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Pyrolysis Nozzles Coupled to a Microwave Spectrometer with Stark Modulation for the Detection of Transients Species in a Supersonic Expansion

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Dedicated to Prof. Dr. Dr. h. c. mult. Jürgen Troe on the occasion of his 60th birthday

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Two types of pyrolysis nozzles have been constructed and coupled to a new Stark modulated microwave spectrometer. The nozzles were tested on their ability to generate rotationally cooled transient species through a supersonic expansion. The transients species vinylamine, thioketene and ketene were generated and detected using nozzle temperatures ranging from 400-800 °C. Pyrolysis temperatures were generally lower than those used in normal flow pyrolysis experiments and rotational temperatures of ca. 10 K were achieved. A preliminary investigation of the jet nozzle pyrolysis of 3-methyl-4-hydroxy-iminoisoxaline-5-one was carried out and showed a different distribution of CHNO pyrolysis products to that observed in previous low pressure studies.

1. Introduction

Microwave spectroscopy is a powerful tool for the characterization of molecules with molecular properties such as rotational constants, structural parameters, dipole moments and hyperfine constants derivable from the observed microwave spectrum. It also is capable of being used to analyse short lived molecules, although the use of microwave spectroscopy to analyse true transient species with lifetimes of the order of seconds or shorter,

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however, has been limited. The first transient species to be studied with a microwave spectrometer was the OH' radical by Dousmanis *et al.* in 1955 [1]. Other studies can be found in the reviews by Hirota [2, 3] and Bernath [4] which provide a good overview of the work in the field of microwave spectroscopy of transient molecules.

Transient species can be generated for analysis by microwave spectroscopy in a variety of ways: electrical discharge, pyrolysis (flash vacuum pyrolysis), flash photolysis and photoionization [4]. The pyrolysis method has been used successfully to generate a number of short lived or transient species with subsequent spectroscopy using a flow through conventional Stark modulated spectrometer. Molecules such as benzyne [5], vinylamine [6] and ketene [7] have been studied in this way. The generation of highly reactive short lived transients however requires very short transit times and little opportunity for reaction of the resultant transients between the furnace and the detection region. One such method that meets these requirements is a supersonic jet coupled to a pyrolysis oven. The use of a supersonic jet is advantageous in the generation of transients in two ways. Firstly spectra are dramatically simplified and secondly there is the possibility of "freezing" the transient species in the expansion. The second advantage is highly desirable when investigating highly reactive species. Supersonic cooling is known to stabilize fragile and highly reactive species such as Van der Waals molecules, radicals and ions [8]. Also the short time scale of the expansion allows the preparation of short lived transients and metastable species.

Several investigations using pyrolysis in conjunction with a supersonic free jet have been made to examine some complex transient molecules at near absolute zero temperature using techniques such as laser induced fluorescence [9–12]. The first study using a pyrolysis nozzle and a microwave spectrometer was by Gutowsky *et al.* [13]. They observed the transient species 1,1-dimethylsilaethylene (entrained in argon) from the pyrolysis of 1,1-dimethylsilacyclobutane at ca. 1000°C using a Balle-Flygare Fourier transform spectrometer (frequency range 5–30 GHz). The gas mixture was pulsed into a Fabry-Perot cavity through a 1 mm diameter nozzle.

Recently Harmony *et al.* [14] have designed and built a pulsed nozzle (heatable to ca. 1000°C) Fourier transform microwave spectrometer (5–37 GHz) and examined the excited vibrational states of OCS and chloroketene, a reactive intermediate formed by the pyrolysis of chloroacetylchloride. Fourier transform spectrometers are limited in their frequency range (typically only 30 GHz) due to the transmission characteristics of the microwave resonator. To characterise a molecule properly the assignment of several transitions are required. With small molecules like N₂S, whose groups of lines are widely spaced, only a small number of transitions may be observed with a Fourier transform instrument. Conventional sub-millimetre spectrometers typically have the ability to scan \geq 25 GHz regions over a frequency range from 50–600 GHz [15], which is more desirable than typi-

cal Fourier transform instruments. The aim of this work was to design and build a rapid scanning Stark modulated microwave spectrometer coupled to a pyrolysis nozzle for the examination of transient species.

