

A compact hot-nozzle Fourier-transform microwave spectrometer

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A newly constructed pulsed nozzle, Fourier-transform microwave spectrometer utilizes a Fabry–Perot cavity consisting of spherical resonators having diameters of only 10 cm. Tests of this very compact-cavity system show that its sensitivity is only slightly lower than that of a comparably configured system of the Balle–Flygare design having resonators with diameters of 36 cm. With a volume 50 times smaller than in conventional systems, the compact cavity also requires a much smaller vacuum chamber which can be pumped by a relatively small 6 in. diffusion pump. The system includes an integral ceramic nozzle which can be heated to temperatures above 1000 °C. Spectrometer characteristics have been demonstrated by means of experiments on OCS isotopomers in ground and excited vibrational states, ArOCS complexes, and chloroketene, a reactive intermediate formed by pyrolysis of chloroacetylchloride. © 1995 American Institute of Physics.

I. INTRODUCTION

The technique of pulsed-nozzle Fourier-transform microwave (FTMW) spectroscopy has been used extensively since its introduction and development in 1979 by Flygare and co-workers.^{1–6} The original design has been reproduced in many labs around the world^{7–15} with various modifications and improvements but in most cases with no major changes in the design of the Fabry–Perot microwave cavity or the high-speed pumping system. In particular, it has apparently been widely assumed that the large cavity volume (60–70 ℓ) and high-capacity pumping system (8000 ℓ/s) of the Balle–Flygare design were more-or-less immutable design parameters for a high-sensitivity, pulsed supersonic free-jet FT instrument. Actually, some slightly scaled down versions have been reported,^{12,14,16} as well as one whose cavity is nearly twice as large.¹³ Naively, a large microwave cavity volume provides the ability to polarize, and subsequently capture the transient emission from a large number of free-jet molecules at relatively low density. At the same time the high-speed pumping system along with the large free volume of the cavity permits a more-or-less classic example of an unimpeded supersonic free-jet expansion,^{17,18} leading to very low translational and rotational temperatures. While these notions are certainly not false, we show in the following work that they are an oversimplification. Furthermore, it is shown that an experimental system with a Fabry–Perot cavity reduced in volume by a factor of 50 and a pumping system reduced in capacity by a factor of 6 yields FT microwave spectra of a quality comparable in most regards to those produced by the Balle–Flygare design. The work also highlights some key experimental characteristics such as transit time and Doppler doubling.^{3,4}

Finally, the compact FT experimental system described here incorporates as an integral part a ceramic nozzle capable of heating the carrier gas and its active chemical constituents to ≈1000 °C prior to supersonic expansion. Such a hot nozzle, whose most obvious application is for the production of transient chemical species by pyrolysis, has been used seldomly in FT microwave studies although a few such experiments have been reported.¹⁹ Hot-nozzle pyrolysis super-

sonic free-jet methods have been more extensively used in other areas of spectroscopy, notably laser-induced fluorescence excitation spectroscopy,^{20,21} and photoelectron spectroscopy.²² In the present work we demonstrate how the hot nozzle can also be exploited to probe excited vibrational states via the ineffective cooling of molecular vibrational modes in supersonic expansions.²³

II. SIZE SCALING CONSIDERATIONS

A. Frequency

The theory of the Fabry–Perot cavity with spherical concave reflectors has been extensively discussed.^{3,4,6} The desired mode structure for reflectors having a radius of curvature R is obtained when the reflector separation $d \leq 2R$ (see Fig. 1). When $d = R$ the cavity is said to be confocal. In order that diffraction losses be not more than a few percent, the microwave frequency should satisfy

$$\nu \geq \frac{cR}{a^2}, \quad (1)$$

where a = reflector radius and c = speed of light. Thus, a cavity with a given resonator design (a and R) has a practical low-frequency limit but essentially no high-frequency restriction. However, as ν increases the beam waist radius (w_0) decreases, so the active cavity volume decreases and the microwave electric field strength increases. In practice, the condition in Eq. (1) is easily satisfied for a broad range of (a, R) values. The Balle–Flygare system⁶ (with $a = 18$ cm and $R = 84$ cm) was usable down to 4500 MHz and was operated typically with $d \approx 70$ cm. The compact system used in our work ($a = 5$ cm, $R = 15$ cm) operates down to approximately 15 000 MHz with $d \approx 13$ cm. With slightly larger reflectors ($a = 7.5$ cm, $R = 15$ cm), operation to below 7000 MHz should be achievable. Thus it is clear that while low-frequency operation generally requires larger reflectors, there is no need for them to be as large as in most conventional systems.

