3 ms, following which the ion signals gradually decreases with no noticeable changes after 4 ms, it is suggested that the most aggressive reaction (ignition) happens within ~4 ms, and the whole reaction lasts ~9 ms.

For a second example we present results for the ignition and combustion of RDX. Similar to the nitrocellulose experiment, we use a sampling rate of 100 μs per spectrum (10,000Hz) to capture the progression of the reaction. The heating pulse is about 8 ms at a heating rate of ~1.5×10^5 K/s, and a total of 95 spectra obtained. Figure 5 shows that species, other than background (water/N_2/O_2), only appear from 0.7 ms - 2.6 ms, which corresponds to a wire temperature of 370K to 670K. These results clearly show as expected that RDX is more facile than Nitrocellulose, and occurs over an interval of only ~2 ms. Although a m/z range up to 400 was recorded for each spectrum, no heavy 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. Small peaks of m/z +14, +16, +41, +43, +81, +120 are also found in some spectra.

Based on the experimental results presented above, it can be clearly see that the characteristic reaction time for energetic materials decomposition/combustion is in 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 ~ 30 kHz. The experimental results suggest that the time-resolved spectra obtained using T-jump/TOF mass spectrometer shod have sufficient sensitivity, and time resolution to probe the reaction dynamics of extremely fast condensed state reactions at high heating rates.

CONCLUSION

A new Time-of-Flight mass spectrometer (TOFMS) 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/sec, 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 solid-state reactions in a time resolved manner.

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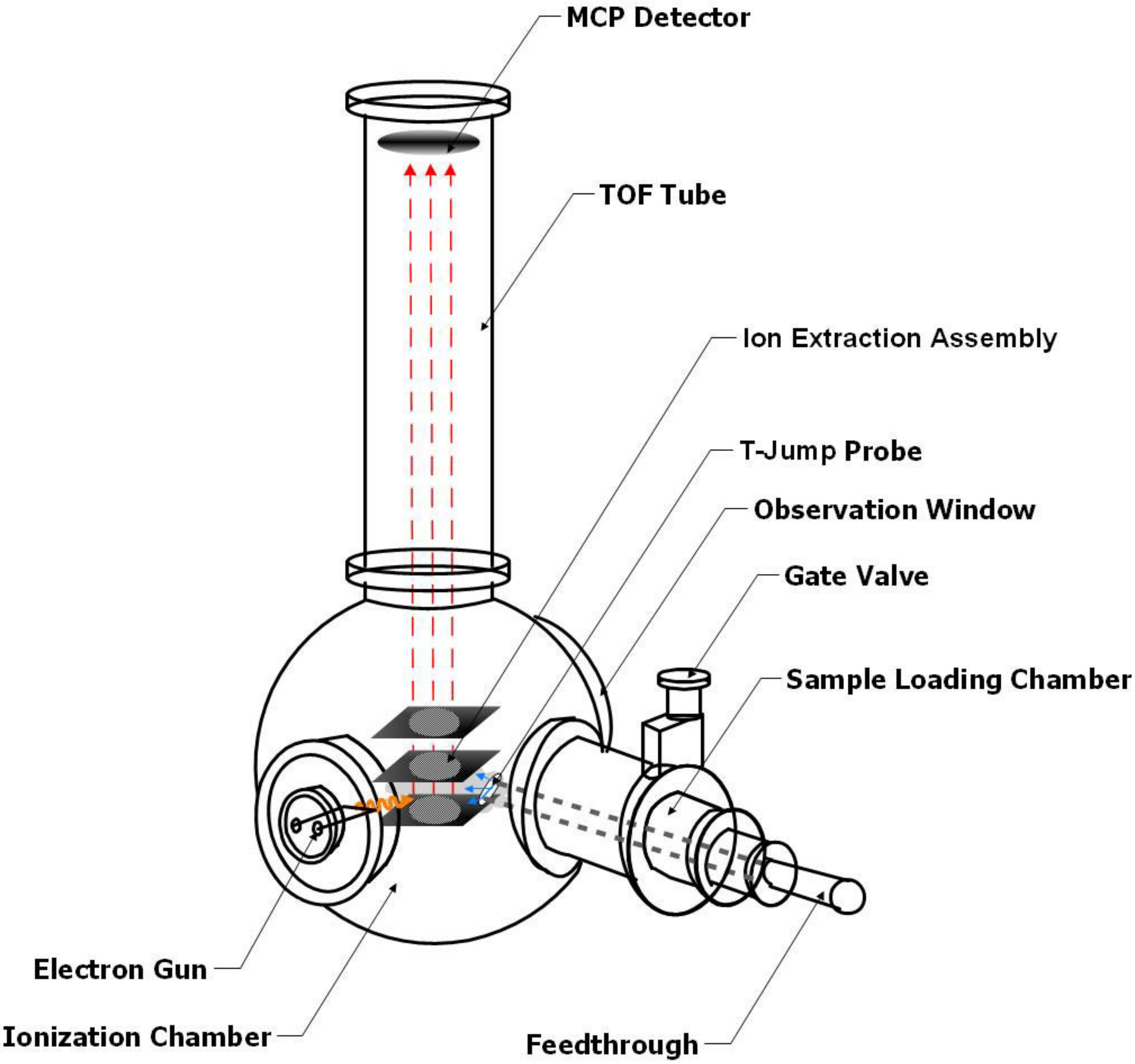

