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Determination of nuclear spin–rotation coupling constants in CF_3I by chirped-pulse Fourier-transform microwave spectroscopy

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ABSTRACT

The rotational spectrum of CF_3I in the ground vibrational state has been re-measured using a chirped-pulse Fourier-transform microwave spectrometer recently constructed at the University of Bristol. The new spectrometer provides the capability to acquire broadband rotational spectra throughout an operational frequency range of 7–18 GHz. The frequencies of ninety-nine $F_1'–F_1'$ transitions in three distinct $J_K'–J_K''$ bands have been recorded during an experiment which required only a couple of hours of data collection. Many of these transitions have additionally been re-measured using a Balle–Flygare, Fourier-transform microwave spectrometer. Fitting the data to the Hamiltonian for a C_{3v} prolate, symmetric top has allowed the determination of new spectroscopic parameters. The rotational constant, B_0, and nuclear quadrupole coupling constant, $\chi_{aa}(I)$, are consistent with the results provided in earlier works. The nuclear magnetic spin–rotation constants, $C_{perp.}(I)$ and $C_{perp.}(F)$, have been independently determined for the first time. These parameters are evaluated as 6.92(5) kHz and 2.37(11) kHz respectively. A technical description of the new CP-FTMW instrument is presented.

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1. Introduction

The Balle–Flygare design of Fourier-transform microwave (FTMW) spectrometer [1], exploiting a Fabry–Perot cavity, is widely used to measure the rotational spectra of molecules between six and eighteen gigahertz. This instrument provides high resolution compared with earlier, sweep absorption methods and allows the measurement of rotational transitions across a twelve gigahertz frequency interval. The use of a Fabry–Perot cavity limits the bandwidth achieved in individual measurements to approximately one megahertz and requires the entire spectrum to be re-constructed from many distinct measurements which are each narrower than one megahertz in bandwidth. Since the initial development of the Balle–Flygare FTMW spectrometer, electronic sampling and computing technology has advanced considerably. It is now possible to measure, digitise and Fourier-transform a molecular free induction decay at frequencies significantly greater than one gigahertz. The opportunities presented by this improved capability have been exploited by Pate and co-workers for the construction of a novel chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer [2–4]. The Pate design of CP-FTMW spectrometer allows acquisition of a microwave spectrum across a broad, twelve gigahertz frequency interval in a single measurement. A chirped excitation pulse can be prepared to deliver highly uniform intensity across the entire bandwidth, allowing the intensities of rotational transitions to be accurately measured and compared.

The SACI (search-accelerated correct-intensity) [5] variant of CP-FTMW spectroscopy exploits the opportunity to collect data for the determination of molecular structure with greater speed and efficiency of sample consumption than achieved in conventional Balle–Flygare FTMW spectrometers. The data can be interpreted to yield rotational and hyperfine coupling constants to provide information about the molecular structure. The development of the CP-FTMW spectrometer has prompted the application of microwave spectroscopy to study an expanded range of chemical and physical phenomena. For example, the isomerisation dynamics of cyclopropane carboxaldehyde has been studied on the picosecond timescale [4]. New methods are being developed to apply CP-FTMW to the study of conformational isomerisation in biomolecules [6]. Very recently, a new version of the CP-FTMW spectrometer has been developed at a significantly reduced cost [7]. The many opportunities presented by this emergent technique have motivated the construction of a CP-FTMW spectrometer covering a frequency band between seven and eighteen gigahertz within our group. This work will present the design and technical details of the new instrument which has been evaluated and optimised through a study of the nuclear magnetic coupling constants in trifluoroiodomethane (CF_3I) by CP-FTMW spectroscopy.

The first study of CF_3I was completed by Sheridan and Gordy [8]. This was soon followed by a report providing a determination of the iodine nuclear quadrupole coupling constant through

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measurement of the pure quadrupole spectrum of the molecule [9]. CF_3I is a C_{3v} prolate symmetric top which possesses three distinct J_K'–J_K'' transitions between seven and eighteen gigahertz, each displaying extensive hyperfine structure. The molecule is notable for possessing a nuclear quadrupole coupling constant for iodine, $\chi_{aa}(I)$, similar in magnitude to the rotational constant, B_0. Cox et al. [10] and Jones and Kohler [11] studied the molecule using Stark-modulated microwave spectroscopy and infrared-microwave double resonance respectively. Walters et al. [12] were able to improve on the accuracy of the rotational parameters in the vibrational ground state and further studied excited vibrational states of the molecule. This work presents several new parameters determined through measurements exploiting the new CP-FTMW spectrometer and also an existing Balle–Flygare FTMW spectrometer. The nuclear spin–rotation constant, $C_{perp.}(I)$, for the iodine atom and nuclear spin–rotation constants, $C_{perp.}(F)$, for each of the fluorine atoms have been determined for the first time.