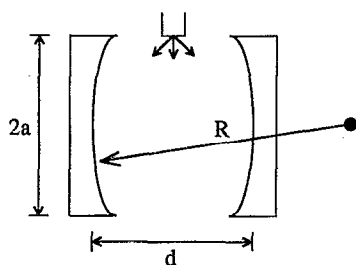


FIG. 1. Fabry-Perot cavity parameters.

B. Sensitivity

Flygare and co-workers have presented the general theory of pulsed-nozzle FTMW spectroscopy in several publications.^{2-4,6} While the general principles are well established, the experimental results depend to some extent upon exactly how the experiment is performed (e.g., supersonic free-jet conditions, sampling decay time, etc.). If one focuses on the key issues of the cavity experiment that relate to geometry, the observed signal (the voltage at the input to the analog-to-digital converter (ADC), for example, see Fig. 2), may be written as

$$S \propto (\nu Q V)^{1/2} f(P_0, T_0, D, \mu, \dots), \quad (2)$$

where ν , Q , and V are, respectively, the microwave frequency, quality factor, and effective volume of the on-resonance cavity. $f(P_0, T_0, \dots)$ reminds us that the signal depends on numerous other variables including, but not limited to, the pressure and temperature of the reservoir gas, the nozzle diameter, and the transition dipole moment for the resonant molecular states. For the Fabry-Perot cavity, Q scales with reflector separation (d),⁶ so $(QV)^{1/2}$ introduces $(l \times l^3)^{1/2} = l^2$, scaling with linear dimension l . But in practice Q is often determined by input/output coupling (loading) and thus the theoretical size scaling is not important. Also, the useful

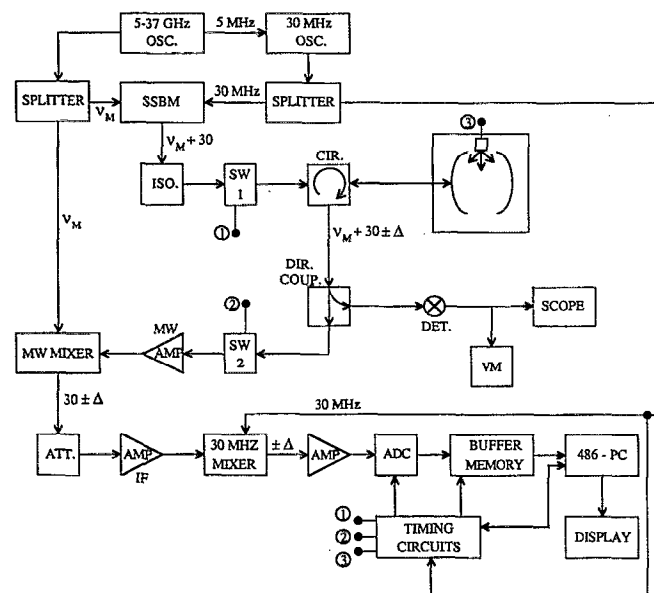


FIG. 2. Block diagram of the Fourier-transform microwave spectrometer.

cavity volume involves that within the beam waist. This volume is $V \approx \pi w_0^2 d$, which for resonant frequency ν ($\nu = c/\lambda$) varies as $R^2 \lambda$ in the confocal case. Thus, $(QV)^{1/2}$ varies more like $(l^0 \times l^2)^{1/2} = l$ in practice. If ν and all the factors in F are constant, then the Balle-Flygare spectrometer would be more sensitive than ours by a factor of $\approx 4-5$ since the ratio of reflector radii is $18/5 \approx 4$ and the ratio of reflector separation is $\approx 70/13 \approx 5$. This estimate is a fairly good approximation as we shall see later.