Figure 1. Diagram of T-Jump/TOF mass spectrometer.

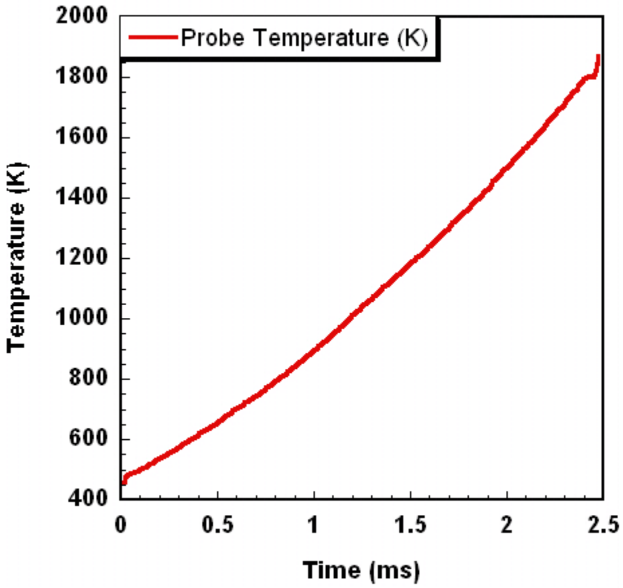

Figure 2 Estimated probe temperature from electrical resistance

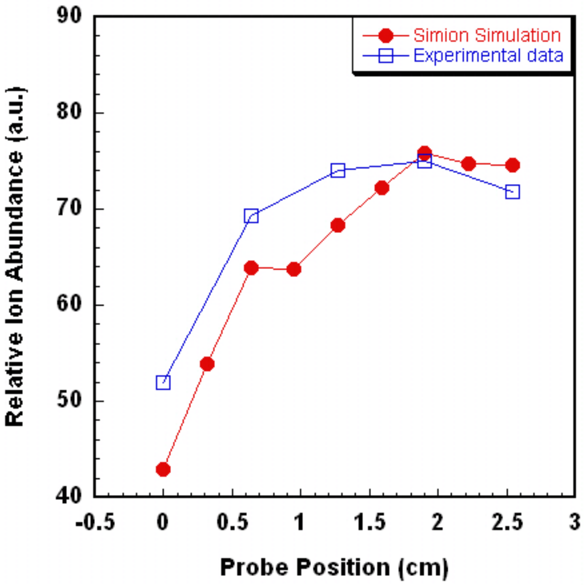

Figure 3 Relative water ion abundance as a function of the probe filament position.