2. Experimental

The CP-FTMW spectrometer shares many of the characteristics of that previously described by Brown et al. [2]. Many of the components used to prepare the microwave excitation pulse and detect the molecular emission are the same as those chosen by Brown et al. while the vacuum chamber has been uniquely designed and constructed to meet the specific needs of our group. The operation of this instrument will be described extensively in Sections 2.1–2.3 and a brief description of the existing Balle–Flygare FTMW spectrometer will be provided in Section 2.4. Details of the microwave circuit and vacuum chamber of the CP-FTMW spectrometer are provided in Figs. 1 and 2.

2.1. Generation and amplification of chirped microwave pulses

A complete circuit diagram of the new instrument is shown in Fig. 1. An arbitrary waveform generator (Tektronix, AWG7102B) is used for initial generation of the chirped microwave pulse. This AWG has a sampling rate of 20 GS/s when operated in the interleaved mode and allows the generation of chirped pulses of frequencies between 0 and 10 GHz. Mixing of the primary pulse with the AWG internal clock generates an image sweep with frequency of $20\ GHz - x$ (where x is the programmed frequency sweep). This image sweep allows chirped pulses to be generated with frequencies between 10 and 12 GHz. Pulse durations between 0.5 and 1 μs were employed during the present study with a duration of 1 μs found to give the most intense signals. The pin diode switch required to protect the low-noise amplifier from the high-intensity chirped excitation pulse is specified to open for a maximum duration of one microsecond. For this reason, excitation pulses of greater duration were not used. It is anticipated that
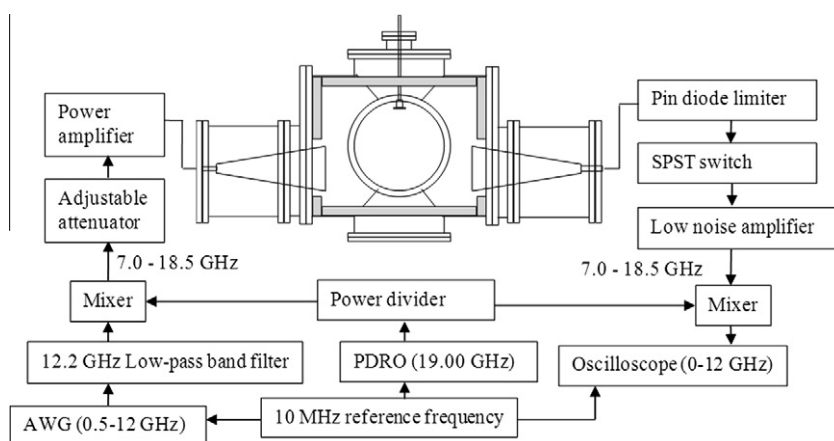
Fig. 1. Circuit diagram of the CP-FTMW spectrometer. The dimensions of the vacuum chamber are shown in Fig. 2.
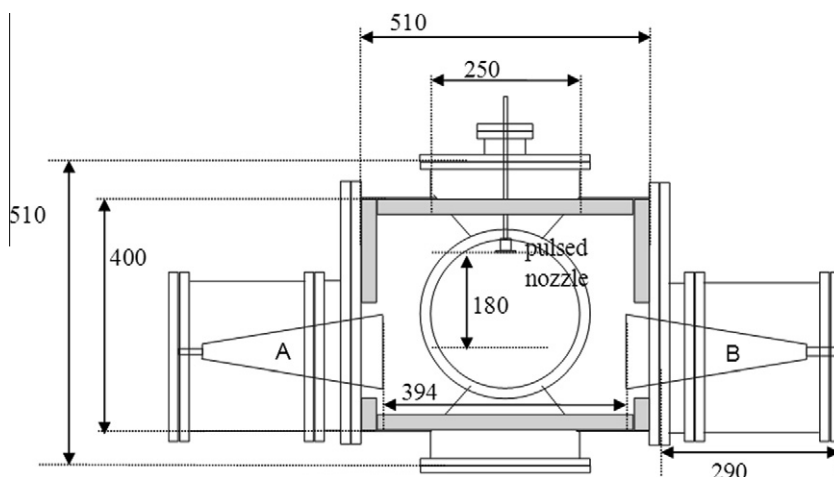
Fig. 2. Schematic diagram of the vacuum chamber used in the CP-FTMW spectrometer. All dimensions are given in millimetres. The microwave-absorbent foam is shaded grey and the two horn antennae are labelled A and B respectively. The output of each horn antenna is 127 mm by 178 mm (5″ by 7″).

excitation pulses of slightly greater duration may yield more intense signals [5].