2. Instrumentation

The transient species spectrometer is shown schematically in Fig. 1 and its basic construction follows that of the system designed by Brown et al. for the study of molecules of low volatility [16]. It consists of a circular aluminium sample chamber with several ports. Two ports are used for mounting the conical horns and accompanying teflon lenses used to form a microwave beam-waist at the centre of the chamber. The chamber itself is fitted onto a custom built gate valve which is bolted directly onto a frame structure. A Varian[®] HV-12 cryo-pump is located on the lower side of gate valve and is linked to a mechanical "roughing" pump. The top plate (shown in Fig. 2) of the chamber is removable. Connected to this plate are the pyrolysis nozzle, pressure gauge port, and electrical feed throughs for the Stark plates (aluminium: $107.2 \text{ mm} \leftrightarrow 50.0 \text{ mm} \leftrightarrow 0.7 \text{ mm}$), the nozzle heater and thermocouple. On the underside of this plate two stainless steel tubes, used to support the Stark plate assembly are attached. To overcome Stark discharge problems closely spaced grounded aluminium guard plates are installed behind each of the aluminium Stark plates. Both plates are secured by Delrin rods which are connected to the stainless steel tubes by Teflon insulators. Stark plate spacing can be varied but the minimum distance to achieve a uniform field and allow the semi-focussed beam through the system is ca. 50 mm. This wide plate spacing can lead to under modulation of lines with slow Stark effects.

The supersonic free jet travels transversely to the direction of both the millimetre-wave radiation and the electric field of the Stark plates. Absorption signals are modulated through the Stark effect by means of a 33 kHz applied square-wave electric field and the electric field vector of the millimetre-waves is parallel to the applied electric field so only $\Delta M = 0$ selection rules are involved for the observed rotational transitions.

The radiation source is a YIG-tuned (Yttrium Iron Garnet) microwave oscillator which produces frequencies in the range of 12-18 GHz, with a frequency quadrupler used to generate the actual frequency range accessible with the spectrometer, 48-72 GHz. The oscillator is phase-locked to a synthesiser that is referenced to a 5 MHz laboratory frequency standard, allowing frequency measurements accurate to within 1 part in 10^8 . The transition from waveguide radiation propagation to a quasi-optical millimetre wave beam was achieved by Teflon-lens corrected horns connected to the chamber which produced a beam waist of 37 mm diameter between the Stark plates. The radiation was detected by a Schottky diode, the output of which was fed to a pre-amplifier and phase-sensitive detector (PSD).





Fig. 1. Microwave spectrometer.

The analogue output signal of the PSD was connected to a strip-chart recorder for broad-band scanning. Precise line frequency measurements of detected absorption lines were obtained by signal averaging using a micro-computer-based data acquisition system fed by the digital PSD output. A PSD filter time constant of 100 ms, 20 kHz millimetre-wave frequency step size and 3.33 step s⁻¹ were the conditions used for computer averaging.





Fig. 2. Top nozzle and nozzle position.

Computer averaged line profiles were then fitted to a Lorentzian function using the Macintosh software package KaleidagraphTM (version 2.1.1) to obtain the centre frequency of the observed transition and its line width (typically 250 kHz). The standard deviation of the transition frequency of a well resolved line was estimated to be equal to one tenth the line width; undermodulated lines were given a standard deviation of one quarter the

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line width. Severely undermodulated lines and poorly resolved lines were given a standard deviation equal to the line width.

3. Discussion

3.1 Nozzle design mark I

In designing the hot nozzle various requirements had to be taken into account. The main two requirements being: (1) the nozzle needed to maintain high temperatures ($600 \,^\circ\text{C}$ +) for long periods of time; (2) the nozzle needed to achieve rotational temperatures in the range 5–15 K.

The pyrolysis nozzle mark I is shown in Fig. 3. Nichrome[®] wire was coiled around four quartz rods held in position by two Macor[®] discs. The Nichrome wire and quartz rods were then placed in a stainless steel tube and enclosed by several layers of shimmed stainless steel sheet which acted as a heat shield. The stainless steel tube screwed on to a platform which was connected to three insulated stainless steel supports. The ends of the Nichrome wire were connected to a ceramic electrical contact block which was fixed on to the platform. A stainless steel tube was used to guide a K-type thermocouple to a region near the centre of the heater and close to the surface of the nozzle. The final resistance of the Nichrome winding was measured as 1.4Ω . The Nichrome wire was resistively heated using a Variac regulator connected to a step-down transformer (240-32 V).