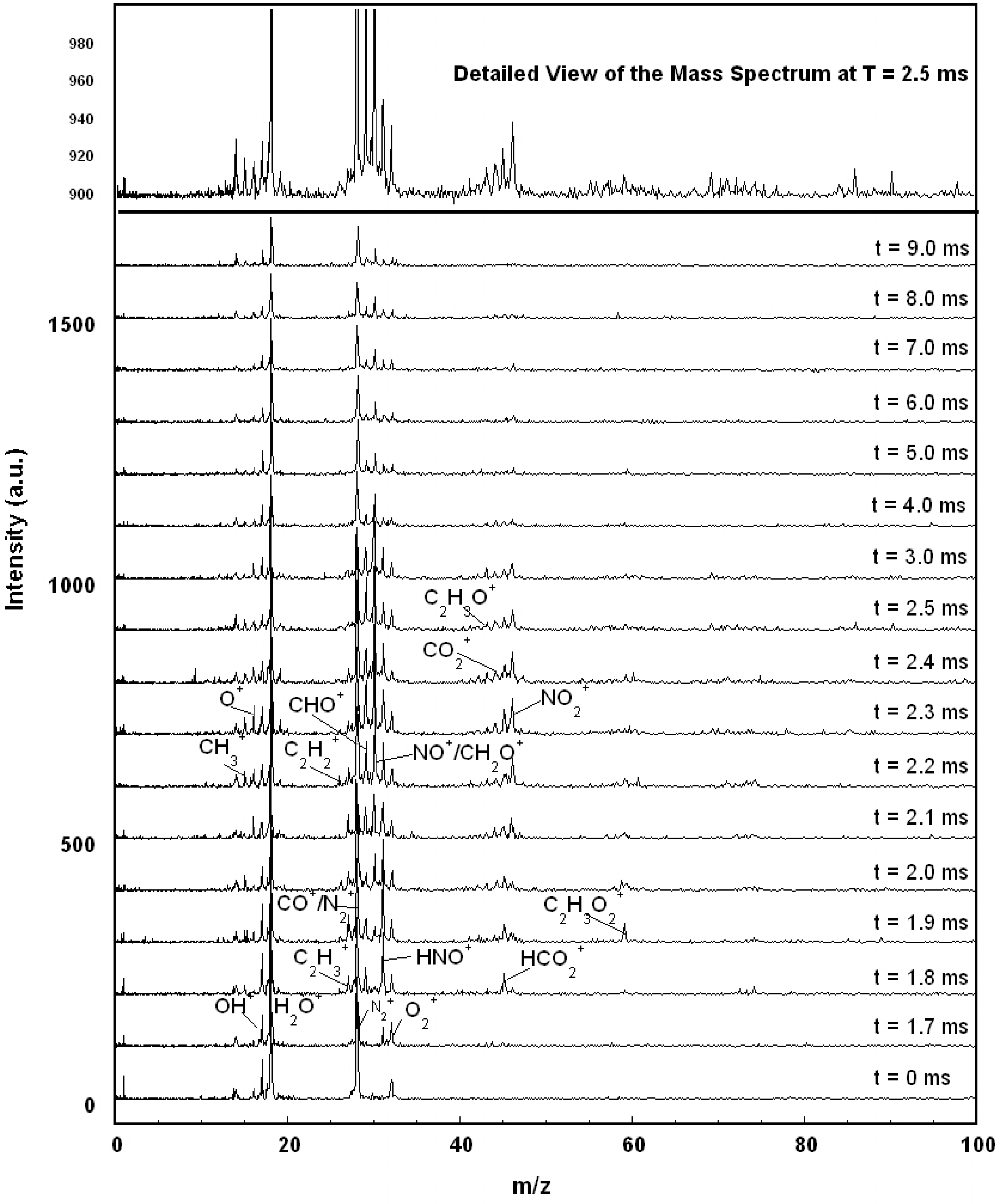

Figure 4. Time resolved mass spectrum from rapid heating of nitrocellulose. Heating rate ~ 1.3 ×10^5 K/s