The AWG output passes through a low-pass filter (12.2 GHz, Lorch 11LA-12200-s) to remove unwanted image frequencies above 12 GHz. A phase-locked dielectric resonant oscillator (Herley CTI, XPDRO-14373) supplies a 19.00 GHz signal to the local oscillator of a triple-balanced mixer in order to convert the AWG output into frequencies within a 7–18 GHz range. The AWG and phase-locked dielectric resonant oscillator (PDRO) are each phase-locked to a 10 MHz frequency reference (Symmetricom 58533A, GPS time and frequency reference receiver) accurate to 1 part in 10^{12}. Adjustable attenuators (Agilent 8494B and 8495B) allow the intensity of the pulse to be optimised with respect to the intensity of the observed molecular emission. The specifications of amplifier necessary to simultaneously excite transitions over a 12 GHz bandwidth are discussed by Brown et al. [2]. The data presented herein were acquired using a 5 W solid-state amplifier (Microwave Power, 0818-37). Consistent with the previous study [2], this model of amplifier did not yield excitation pulses sufficiently intense to yield strong molecular emission signals when used in conjunction with a chirped pulse sweeping 10 GHz in frequency.

CF_3I possesses a comparatively large value [10] for μ_a of 1.048(3) D and the molecular emission signal following chirped pulse excitation scales with the square of the dipole moment [2]. Amplified frequency chirps prepared to sweep over a 0.8 GHz frequency range were found to allow the observation of strong lines in the $J_{K'}'–J_{K''}'' = 5–4$ transition of CF_3I after fewer than ten averaging cycles. The amplifier is activated by a 5 V TTL pulse synchronised to coincide with the chirped pulse. Pulsing the amplifier ensures that the level of amplified noise transmitted into the chamber and detected while measuring the molecular emission is minimised. The cooling which is required to prevent the amplifier overheating is also reduced when this device is operated in pulsed mode.

2.2. Interaction of chirped excitation pulse with the molecular beam

The CP-FTMW spectrometer has been constructed with the aim of studying the microwave spectra of rotationally-cold, gas phase molecules that are generated within a supersonic jet. An evacuated chamber provides the necessary environment for generating and interrogating such cold, molecular complexes. The current design of vacuum chamber (Fig. 2) is flexible enough to allow optimisation of the instrument with respect to the positions and orientations of the pulsed nozzle and horn antennae. The design will further allow future development of the instrument to include a laser ablation source for the study of metal-containing complexes. The vacuum chamber consists of a six-way cross with four ISO 250 ports. The chamber is evacuated using a diffusion pump (Edwards, Diffstak 250) mounted on one of these ports. Two larger ISO 400 ports are positioned on opposite sides of the chamber. Each of these larger ports is mated to an offset reducing adapter and tubular section which encloses one of the broadband horn antennae (ATM, 750-442-C3) used for the transmission and detection of microwave radiation. These horns are each mounted on an ISO 250 flange at a bulkhead (ATM, 750-130-3.75-G3-G3) with waveguide feedthrough. Each feedthrough is connected directly to either the excitation or detection circuit using a double-ridged waveguide (WRD 750) to SMA co-axial adapter (ATM, 750-251-C3).

The pulsed nozzle (Series 9, General Valve) is mounted on an ISO 250 flange which is positioned approximately half-way between the two horns. This nozzle is oriented so that complexes generated within the supersonic jet travel perpendicular to the propagation of the microwave excitation pulse. The gas sample contains ~1% CF_3I in a balance of argon at a backing pressure of 1 atm. Two different arrangements of pulsed nozzle source and driver were tested while configuring the instrument to generate a supersonic expansion and observe the rotational spectrum of CF_3I. The spectra presented herein were all obtained using a nozzle driven by an Iota One driver (Parker Hannifin) with typical nozzle pulse durations of 320 µs. An equally intense rotational spectrum was also observed using the same model of nozzle instead driven by a 20 V output pulse of ~3.5 ms supplied directly from a delay generator (Quantum Composers, 9518+). It has been shown that the molecular emission signal scales linearly with the number of nozzles employed in a CP-FTMW spectrometer [2]. If it proves possible to generate a wide variety of rotationally-cold molecules and complexes while driving more than one nozzle directly from a single delay generator, the cost of adding nozzles to the present design of spectrometer will be significantly reduced.