3.2 Test of spectrometer and cold-nozzle

1,1,1,2-tetrafluoroethane (HFC-134a) was used to test the newly constructed spectrometer detection system and to evaluate the amount of cooling achieved by the jet-expansion. The gas was obtained commercially from CIG Australia and used without further purification. Microwave transition frequencies and intensities were predicted at a range of temperatures around 10 K in the region 48-72 GHz using the rotational constants given by Ogata and Miki [17]. A mixture of both welding grade argon and HFC-134a gas was then passed through the nozzle (Pyrex, with a ca. 300 µm pin hole). Pressure inside the chamber was maintained at ca. 0.04 Pa with a backing pressure of ca. 10 kPa. The argon/HFC-134a mixture was approximately 10:1, thus resulting in a temperature cooler than if pure HFC-134a was used. A total of 114 transitions were assigned ($J \le 20, K_a \le 11$). A result of jet cooling is that transitions usually not observed at ambient temperatures are observed. During this work Xu et al. [18] recorded and assigned a number of lines of HFC-134a at room temperature in the region 7-25 GHz and obtained a much improved set of rotational constants compared with those from the work of Ogata and Miki [17]. We have combined their data with ours and fitted it to Watson's S-reduced Hamiltonian [19] to





Fig. 3. Pyrolysis nozzle Mk. I.

achieve a comparable but slightly better determined set of constants. The constants are given in Table 1 and the good fit with the data of others validates the spectrometer system and procedures. From a comparison of the line intensities of the observed spectrum against that predicted, a rotational temperature was estimated for HFC-134a of 7.5 ± 2.5 K. Colder samples were achieved with further dilution in argon but at the expense of S/N.

3.3 Hot nozzle experiments

To gain some understanding of the limits of the system, analyses of some known transient species were performed. The transient species vinylamine