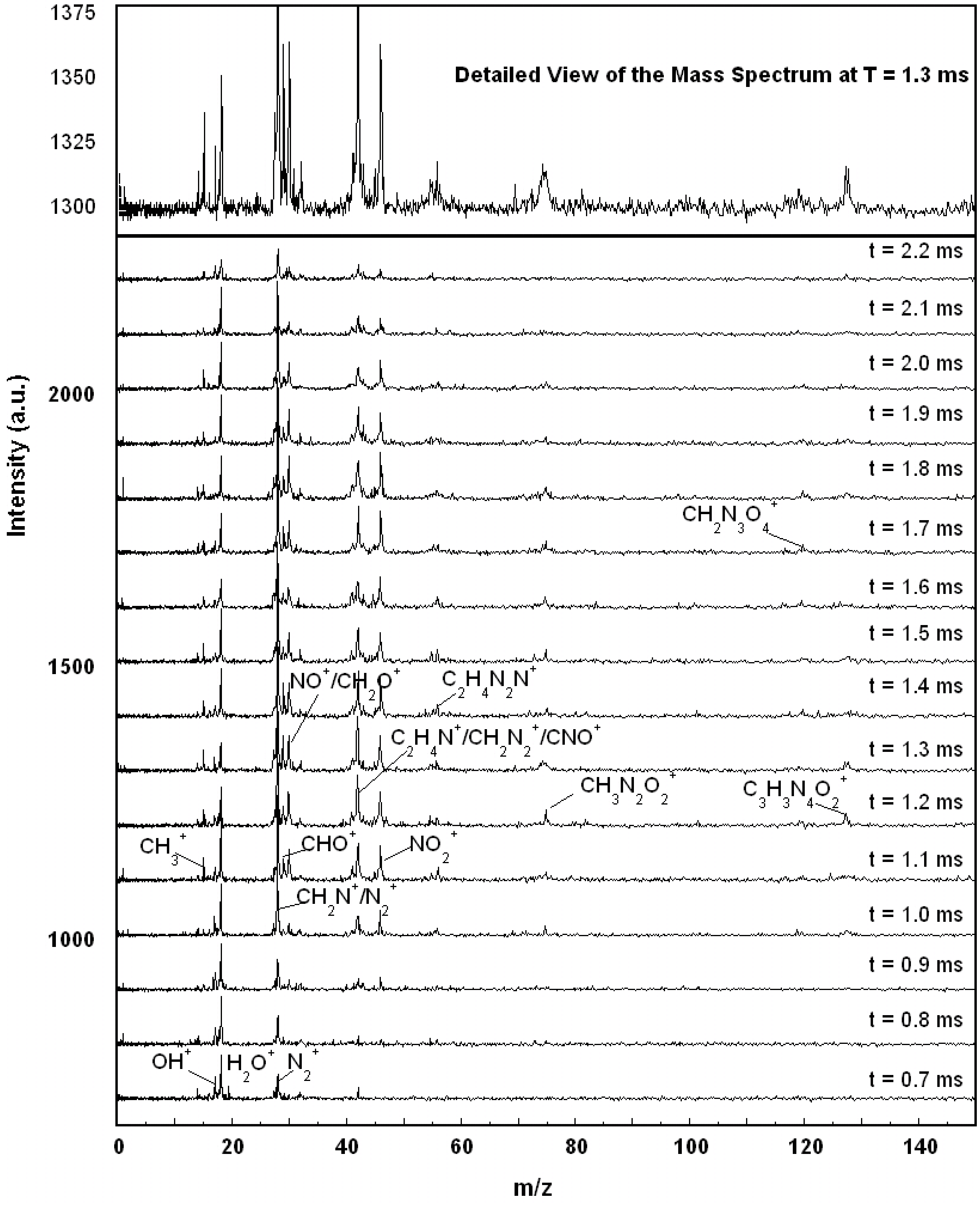

Figure 5. Time resolved mass spectrum from rapid heating of RDX. Heating rate ~1.5 ×10^5 K/s