The axis of the detection horn is aligned to be co-linear with the axis of the excitation horn thus allowing the transmitted power of the chirped excitation pulse to be monitored during optimisation of the switch and power amplifier timings. Transmission loss between the two horns is measured to be 5–7 dB in the current arrangement. Operation of the CP-FTMW spectrometer requires the chirped excitation pulse to be overlapped spatially and temporally with a supersonically-expanding jet of gas from a pulsed nozzle. The nozzle pulse duration and the distance from the pulsed nozzle to the horn axis can be easily adjusted and optimised to yield rotationally-cold molecules which display transitions in the required frequency range. The programmable delay generator is used to delay the chirped excitation pulse with respect to the nozzle pulse. The optimal delay time was identified to be between 900 and 1100 µs for the experiments described herein.

Rotationally-excited molecules within the expanding jet begin to coherently emit microwaves soon after absorbing a fraction of the incident radiation from the excitation pulse. However, the presence of reflective metal surfaces inside the chamber causes intense resonances that persist significantly beyond the duration of the pulse. It is therefore not possible to begin measurement of the molecular emission until these chamber resonances have completely dissipated. Two flat sheets of microwave-absorbent, carbon-loaded polyurethane foam (Emerson and Cuming, Eccosorb HR-1) cover the surfaces of the two opposed ISO 400 flanges. A rectangular hole is cut in each of these sheets to accommodate the output of each horn. A thin metal sheath is rolled to fit inside the length and sixteen inch diameter of the chamber. This sheath is covered with the foam to comprehensively cover the inside of the chamber thus minimising the number of reflective surfaces present to support chamber resonances. Thus, the delay necessary between deactivation of the pulse and measurement of the molecular free induction decay is reduced to less than a microsecond. A 400 mm orifice immediately above the diffusion pump is uncovered by foam. A fine mesh prevents any detached foam from falling into the diffusion pump while still allowing efficient evacuation of the chamber. A much smaller orifice in the top of the sheath allows the nozzle to be positioned within the chamber.

2.3. Detection and transform of the free induction decay

A fraction of the total molecular emission is directed toward the receiving horn and hence transmitted into the detection circuit. The intensity of the measured molecular emission is significantly lower than that of the chirped excitation pulse which also enters the receiving horn. Several components are used to protect the sensitive, low-noise amplifier from the high intensity, chirped excitation pulse prior to detection of the molecular emission. A pin diode limiter (ACLM-4539C6R1K) is located immediately after the receiving horn. A single-pole, single-throw (SPST) pin diode switch (Arra, H8753-80D) is synchronised to effectively block the chirped excitation pulse during its transmission.

After decay of the chirped excitation pulse and the associated chamber resonances, the SPST switch is closed to allow the amplification and measurement of the molecular free induction decay. The free induction decay between 7 and 18.5 GHz is mixed down against the same 19.00 GHz reference signal used by the excitation circuit yielding frequencies between 0.5 and 12 GHz. A power divider (ATM, P218) is used to split the 19.00 GHz signal from the PDRO, so that it may be used in both the excitation and detection circuits. A digital oscilloscope (Tektronix, DPO71254) is used to digitise the free induction decay which is then Fourier-transformed to yield the power spectrum. The free induction decay can be averaged over many nozzle pulses to improve the signal/noise ratio of measurements. Measuring and averaging many consecutive free induction decays of several gigahertz in frequency requires a measurement trigger that is stable and reproducible on a timescale of picoseconds. A marker channel on the AWG provides this level of stability and is used to supply the measurement trigger to the oscilloscope. The oscilloscope is phase-locked to the same 10 MHz external frequency reference used by the PDRO and AWG.

The observed hyperfine components of CF_3I have a linewidth (Full width at half maximum) of approximately 80 kHz. At this resolution, the achievable linewidth is limited by the maximum duration of free induction decay which can be measured without degradation of the signal/noise ratio seen in the power spectrum. Experiments conducted on OCS confirm that the free induction decay can be measured over a long period, significantly reducing the linewidth in the power spectrum, where a strong molecular emission signal can be detected. In the present spectrometer, where the propagation of microwaves and the supersonic jet are arranged to be mutually perpendicular and where argon is typically used as a backing gas, Doppler broadening becomes significant (particularly at higher frequencies) if a digital resolution on the order of 40 kHz can be achieved. This order of linewidth has been obtained in several measurements of the intense transition of $^{16}O^{12}C^{32}S$ at 12162.979 MHz.