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Paran	neters	Thi	This work			Previous work ^b		
Α			5355.61897(26)			5355.61817(51)		
В		279	2799.22113(12)			2799.22085(31)		
С		275	2759.43382(11)			2759.43294(31)		
$\Delta_{ m \prime} imes 10^{-4}$			5.2066(67)			5.012(87)		
$\Delta_{IK} imes 10^{-3}$			4.3212(49)			4.3132(55)		
$\Delta_{\kappa} imes 10^{-3}$			-3.3691(31)			-3.396(15)		
$\delta_{\kappa} imes 10^{-3}$			1.593(30)			1.766(32)		
$\Phi_{\scriptscriptstyle JK} imes 10^{-7}$			1.02(21)					
Stand	ard deviati	on	1.023					
RMS error			0.00370					
No. o	f transitior	ns 17	/3					
elation ma	atrix :							
Α	В	С	Δ_J	$\Delta_{\scriptscriptstyle JK}$	$\Delta_{\!\scriptscriptstyle K}$	$\delta_{\scriptscriptstyle K}$	$\varPhi_{_{JK}}$	
1.00								
0.75	1.00							
0.77	0.69	1.00						
0.53	0.70	0.53	1.00					
0.75	0.39	0.50	0.28	1.00				
0.34	0.00	-0.09	0.19	0.20	1.00			
0.03	0.44	-0.31	0.28	-0.17	0.15	1.00		
0.54	0.11	0.40	0.13	0.84	0.19	-0.30	1.00	
	Param A B C $\Delta_J \times 1$ $\Delta_{JK} \times$ $\Delta_{K} \times 1$ $\Phi_{JK} \times$ Stand RMS No. o elation ma A 1.00 0.75 0.77 0.53 0.75 0.34 0.03 0.54	Parameters A B C $\Delta_{J\kappa} \times 10^{-3}$ $\Delta_{K} \times 10^{-3}$ $\Delta_{K} \times 10^{-3}$ $\Phi_{J\kappa} \times 10^{-7}$ Standard deviati RMS error No. of transition elation matrix : A B 1.00 0.75 0.53 0.75 0.34 0.00 0.34 0.54	Parameters Thi A 535 B 279 C 275 $\Delta_{JK} \times 10^{-4}$ $\Delta_{JK} \times 10^{-3}$ $\Delta_{K} \times 10^{-3}$ $ \delta_{K} \times 10^{-3}$ $ \delta_{K} \times 10^{-7}$ Standard deviation RMS error No. of transitions 17 elation matrix : A B C 0.75 1.00 0.75 0.53 0.77 0.69 1.00 0.53 0.75 0.39 0.50 0.34 0.00 -0.09 0.03 0.44 -0.31 0.40 -0.31 0.40	Parameters This work A 5355.61897(2) B 2799.22113(2) C 2759.43382(2) $\Delta_{J} \times 10^{-4}$ 5.2066(6) $\Delta_{JK} \times 10^{-3}$ 4.3212(4) $\Delta_{\kappa} \times 10^{-3}$ -3.3691(3) $\delta_{K} \times 10^{-3}$ 1.593(30) $\Phi_{JK} \times 10^{-7}$ 1.02(21) Standard deviation 1.023 RMS error 0.00370 No. of transitions 173 elation matrix : A B C Δ_{J} 1.00 0.75 1.00 0.75 0.50 0.28 0.34 0.00 -0.09 0.19 0.03 0.44 -0.31 0.28 0.54 0.11 0.40 0.13 0.13 0.13	Parameters This work A 5355.61897(26) B 2799.22113(12) C 2759.43382(11) $\Delta_{J} \times 10^{-4}$ 5.2066(67) $\Delta_{J\kappa} \times 10^{-3}$ 4.3212(49) $\Delta_{\kappa} \times 10^{-3}$ -3.3691(31) $\delta_{\kappa} \times 10^{-3}$ 1.593(30) $\Phi_{J\kappa} \times 10^{-7}$ 1.02(21) Standard deviation 1.023 RMS error 0.00370 No. of transitions 173 elation matrix : A A B C Δ_J 0.75 1.00 0.75 0.75 0.69 1.00 0.75 0.75 0.39 0.50 0.28 1.00 0.75 0.39 0.50 0.28 1.00 0.75 0.39 0.50 0.28 1.00 0.34 0.00 -0.09 0.19 0.20 0.03 0.44 -0.31 0.28 -0.17 0.54 0.11 0.40 0.13 0.	Parameters This work Previo A 5355.61897(26) 5355.6 B 2799.22113(12) 2799.2 C 2759.43382(11) 2759.4 $\Delta_{J} \times 10^{-4}$ 5.2066(67) 5.0 $\Delta_{J\kappa} \times 10^{-3}$ 4.3212(49) 4.3 $\Delta_{\kappa} \times 10^{-3}$ -3.3691(31) -3.3 $\delta_{\kappa} \times 10^{-3}$ 1.593(30) 1.7 $\Phi_{J\kappa} \times 10^{-7}$ 1.02(21) 5 Standard deviation 1.023 RMS error 0.00370 No. of transitions 173 173 2 elation matrix : A B C Δ_J $\Delta_{J\kappa}$ Δ_{κ} 1.00 0.75 1.00 0.75 0.53 1.00 0.75 0.39 0.50 0.28 1.00 0.34 0.00 -0.09 0.19 0.20 1.00 0.03 0.44 -0.31 0.28 -0.17 0.15 0.54 0.11 0.40 0.13 0.84 0.19	Parameters This work Previous work ^b A 5355.61897(26) 5355.61817(51) B 2799.22113(12) 2799.22085(31) C 2759.43382(11) 2759.43294(31) $\Delta_{J} \times 10^{-4}$ 5.2066(67) 5.012(87) $\Delta_{J\kappa} \times 10^{-3}$ 4.3212(49) 4.3132(55) $\Delta_{\kappa} \times 10^{-3}$ -3.3691(31) -3.396(15) $\delta_{\kappa} \times 10^{-3}$ 1.593(30) 1.766(32) $\Phi_{J\kappa} \times 10^{-7}$ 1.02(21) Standard deviation 1.023 RMS error 0.00370 No. of transitions 173 elation matrix: A B C Δ_J Δ_{κ} δ_{κ} 0.75 1.00 0.77 0.69 1.00 0.75 0.39 0.50 0.28 1.00 0.75 0.39 0.50 0.28 1.00 0.34 0.00 -0.15 1.00 0.34 0.00 -0.09 0.19 0.20 1.00 0.54 0.11 0.40 0.13 0.84	

Table 1. HFC-134a ground state parameters (in MHz)^a.