It is perhaps useful to note also the frequency dependence of the $(\nu Q V)^{1/2}$ factor based on the preceding discussion. We have from V a factor $\lambda \propto \nu^{-1}$ so that $(\nu V)^{1/2}$ varies as $(\nu^0)^{1/2}$, that is, it is independent of frequency. The cavity Q has only a modest $\nu^{1/2}$ dependence⁶ so $(\nu Q V)^{1/2}$ varies only as $\nu^{1/4}$. Thus there is no substantial direct frequency dependence although it may arise incidentally. (For example, at a higher frequency one may be dealing with transitions having larger dipole matrix elements.)

C. Pumping rate

The principle requirement for maintaining a pulsed supersonic free-jet expansion is that the pumping system must have the capacity to evacuate the vacuum chamber between pulses.¹⁷ This will depend then upon a number of design criteria such as chamber size (determined in this case by the size of the Fabry-Perot cavity), nozzle diameter, pulse length, and repetition rate. A typical 1-mm-diam nozzle operating with reservoir conditions of 1 atm and 300 K will emit approximately 4×10^{21} molecules.¹⁸ If a pulse width of 250 μ s is selected, the valve will then emit 1×10^{18} molecule/pulse. In a "compact" chamber with a volume of 10 ℓ , this will produce a pressure pulse of about 2 mTorr. A nominal 6 in. diffusion pump with a capacity of 1500 ℓ /s can reduce this to $\approx 10^{-6}$ Torr in a time of 50 ms.²⁴ Thus, one would predict that this pump could handle a pulse repetition rate of 10-20 pulses/s. The valve/pumping system/vacuum chamber used in the present work is designed around these criteria. It is typically operated at a repetition rate of 5 Hz although there is only slight deterioration at 10-15 Hz. All indications are that the free jet reaches rotational temperatures near 1 K and there is no evidence of any intrusion by warm background gas.

Most large-cavity systems have vacuum chambers with volumes near 100 ℓ and utilize pumps in the range of 5000-8000 ℓ /s. The large pumps may permit somewhat higher repetition rates and longer pulse widths but these capabilities are often not utilized. It is true that for the large volume chambers a larger pump is needed (all other factors being identical).

D. Linewidth

One characteristic feature of cavity scale down is the fact that the transit time of molecules through the cavity is substantially shortened. In the Balle-Flygare design with 36-cm-diam reflectors, the beam waist radius at 18 GHz is $w_0 \approx 4.7$ cm, while in the compact system with 10-cm-diam reflectors reported here, $w_0 \approx 2.2$ cm at 18 GHz. With argon as the free-jet carrier gas, a terminal velocity of 5.4×10^4

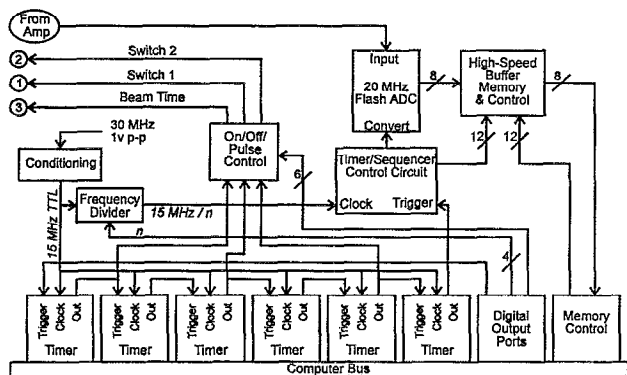


FIG. 3. Schematic of the control/acquisition subsystem. This represents essentially the boxes labeled ADC, Buffer Memory, and Timing Circuits in Fig. 2.

cm/s is reached for an expansion from a nozzle at 300 K. For the large cavity, the nominal transit time through the beam waist diameter would be $\approx 170 \mu\text{s}$, while the value for the small cavity would be $\approx 80 \mu\text{s}$. Since the fundamental polarization relaxation time T_2 is typically about $100 \mu\text{s}$, it is obvious that transit time decay becomes increasingly important for small cavities. The principal result of the shortened transit time is a shortened free-induction decay (FID) emission time. Thus for the small cavity of this work the FID has decayed to the few percent level in typically 30–40 μs , whereas the larger cavities permit observation times about twice as long. In the frequency domain, after Fourier transformation, the shorter relaxation time translates to an increased linewidth. Thus one may expect that cavity scale down will lead to broader lines.