2.4. The Balle–Flygare FTMW spectrometer

The Balle–Flygare Fourier-transform microwave spectrometer is described in a previous work [13] so only a brief description will be provided here. A gas sample is pulsed from the orifice of a supersonic nozzle source and expands into the Fabry–Perot cavity through an orifice in the centre of a stationary mirror. The cavity consists of two spherical aluminium mirrors (diameter = 35 cm; radius of curvature = 84 cm) separated by approximately 70 cm. A gas sample of ~0.5% CF_3I in argon at a pressure of 1 atmosphere is used. The parallel propagation of the gas and microwave pulses enhances the resolution and sensitivity of the instrument but also increases the well-known Doppler splitting of each hyperfine component so that two peaks are observed for each spectral transition. The line frequency is determined by finding the average of the frequencies of the two Doppler components. Molecules are excited to higher rotational states by the microwave pulse if the transition from the lower state is resonant or nearly resonant with the radiation and subsequently undergo relaxation by spontaneous coherent emission at the transition frequency. The free induction decay is detected and Fourier-transformed to yield a plot of emission intensity against frequency. The experimental cycle described above is repeated and averaged as necessary to obtain a satisfactory signal-to-noise ratio for measured lines. A repetition rate of 4 Hz was used for the described experiments. All frequency measurements are referenced to an external source that is accurate to 1 part in 10^{12}. The same frequency reference source is employed on both the Balle–Flygare and the CP-FTMW spectrometer. Individual hyperfine components have a full width at half height of 5 kHz

and their frequencies are consequently measured with an estimated accuracy of ±0.5 kHz.

3. Results

### 3.1. CP-FTMW spectroscopy of CF_3I

CF_3I is a prolate, C_{3v}, symmetric top which possesses a microwave spectrum with intense a-type transitions. Values for the B_0 rotational constant determined previously [8–12] are consistent with a spectrum containing three J_K'–J_K'' transitions between 7 and 18 GHz. All three J_K'–J_K'' transitions can be observed simultaneously using the broadband capability of the CP-FTMW spectrometer. All three transitions were observed in a spectrum which used an excitation pulse chirped from 9 to 18.5 GHz and 1 µs in duration. Under these experimental conditions, only the strongest hyperfine components of each transition were observed after five minutes of averaging at a repetition rate approaching 3 Hz. As discussed above, the present amplifier does not provide sufficient gain to optimally acquire spectra across the full bandwidth of the instrument. Molecular emission signals that follow the chirped pulse excitation decrease with the square root of the excitation pulse bandwidth [14]. Reducing the frequency sweep of the excitation pulse ensures more efficient excitation of transitions within the selected bandwidth.

Three different chirped excitation pulses were therefore used in distinct measurements of the $J'–J'' = 5–4$, $J'–J'' = 4–3$ and $J'–J'' = 3–2$ transitions. In each case, the chirped excitation pulse covered a very broad frequency range appropriate to the expected hyperfine structure. Thirty-six hyperfine components were identified in the $J'–J'' = 5–4$ transition (Fig. 3) after averaging approximately three thousand nozzle pulses (about half an hour). The strongest components in this transition can be clearly seen after a few seconds of averaging (about 10 nozzle pulses). The molecular emission signals measured at lower frequencies are less intense and require greater acquisition times. Observation of the strongest hyperfine components in the $J'–J'' = 3–2$ transition requires fifty averaging cycles corresponding to approximately thirty seconds of time. Thirty-nine hyperfine components have been assigned to the $J'–J'' = 4–3$ transition and twenty-four components to the $J'–J'' = 3–2$. The observed transitions have been fit to the Hamiltonian for a symmetric top using the PGOPHER program [15]. The quantum number assignments used are $\mathbf{J} + \mathbf{I}_I = \mathbf{F}_1$.