 $^{\rm a}$ The number in parentheses are 1 standard deviation (expressed in the last two digits) from the least squares fit.

^b Reference: Xu et al. [18].

was thought to be a good test of the system since it needs a relatively high-temperature to be generated (ca. 850-900 °C from previous studies). Vinylamine has been studied a number times in the microwave region from the pyrolysis of cyclobutylamine, the most recent study being by Brown *et al.* [6]. The nozzle temperature was set to ca. $700 °C^{1}$, and argon bubbled through the cyclobutylamine (98% purity, Aldrich[®], held at room temperature) with a backing pressure of 10 kPa. Observed frequencies agreed with the work of Brown *et al.* [6] and the $3_{0,3} \leftarrow 2_{0,2}$, $3_{1,3} \leftarrow 2_{1,2}$, $3_{1,2} \leftarrow 2_{1,1}$, $3_{2,2} \leftarrow 2_{2,1}$ and $3_{2,1} \leftarrow 2_{2,0}$ transitions from both the 0⁺ and 0⁻ vibrational states were observed. All lines were not well resolved due to hyperfine structure and also undermodulated, allowing only an approximate estimation of the line frequency, intensity and hence rotational temperature.

¹ The temperature (°C) refers to the temperature at the hottest zone inside the nozzle. Since the nozzle is being heated radiatively the actual temperature of Nichrome wire could well in excess of 1000-1100 °C. Nichrome wire has a temperature rating (in air) of 1150-1250 °C.

The Nichrome[®] wire could maintain the temperature of ca. 700 °C for approximately three hours before deteriorating. From a comparison of the intensities of the weakest and strongest lines with the line intensities predicted at a range of temperatures a rotational temperature between 10 ± 5 K was estimated.

Another test of the system was in the generation of ketene. Ketene can be generated by the pyrolysis of acetic anhydride at temperatures between 650-1000 °C [7]. The nozzle was set to ca. 500-550 °C, and argon was bubbled through acetic anhydride (+99% purity, Aldrich[®]). Stark voltages between 1500-3000 V and backing pressures between 10-30 kPa were used. The ground state lines $3_{0,3} \leftarrow 2_{0,2}$, $3_{1,3} \leftarrow 2_{1,2}$ and $3_{1,2} \leftarrow 2_{1,1}$ of ketene were observed. No lines from the $K_a = 2$ state were observed. All lines were well resolved and well modulated. Since no lines belonging to the $K_a = 2$ state were observed, an upper estimate of the rotational temperature could be obtained. The signal to noise of the $3_{1,2} \leftarrow 2_{1,1}$ line was estimated to be $150:1^2$. Therefore the instrument should be able to detect lines of ketene that are up to 150 times less intense than the $3_{1,2} \leftarrow 2_{1,1}$ line. An upper rotational temperature for ketene of 11 K was estimated.

The jet-nozzle mark I has the capacity to generate transient species such as vinylamine and ketene, from precursors that are a relatively volatile liquid or gas using temperatures below those employed in low pressure studies. Attempts to use this nozzle for the generation of transients from solid precursors were not successful due to: (1) the small diameter of the inlet tube (4 mm i.d.) resulted in insufficient sample being heated and hence insufficient vapour pressure over a long period of time; (2) deposition of the sample on the inside of the sample tube because the tube is only heated at its tip; (3) the Nichrome[®] wire was unsuitable for maintaining high nozzle temperatures (>700 °C). In order to rectify these problems and obtain spectra of transients from solid precursors a new design was developed and constructed.

3.4 Nozzle design mark II

The new pyrolysis nozzle apparatus is shown in Fig. 4. The pyrolysis nozzle is made up of two stages. The first, wider stage is a stainless steel tube (23.7 mm i.d.) which has 3 mm diameter AEROCOAX[®] wire (ARI Industries, Inc.), a biaxial insulated heating wire, brazed on to it. The final resistance of the wire measured 80 Ω . This stage is wide enough to allow the heating of a few grams of solid. The heating wire wrap is tapered to allow a gradual increase in temperature towards the nozzle end. The second stage contains the main heater which consists of a stainless steel tube (0.7 mm i.d.) with 1 mm diameter AEROBIAX[®] heating wire (ARI Industries, Inc.)