III. EXPERIMENT

Figure 2 presents a block diagram of the newly constructed pulsed-valve, Fourier-transform microwave spectrometer. The electronics and system operation are essentially conventional and are based upon the Balle–Flygare⁶ design with the modification of Suenram *et al.*,⁹ which incorporates a single-side band modulator (SSBM) in place of a second microwave source (local oscillator). The microwave source is capable of generating frequencies in the 5–37 GHz region with accuracies of a few kHz. The “source” consists of an HP-8673H synthesized signal generator covering 5–18.5 GHz with active Avantek doublers which extend operation into the *K* and *R* bands. A 5 MHz signal from the 8673H serves as the phase coherent reference for the 30 MHz synthesized generator which itself drives the pulse-timing circuitry coherently.

The timing circuitry and all data collection and processing software were developed by the University of Kansas Instrumentation Design Laboratory. The pulse sequencing for the pin-diode microwave switches (American Microwave Corp.), pulsed valve (General Valve Corp.), and ADC is all conventional.

The control/acquisition subsystem (see Fig. 3) was custom designed for a 486 PC to achieve acquisition rates up to 10 MHz with precision timing of both the control signals and

the data acquisition. Real time software facilitates data processing during the acquisition. The control/acquisition clock is derived from the system’s 30 MHz source which is amplified and fed to a comparator. Six programmable countertimers precisely generate the switch control signals and delays and feed the ADC control. A high-speed (flash) ADC is synchronized to the 30 MHz clock, and the data array for a single FID is stored in onboard memory. At the end of the acquisition of a single FID, the circuit requests an interrupt. Within the interrupt service routine (ISR), the data array is added to the signal-averaging array. The process can be repeated at rates up to 20 Hz. Because the signal averaging takes place in the ISR, the main routine is free to display the averaged FID wave form, to accept changes to experimental variables, to perform fast Fourier transforms, and to display the results during the course of the experiment. The software was written in C++ (Borland International) with third-party GUI tools.

The first of the two major unique features of the spectrometer is the small Fabry–Perot cavity and pumping system mentioned earlier. The cavity consists of two 10-cm-diam aluminum reflectors, each having one surface machined with a 15 cm concave radius of curvature. In typical operations, the two reflectors have a separation near 13 cm. In the notation of Fig. 1, $a=5$ cm, $R=15$ cm, and $d=13$ cm. Microwave radiation is coupled into the cavity by means of a coupling iris (5/32 in. diam) fed by a standard piece of a rectangular *K*-band brass waveguide. The cavity should operate down to 15 GHz, but to date we have stayed in the 18–26 GHz range. As described earlier, the reflectors need a minor modification to reach lower frequencies, namely, either an increase in diameter a or a decrease in radius of curvature R according to Eq. (1).

In the present design, the reflector used for microwave input/output is fixed while the opposite reflector can be translated for a distance of ± 1.2 cm by means of a micrometer drive. Either manual or automated stepper-motor operation is possible. The loaded cavity Q is approximately 10 000 and the beam waist diameter is approximately 3.6 cm near mid-band (22 GHz). Note that the gross cavity volume is approximately 1.0 ℓ while the effective volume ($\pi w_0^2 d$) is 0.13 ℓ at 22 GHz.

This cavity is housed in a small vacuum chamber consisting of a six-arm stainless steel cross (6-in. diam arms, nominally) with a total volume of about 10 ℓ . A 6 in. un baffled oil-diffusion pump (Varian M-6) rated at 1500 ℓ/s pumps the system at a rate of 5×10^{19} molecules/s at 1 mTorr pressure. As described earlier, this pump rate is sufficient to handle the gas load from a 1-mm-diam nozzle operated at 5–10 Hz at backing conditions of 1 atm, 300 K and pulse widths of 250 μs .

The second unique spectrometer feature is the incorporation of a ceramic nozzle which can be heated to at least 1000 °C. The nozzle, sketched in Fig. 4, consists of a 1-mm-i.d. alumina tube which is resistively heated over a length of 2 cm. This tube is cemented into a brass fitting which connects to a water-cooled adaptor which in turn is connected via an O-ring vacuum seal to a conventional General Valve Corp. series 9 pulsed valve. A heating coil consisting of an