Walters et al. [12] precisely determined the centrifugal distortion constants, Δ_J and Δ_{JK}, through measurements of transitions at higher frequencies than those measured during the present work. These parameters were therefore held fixed at the values provided by Walters et al. A fit of B_0 and $\chi_{aa}(I)$ to the frequencies of the $F_1'–F_1''$ transitions yields values for these two parameters which are consistent with those presented in earlier works [8–12]. However, the observed residuals are found to be greatest in respect of transitions with the highest F_1 quantum numbers and a comparatively high standard deviation of 17 kHz is obtained. The inclusion of one of the nuclear magnetic spin–rotation constants of iodine, $C_{perp}(I)$, yields precisely-determined values for all parameters and significantly reduces the standard deviation of the fit to ~6 kHz, consistent with the ~80 kHz width of the observed spectral lines. Inclusion of the $C_{aa}(I)$ constant does not yield a well-determined value for this parameter. The results of the fit to the data acquired using the CP-FTMW spectrometer are shown in Table 1.

Hyperfine components in the $J'–J'' = 5–4$ transition are displayed in Fig. 3 above a simulation prepared using PGOPHER and the evaluated constants. The large value of $\chi_{aa}(I)$ for iodine causes the hyperfine structure associated with this transition to be spread over 350 MHz in frequency. The observed spectrum is in good
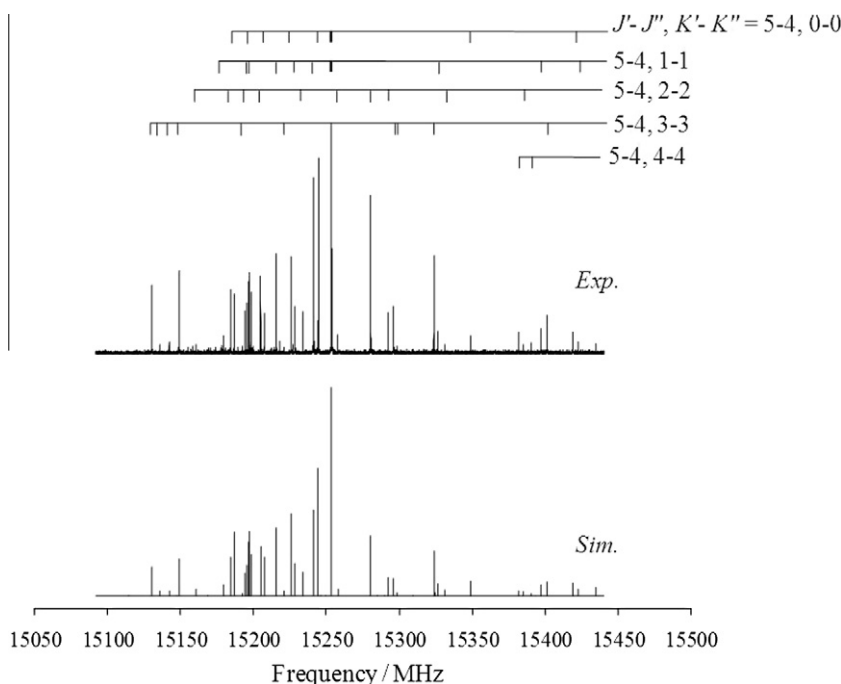
Fig. 3. Measured and assigned transitions for the J'–J'' = 5–4 transition of CF_3I. The observed spectrum (top) after ~3000 nozzle pulses (half an hour of averaging) is compared with a simulation (bottom) which assumes a temperature of 1 K and A_0 = 5600 MHz.

Table 1
Rotational, centrifugal distortion and hyperfine coupling parameters evaluated from the observed rotational spectrum. Numbers in parentheses are one standard deviation in units of the last significant figure.

	CF_3I(CP-FTMW)	CF_3I(Balle–Flygare)	CF_3I(Ref. [12])
B_0 (MHz)	1523.28226(9)	1523.28287(2)	1523.28267(9)
Δ_J (kHz)	0.16462[a]	0.16462[a]	0.16462(2)
Δ_{JK} (kHz)	0.9925[a]	0.9925[a]	0.9925(4)
χ_{aa}(I) (MHz)	−2145.017(11)	−2144.9949(28)	−2145.207(3)
$C_{perp.}$(I) (kHz)	6.88(25)	6.92(5)	4.7(6)
$C_{perp.}$(F) (kHz)	–	2.37(11)	–
N	99	51	
σ_{rms} (kHz)	6.1	0.9	

[a] Fixed at the value of the parameter determined in Ref. [12].