² The signal to noise was estimated by calculating the intensity of the main peak against the standard deviation of the noise in the baseline.

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Fig. 4. Pyrolysis nozzle Mk. II.

coiled around it giving a final resistance of 50 Ω . The tube is then encased in an outer stainless steel tube equipped with a heat shield (shimmed stainless steel). This tube is supported by a stainless steel platform. Two electrical connectors are also fixed on to the platform, which is held in place by three stainless steel tubes connected to the top plate of the heater. The nozzle is made from quartz with a ca. 300 µm diameter hole at the tip. The quartz nozzle was made to fit snugly inside the stainless steel tubing of both sections, and is sealed by an O-ring at the top. A K-type thermocouple is connected to the bottom of the first stage.



On initial testing of the system a thermocouple probe was lowered inside the hot zone of the nozzle and a current/temperature relationship established. It was found that radiation from the main heater, when at high temperatures, also heated the pre-heater section, thereby making the temperature of the pre-heater uncontrollable. A stainless steel spacer was added to increase the distance between the second and first stage and a Macor[®] disc inserted between the two stages to help minimize the radiative transfer of heat.

In order to test the nozzle at relatively high temperatures the generation of thioketene was undertaken. Thioketene can be generated from the pyrolysis of 1,2,3-thiadiazole at a temperature of 850°C [20, 21]. 1,2,3-thiadiazole was cooled to ice temperature to reduce the vapour pressure, argon was bubbled through it and then passed through the nozzle. Transition frequencies at a rotational temperature of 10 K were predicted using the molecular constants given by Winnewisser and Schäfer [22]. At a nozzle temperature of ca. 700°C, backing pressure of 10 kPa, and Stark voltages between 1500-3000 V no transitions from thioketene were observed. Upon increasing the backing pressure to 80 kPa several transitions of thioketene were observed. The relationship between the nozzle temperature and the intensity of thioketene lines was investigated and it was found that a nozzle temperature of ca. 500-550°C produced the highest signal. The use of the higher backing pressure, which increases the collision rate of molecules with the nozzle wall, seems to allow the use of a much lower nozzle temperature than that used in the low pressure studies of Brown et al. [7]. No transitions belonging to $K_a = 2$, 3 and 4 levels were observed, allowing a range for the rotational temperature to be obtained. Transition intensities were predicted at various temperatures to estimate the rotational temperature and an observed rotational temperature for thioketene was found to be 9 ± 4 K.

Generation of CHNO isomers

As a final test the jet nozzle pyrolysis of 3-methyl-4-hydroxy-iminoisoxaline-5-one (referred to as MHI; m.p. 147°C (dec)), a solid phase precursor known to generate fulminic acid (HCNO) in high yield was investigated. Fulminic acid, although not a short lived transient, nevertheless readily isomerises into the more energy favourable isocyanic acid (HNCO). Detection of this species would show that generation of a transient species from a solid precursor is possible, and that the system is able to modulate transitions from a linear molecule.

The simplest "organic" molecules containing the elements carbon, hydrogen, nitrogen and oxygen are the molecules with the empirical formula CHNO. It has been shown that 38 possible topologically different CHNO

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3-methyl-4-hydroxyiminoisoxazolin-5-one

Scheme 1. Pyrolysis of 3-methyl-4-hydroxy-iminoisoxaline-5-one.

structures may exist [23]. Of these only four isomers HNCO (isocyanic acid), HOCN (cyanic acid), HCNO (fulminic acid), and HONC (isofulminic acid) have been observed experimentally.

To date only HNCO and HCNO have been observed in the gaseous phase whilst HOCN and HONC have been observed only under matrix isolation conditions [24]. Theoretical predictions on the relative energies and geometries of the isomers of CHNO are plentiful with numerous publications on the subject each year. Teles *et al.* [24], East *et al.* [25] and Mebel *et al.* [26] give good accounts of the state of theoretical predictions of these species.