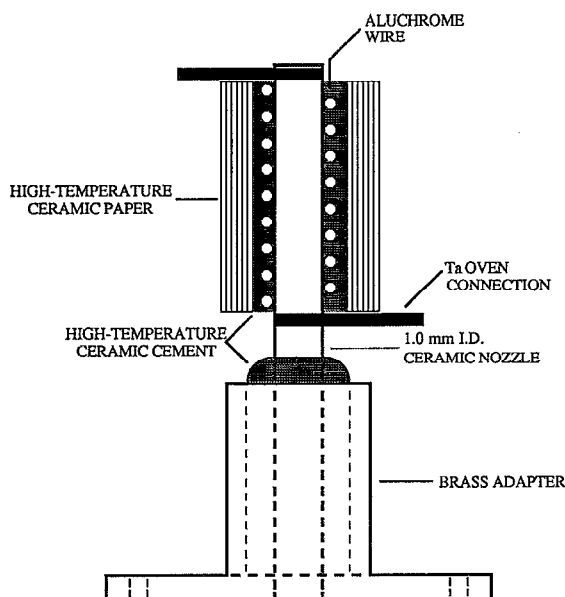


FIG. 4. A sketch of the heated ceramic nozzle assembly, not drawn to scale. The heated section has a length of approximately 2 cm.

Aluchrome resistance wire is insulated for efficiency by ceramic paper. Temperature calibrations have been performed by means of an imbedded chromel–alumel thermocouple. In practice, the dc power input to the coil is measured and converted to temperature by means of a calibration curve. A power input of 20 W leads to a temperature of approximately 1200 °C. The general characteristics of such hot nozzles have been described by Chen *et al.*²² We have found the nozzles especially useful for the production of simple carbenes for LIF studies.^{20,21}

IV. RESULTS

In order to demonstrate the key spectrometer characteristics discussed previously, tests have been made using several well-characterized molecular systems. In the following, results are presented for OCS, OCS·Ar, and ClHC=C=O (chloroketene).

A. OCS

The isotopic species of carbonyl sulfide provide excellent sensitivity tests. Most recently, FTMW spectra of the various isotopomers have been reported by Lovas *et al.*⁸ The $^{16}\text{O}^{12}\text{C}^{36}\text{S}$ and $^{18}\text{O}^{13}\text{C}^{32}\text{S}$ isotopomers, with natural abundances of 0.014% and 0.002% were among those studied in the earlier work. We have observed the $J = 2 \leftarrow 1$ transitions (ground vibrational states) of these isotopomers at 23 198.7 and 22 764.2 MHz, respectively,²⁵ with signal/noise (S/N) ratios near 30/1 and 4/1 after 1000 repetitions. (Note that at a 5 Hz repetition rate, this requires just over 3 min.) In their initial instrument paper, Lovas and Suenram⁸ report a S/N near 10/1 after 5000 repetitions for the $^{18}\text{O}^{13}\text{C}^{32}\text{S}$ $J = 1 \leftarrow 0$. With later improvements to their system⁹ (the inclusion of a SSBM and microwave amplifier, which makes the system comparable to ours), we estimate their S/N to be near 20/1 after 5000 repetitions, which would be 9/1 after

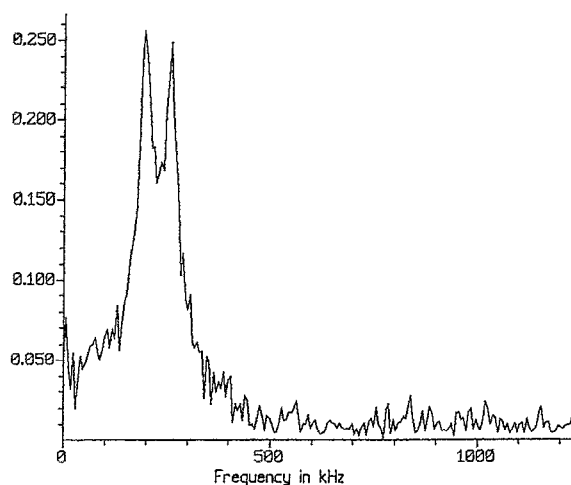


FIG. 5. $^{18}\text{O}^{13}\text{C}^{32}\text{S}$ $J = 2 \leftarrow 1$ ground state transition at 22 764.223 MHz. The argon carrier gas is at ~ 1 atm pressure and the nozzle temperature is ambient. The figure shows FT after 4000 repetitions of FID.