agreement with the simulation which assumes a rotational temperature of 1 K. Fig. 4 compares the simulation with an expanded portion of the observed spectrum. The plots shown in both figures
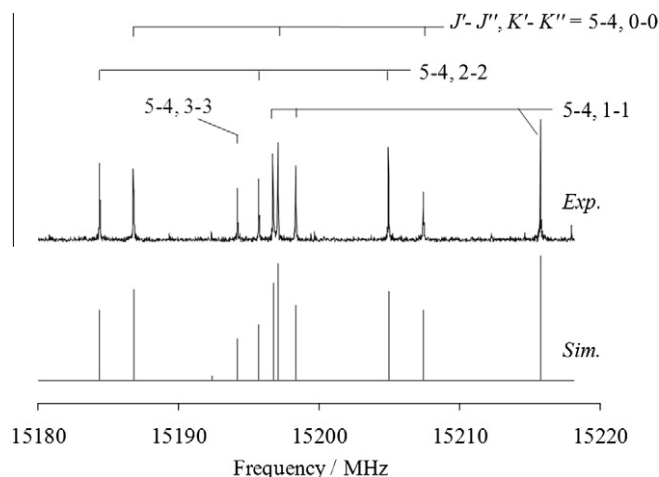

Fig. 4. Expanded section of the J'–J'' = 5–4 transition shown in Fig. 3. The observed spectrum (top) is compared with the simulation (bottom).

demonstrate several advantages of the CP-FTMW technique. Firstly, there is excellent agreement between the intensities of lines in the simulation and those measured experimentally. Secondly, peaks which cannot be assigned to the rotational spectrum of CF_3I are extremely scarce within the observed spectra. Given the comparatively high resolution of the technique, coincidences between individual transitions for different molecules and isotopologues will be extremely rare in most spectra. A small proportion (<5%) of the peaks identified in the spectra do not assign to transitions in the rotational spectrum of the vibrational ground state of CF_3I. These do not readily assign to rotational transitions in the vibrational ground state of $^{13}CF_3I$ or to the vibrationally-excited states of CF_3I characterised by Jones and Kohler [11] and Walters et al. [12]. Attempts to identify their origin were unsuccessful. It is possible that the unassigned transitions indicate the formation of complexes formed between CF_3I and argon atoms within the carrier gas. Alternatively, dimers and higher clusters of CF_3I may also be present.

3.2. Balle–Flygare FTMW spectroscopy of CF_3I

The frequencies of a range of F_1'–F_1'' transitions were re-measured using a Balle–Flygare FTMW spectrometer to evaluate the performance of the new CP-FTMW spectrometer against benchmark measurements performed at higher resolution. It was necessary to individually measure each transition using the Balle–Flygare instrument owing to the 1 MHz bandwidth of the Fabry–Perot cavity employed. However, the higher resolution of this instrument allows additional coupling effects to be determined with greater precision. Fig. 5 provides an illustration of the additional coupling effects that are apparent in the spectrum when measured at high resolution. Some transitions are observed to be extensively split while others are broader than expected given the instrumental resolution. The splitting was seen in components with all values of J and K probed during this work.

In addition to the I = 5/2 nucleus of iodine, CF_3I contains three fluorine nuclei which each have I = 1/2. These are interchanged
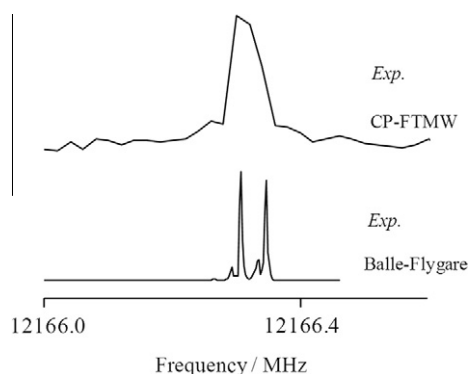
Fig. 5. The $J_K'-J_K''$, $F_1-F_1' = 4_0-3_0$, $\frac{9}{2}-\frac{7}{2}$, transition measured using the CP-FTMW spectrometer (top) and the Balle–Flygare spectrometer (bottom). Approximately 3000 averaging cycles were used to acquire the CP-FTMW spectrum which covered 1 GHz in bandwidth. A narrower, 0.5 MHz interval was probed using the Balle–Flygare spectrometer where 200 nozzle pulses yielded the data shown. In addition to the splitting characteristic of the Doppler effect, further structure yielded by nuclear spin–rotation coupling of the fluorine nuclei is present.