HNCO is the lowest energy species, while HOCN is the second lowest. The relatively low total energy of HOCN suggests that it is a possible contender for observation in the gas phase but due to its kinetic instability HOCN has only been detected in matrix conditions. HCNO and HONC are the least thermodynamically stable isomers. However HCNO is observable in the gas phase. For gas phase work fulminic acid can be generated by the pyrolysis of mercury fulminate or 3-methyl-4-hydroxy-iminoisoxaline-5-one [27] as shown in Scheme 1. Wentrup *et al.* [27] pyrolysed MHI in an attempt to generate HONC (isofulminic acid) but detected only the isomer HCNO (fulminic acid) and very small amounts of HNCO. Depending on the mechanism, generation of HONC in the gas phase using MHI may be possible if HONC can be stabilized before it isomerises. Previous flow through pyrolysis microwave experiments using MHI in this laboratory and others have failed to identify HONC.

A sample of MHI, synthesised by the method of Wentrup [27], was lowered into the first heating stage³, (ca. 200°C) and the nozzle temperature was set to ca. 650°C. In the initial experiments only lines from methyl cyanide were detected, indicating that some MHI was being pyrolysed. The height of the sample in the first section was adjusted while a line from methyl cyanide was monitored. Once appropriate positions and settings were found to maximize methyl cyanide production, a search was made for

³ Sample was held in a pyrex "bucket" which was attached to stainless steel wire. The wire ran through a septum at the top of the nozzle.

HCNO. Line frequencies were predicted at a temperature of 10 K using the constants from Winnewisser and Winnewisser [28] and Yamada [29] respectively for HCNO and HNCO. With a backing pressure of 80 kPa, a Stark voltage of 1500 V and chamber pressure of 0.09 kPa, the $J = 3 \leftarrow 2$ (68813.86 MHz) transition of HCNO was observed. The line intensity was not substantially improved by adjustment of either the backing pressure or the nozzle temperature. The $3_{0.3} \leftarrow 2_{0.2}$ (65944.30 MHz) line from HNCO (isocyanic acid) was also observed with much greater intensity than the line of HCNO. No lines from the $K_a = 1$ or 2 states of HNCO were observed. The rotational temperature of HNCO was estimated to be 8.5 ± 3.5 K.

The rotational constants for the four isomers were predicted using the MP2/6-311G(d,p) and the predicted rotational constants of HONC and HOCN were multiplied by a scaling factor derived using experimental and theoretical results of HNCO and HCNO. Using the program WANGSR transitions were predicted for HONC and HOCN at a temperature of 10 K, the most intense line for HONC being the $3_{0.3} - 2_{0.2}$ transition at 66 167 MHz. A search was made in this region and a very weak line was observed at 66 163.300 MHz with similar modulation characteristics to HNCO, which has the same symmetry. No lines from $K_a = 1$ and 2 states of HONC were observable and the observed line cannot be assigned to any known transitions of HCNO, HNCO or CH₃CN. However with only one peak no justification can be made that isofulminic acid had been observed. Due to the limitations in the sensitivity of the instrument and rotational cooling no other K_a transitions were observable which would help substantiate the detection of isofulminic acid. No lines attributable to HOCN were observed.

4. Conclusion

Microwave transitions from the transient species vinylamine, ketene, and thioketene have been observed using a pyrolysis nozzle coupled with a Stark modulated microwave spectrometer. A supersonic expansion of the molecules, entrained in argon, achieved rotational temperatures in the range 5-15 K. The pyrolysis nozzle mark I could only achieve temperatures of up to 750 °C for ca. 3 hours, while the pyrolysis nozzle mark II was able to achieve and maintain temperatures of up to 1000 °C (typically 750 °C) for more than 6 hours. Pyrolysis of 3-methyl-4-hydroxy-iminoisoxaline-5-one using conventional techniques favours the generation of fulminic acid over that of isocyanic acid. In this work this is reversed, with the generation pathway significantly to allow the formation of normally energy unfavourable species such as isofulminic acid or the temperature conditions in the system are more conducive to isomerization to HNCO. Further investigation with this technique may allow the generation of many unstable and novel

short lived species. This work has shown that a pyrolysis jet nozzle coupled to a Stark modulated instrument can be used in the detection and characterization of transient species. Future work on the system would include working toward increasing sensitivity (which may be achieved by using a MWFT system), increasing the frequency range of the spectrometer, redesigning the nozzle for better handling of the sample, and improving control of the temperature of the nozzle and pre-heater.

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