1000 repetitions. Thus, we see that the present compact FT spectrometer yields a sensitivity within about a factor of 2 of that from the large, conventional Balle–Flygare design. Figure 5 presents the $^{18}\text{O}^{13}\text{C}$ S transition obtained after 4000 repetitions of the free-induction decay.

In Sec. II, we found that the size difference between the Balle–Flygare system and the compact system led to the conclusion that the latter system would be less sensitive by a factor of about 4. Thus, the compact system actually appears somewhat better than even expected. A portion of this minor discrepancy surely comes from the factor $f(P_0, T_0, \dots)$ in Eq. (2). If μ_{ij} and the state populations at 1 K are considered, then the $J = 2 \leftarrow 1$ should gain a factor of approximately 2 compared to the $J = 1 \leftarrow 0$. In any case, the sensitivity of the compact FT system developed in this work is apparently only slightly less than that of the conventional Balle–Flygare spectrometer. In this regard we note that the sensitivity of the original Balle–Flygare spectrometer has been improved substantially by using a neon carrier gas rather than argon,⁸ and by pulsing the nozzle through one of the resonators so that the free jet is coaxial with the microwave cavity.²⁶ Presumably the same gains should accrue for the compact cavity as well.

Figure 6 presents as a typical example a tracing of two of the OCS $J = 2 \leftarrow 1$ excited state transitions observed with argon backing gas at room temperature. Note that the Doppler doubling⁶ in this trace is approximately 80 kHz, which is essentially twice as large as that observed by workers^{4,6,8} who have previously observed the $J = 1 \leftarrow 0$ lines near 12 GHz. This increase is in accord with the discussion of the Flygare group^{4,6} who suggest the splitting should be proportional to frequency. However, as observed by other workers,⁸ we find that the Doppler doubling depends in a complex fashion upon numerous details of the beam dynamics, such as backing pressure, temperature, sampling decay time, and valve pulse length.

The half-width at half-maximum intensity of each component of the doublet is approximately 35 kHz, some 2 or 3

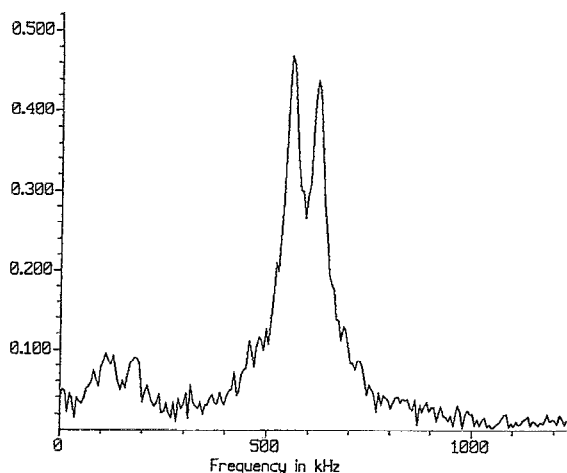


FIG. 6. OCS $J = 2 \leftarrow 1$ transitions in (100) and (002) excited states. The conditions are the same as in Fig. 5 but 3000 repetitions. The most intense (002) transition is at $\nu_0 = 589$ kHz while the weak (100) line appears at $\nu_0 = 149$ kHz, with $\nu_0 = 24\,180.050$ MHz.

times larger than reported by workers using the conventional-size Balle–Flygare FT system. As suggested earlier, this increased linewidth must be attributable to the short transit time through the microwave cavity. If the linewidth were determined by a single relaxation time τ , the required value of τ would be ≈ 5 μs , which is much shorter than the perpendicular transit time (≈ 80 μs) computed simply as $2W_0/v_T$, where v_T is the terminal velocity in the argon expansion. This suggests that the effective transit time is much shorter than even supposed. Physically this must mean that *on average* the emitting molecules couple into the cavity field for a relatively short time on the order of 5 μs . It would appear, therefore, that the compact cavity used here may be near the minimum permissible size for FT experiments. It should also be noted that the use of a nozzle which is coaxial with the cavity axis has been reported to lead not only to enhanced sensitivity but also to narrower lines.²⁶ Thus, it will be especially interesting to make this modification to the compact cavity system at a future time.