by a C_3 rotation such that the nuclear spin–rotation constant $C_{\text{perp.}}(F)$ is equal for all three nuclei. Each additional coupling nucleus increases the number of hyperfine components. The intensity of each $F_1'-F_1''$ transition is thus distributed over many components lying within a narrow (<50 kHz) frequency range. It is clearly not possible to explicitly distinguish between all of these given the resolution of the instrument. However, many of the observed hyperfine components merge into single features which can be resolved and depend sensitively upon the value of $C_{\text{perp.}}(F)$. The frequencies of these transitions have been included in a fit to determine $C_{\text{perp.}}(F)$ for all fluorine nuclei using Pickett's SPFIT [16]. The coupling scheme employed here is $\mathbf{J} + \mathbf{I}_I = \mathbf{F}_1$, $\mathbf{F}_1 + \mathbf{I}_{\text{tot.}} = \mathbf{F}$ where $\mathbf{I}_{\text{tot.}}$ is the vector sum of the spins of the three equivalent fluorine nuclei. Again, the centrifugal distortion constants are held fixed at the values accurately determined by Walters et al. [12]. The rotational constant, B_0, nuclear quadrupole coupling constant, $\chi_{aa}(I)$, and nuclear spin–rotation constants, $C_{\text{perp.}}(I)$ and $C_{\text{perp.}}(F)$, are presented in Table 1. The value of $C_{\text{perp.}}(F)$ is precisely-evaluated as 2.37(11) kHz and the standard deviation of the fit is less than 1 kHz. The inclusion of other nuclear spin–rotation (C_{aa} for iodine or the fluorine atoms) and spin–spin coupling terms does not improve the precision of the fit or yield well-determined parameters. Fits were performed to test whether $\chi_K(I)$ or $\chi_J(I)$ contribute to the frequencies of the observed lines. These did not reveal any measurable dependence of the nuclear quadrupole coupling constant on either K or J.

There is good agreement between the values of $\chi_{aa}(I)$ and $C_{\text{perp.}}(I)$ determined using the CP-FTMW and Balle–Flygare instruments respectively. The rotational constant measured using the CP-FTMW spectrometer is lower than that measured using the Balle–Flygare instrument by a quantity that exceeds the standard deviations of the experimental measurements. It follows that the peak intensities of transitions measured using the CP-FTMW spectrometer have been shifted to slightly lower frequencies (on average) than those measured using the Balle–Flygare instrument by ~10 kHz. Independent measurements of the $J'-J'' = 1-0$ transition of OCS at 12162.979 MHz support this observation. The frequency of this transition is correctly reproduced by the Balle–Flygare spectrometer but the peak intensity of the transition appears lower by ~10 kHz when measured using the CP-FTMW spectrometer. The difference between these measurements can be understood by consideration of the different velocities of the supersonic jets relative to the axes of microwave propagation in the two spectrometers. The supersonic jet is aligned perpendicular to the propagation of the

microwave pulse in the CP-FTMW spectrometer. The implication is that emission from molecules travelling toward the receiving horn antenna is detected with greater intensity than that from molecules travelling toward the transmitting horn. This may result from an asymmetric gas expansion or from more efficient detection of the emission from molecules approaching the detection horn. It will be important to correct or account for this effect when using the new CP-FTMW instrument for further studies. The axis of the supersonic jet in the Balle–Flygare spectrometer is parallel with the propagation of the microwave pulse resulting in two Doppler components which can be averaged to yield precisely the transition frequency. For the purposes of this work, it should be noted that the Balle–Flygare instrument provides the most accurate determination of the transition frequencies and the rotational constant. The value is in reasonable agreement with the value provided by Walters et al. [12] though is not within the experimental error.

4. Conclusions

Three $J_K'-J_K''$ transitions in the rotational spectrum of CF_3I have been measured between 7 and 18 GHz. The sensitivity of the new CP-FTMW spectrometer is sufficient to measure ninety-nine hyperfine components in this frequency range within a single period of data collection requiring only a couple of hours. Hyperfine components within the spectrum have also been measured using a Balle–Flygare FTMW spectrometer. Fitting these data allow determination of the nuclear spin–rotation constants, $C_{\text{perp.}}(I) = 6.92(5)$ kHz and $C_{\text{perp.}}(F) = 2.37(11)$ kHz. The results obtained using the new CP-FTMW spectrometer are consistent with those obtained during earlier works and with the data obtained at high resolution using the Balle–Flygare FTMW spectrometer.

Appendix A. Supplementary data

Supplementary data for this article are available on Science Direct (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jms.2010.06.007.

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