B. ArOCS

The carbonyl sulfide argon van der Waals complex has been observed easily in the K band with a sensitivity comparable to that reported in the earlier studies.^{8,27} We use 1% OCS in argon at pressures of ≈ 1 atm with the nozzle at ambient temperature. Table I summarizes the newly measured transitions with both a - and b -type selection rules. The data illustrate that the new FTMW spectrometer with a compact cavity produces perfectly fine results on van der Waals' complexes, substantiating the performance of the complete spectrometer but in particular the behavior of the free-jet expansion. Relative intensity measurements on several of the reported transitions in Table I suggested free-jet rotational temperatures in the vicinity of 1 K.

TABLE I. ArOCS transitions in K band.

Transition	Obs. (MHz)	Δ (kHz) ^a
1(1,1)→2(2,0)	21 875.090	-3
1(1,0)→2(2,1)	21 581.042	-1
2(1,1)→3(2,2)	24 033.001	-1
2(1,2)→3(2,1)	24 937.019	-7
3(1,2)→4(2,3)	26 341.118	0
6(0,6)→7(1,7)	21 071.348	+13
7(0,7)→8(1,8)	23 054.333	+11
7(1,7)→8(0,8)	18 568.786	-11
8(0,8)→9(1,9)	25 065.691	+5
7(0,7)→8(0,8)	21 064.360	0
8(0,8)→9(0,9)	23 518.937	-12
6(1,5)→7(1,6)	19 969.888	+6
7(1,6)→8(1,7)	22 747.803	-7

^aSee Ref. 27. When the above 13 lines were added to the 37 line fit of Ref. 27, the rotational constants changed by 1 kHz or less and the distortion constants by 0.2% or less. Δ represents the deviation from the predictions of the 50 line fit.

C. OCS satellites

As one test of the hot nozzle, several of the excited vibrational states of the normal isotopomers of OCS have been observed. Table II summarizes our observations for the CS ($00\nu_3$) and CO(ν_100) stretching states. It is, of course, well-known that vibrational modes do not cool efficiently in the supersonic free-jet expansion, so that the vibrational temperature (which may not be Boltzmann at all) is typically much higher than the rotational or translational temperatures. As seen in Table II we are able to see the (001), (002), and (100) states with an unheated nozzle even though these states lie 859, 1711, and 2062 cm^{-1} , respectively, above the ground (000) state. Even the lowest of these three states would be unobservable in our experiments if the vibrational temperature (T_v) were below approximately 100 K. In order to observe the higher states we must, however, heat the nozzle. In Table II we list the nozzle temperature needed to produce a signal comparable in intensity to that of the transition depicted in Fig. 4. We do not at this time have a theoretical understanding of the temperature dependence although it is clear that there is a nice monotonic behavior of nozzle temperature versus state energy. Grabow *et al.*²⁸ have observed OCS excited states by producing an electric discharge in the gas before the supersonic expansion. The present method has the clear advantage of being able to populate successive states selectively by choosing the nozzle temperature.

TABLE II. OCS excited state $J = 2 \leftarrow 1$ measurements.

State	Energy (cm^{-1})	Transition frequency (MHz)	Nozzle T ($^{\circ}\text{C}$)
(001)	859	24 253.387 ^a	23
(002)	1711	24 179.461 ^a	23
(100)	2062	24 180.199 ^a	23
(003)	2556	24 104.011	450
(004)	3394	24 026.883	775
(200)	4101	24 035.439	1120

^aThese transitions have previously been reported at lower precision. See Ref. 25.

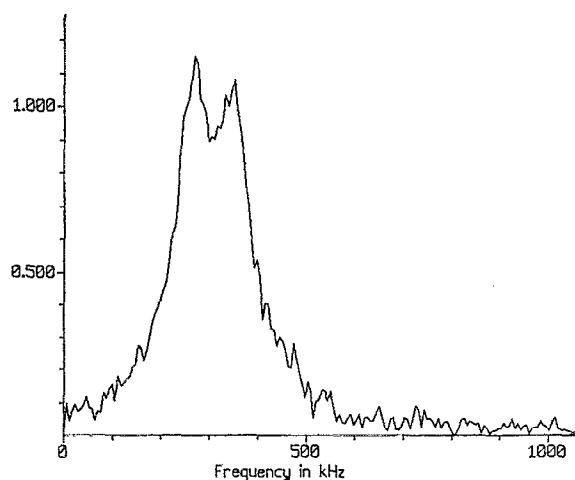


FIG. 7. Chloroketene $J=1_{11} \leftarrow 2_{02}$, $F=3/2 \leftarrow 5/2$ transition at 21 532.096 MHz. Nozzle temperature ≈ 800 °C, 2% chloroacetylchloride in argon carrier gas at 1.5 atm. The spectrum represents 500 repetitions of FID.

D. Chloroketene

As a final example of the hot nozzle we have pyrolyzed chloroacetylchloride ($\text{H}_2\text{CIC}-\text{COCl}$) in argon at temperatures above 500 °C. In accord with earlier work by Gerry *et al.*,²⁹ the pyrolysis leads initially to chloroketene ($\text{HCIC}=\text{C}=\text{O}$) by elimination of HCl. At still higher temperatures (≈ 1000 °C) the chloroketene loses CO to yield the CHCl carbene.²¹ We have observed the chloroketene intermediate at a temperature near 700 °C. This is demonstrated in Fig. 7 where the $J = 1_{11} \leftarrow 2_{02}$, $F = 3/2 \leftarrow 5/2$ line at $\nu = 21\,532.096$ MHz is shown. This line was obtained at a temperature of about 800 °C, which is near its optimum. At higher temperatures the intensity of the line decreases fairly markedly as the second stage pyrolysis sets in. Unfortunately, we cannot see the CHCl species because it has only a pair of $7 \rightarrow 7$ and $8 \rightarrow 8$ transitions available in our spectral region.³⁰ The lower states of these transitions lie rather high in energy (≈ 50 cm^{-1}) and consequently the rotational populations are very unfavorable for rotational temperatures of 1–5 K. Nevertheless the chloroketene observation illustrates nicely the potential of the hot nozzle for pyrolysis studies.

V. DISCUSSION

The design and testing of a new FT microwave spectrometer with a unique compact cavity and small pumping system has been described. The basic sensitivity is excellent in comparison to existing conventional systems with the free-jet operating in the perpendicular position. The greatly reduced size of the vacuum chamber and pumping system lead to a substantially reduced capital cost and also reduced operating and maintenance expenses. Moreover, the complete spectrometer, which includes one-third of a rack of electronics and a computer and display terminal, could be made portable with little effort.

Linewidths from the new spectrometer are greater than in large-cavity systems because of the short transit time of the free-jet molecules through the cavity. In future work it will be important to reposition the nozzle in the coaxial

configuration²⁶ in order to see if the linewidths narrow as expected. The line shape theory recently discussed in detail by Campbell³¹ suggests that this configuration may lead to widths which are limited only by transit time between the reflectors. Even with a short cavity as in the present case ($d \approx 13$ cm), this time is still much longer than the transit time in the perpendicular configuration.

The heated ceramic nozzle provides increased versatility to the FTMW spectrometer. We have demonstrated its use in populating rather high-lying excited states of a molecule such as OCS. It should be noted that an important aspect of these observations is that the rotational temperature remains quite low as the nozzle is heated. Theoretically, the translational temperature should scale directly with nozzle (reservoir gas) temperature¹⁸ and as usual the rotational temperature is expected to remain close to the translational temperature. Thus, we generate vibrationally hot but rotationally cold molecules. An interesting and important future experiment will be to see whether it is possible to populate the excited states of van der Waals' modes. Generally, these states (lying at perhaps 10–50 cm^{-1}) have populations which are too low to detect by FTMW experiments. We note, however, that Chuang and Gutowsky³² were able to detect some van der Waals' excited states even with a nozzle at ambient temperature.

FTMW studies of free radicals have been relatively limited, although nozzle electric discharge^{33,34} and laser vaporization methods³⁵ have had some notable success. Gutowsky also reported the formation of $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ by hot-nozzle pyrolysis. Based on the successful use of the hot-nozzle pyrolysis technique for other spectroscopic studies,^{20–22,36} it should have excellent potential for FTMW spectroscopy. The successful test reported here for chloroketene along with the earlier work of Gutowsky are certainly encouraging first steps. In addition, there exists the possibility that the procedure may be feasible for the production of argon-radical van der Waals' complexes, not unlike the experiment of Iida *et al.*¹⁵ who produced HgOCS complexes with a heated valve.

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