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Rotational spectroscopy of iodobenzene and iodobenzene–neon with a direct digital 2–8 GHz chirped-pulse Fourier transform microwave spectrometer

Justin L. Neill^a, Steven T. Shipman^{a,1}, Leonardo Alvarez-Valtierra^{a,2}, Alberto Lesarri^b, Zbigniew Kisiel^c, Brooks H. Pate^{a,*}

^a Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA, United States ^b Departamento Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain ^c Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland

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ABSTRACT

The design of a chirped-pulse Fourier transform microwave spectrometer operating in the 2–8 GHz frequency range is presented. The linear frequency sweep is generated by an arbitrary waveform generator with a sampling rate of 20 GS/s. After amplification, the microwave pulse is broadcast into a vacuum chamber where it interacts with a supersonically expanded molecular sample. The resulting molecular free induction decay signal is amplified and digitized directly on a digital oscilloscope with a 20 GS/s sampling rate. No frequency mixing or multiplication is necessary in this spectrometer, which allows for very high pulse quality and phase stability. The performance of this spectrometer is demonstrated on the rotational spectrum of iodobenzene. All four distinct singly-substituted ¹³C isotopologues have been detected in natural abundance, as well as two isotopic species of a van der Waals cluster of iodobenzene with a neon atom. Spectroscopic constants and derived structural parameters for iodobenzene and for iodobenzene–Ne are reported. In addition, the use of microwave–microwave double-resonance experiments in this spectrometer to facilitate spectral assignments is presented.

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1. Introduction

Rotational spectroscopy is a powerful technique for the study of gas-phase molecular structure [1–3]. A molecule's rotational spectrum is highly sensitive to small structural changes, and often displays other effects such as nuclear quadrupole coupling and internal rotation splitting that provide structural information. Moreover, through an analysis of the spectra of isotopically substituted species, structural parameters can be experimentally derived from isotopic shifts of the molecule's moments of inertia [4–7].

The development of Fourier transform microwave (FTMW) spectroscopy coupled to a pulsed molecular beam source by Balle and Flygare [8–10] revolutionized the field of microwave spectroscopy due to the enhancement in sensitivity and spectral resolution it provided, as well as its ability to study weakly bound clusters. A number of modifications to their original design have been made by researchers over the years [11–13], including the development of double-resonance spectroscopic techniques to facilitate spectral

interpretation [14–17]. A large number of studies of systems with multiple conformers [18–20], of weakly bound molecular clusters [21–28], of metal-containing molecules [29–32], and of molecules of biological interest [33–35] using this spectrometer design have been reported. The Balle–Flygare FTMW spectrometer employs a Fabry–Perot cavity consisting of two spherical mirrors to amplify both the microwave polarizing pulse and the molecular free induction decay (FID) signal that results when resonant polarization occurs. However, the trade-off for this sensitivity gain is that the cavity can only detect transitions in a narrow bandwidth (typically \sim 1 MHz or less). Therefore, to acquire a spectrum, the cavity length and the frequency of the microwave polarizing pulse must be scanned.

The development of chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy [36], made possible by advances in high-speed digital electronics for microwave signal generation and detection, has dramatically increased the speed with which sensitive, high dynamic range, broadband microwave spectra can be acquired. No resonator is employed; instead, horn antennas are used to broadcast and receive the microwave radiation. However, the lower single-shot signal-to-noise ratio in the CP-FTMW spectrometer is compensated for by the simultaneous measurement of transitions across a large bandwidth (7.0–18.5 GHz in the previously reported configuration) and the ability to perform extensive time-domain signal averaging, making the acquisition

^{*} Corresponding author. Fax: +1 434 924 3710.

E-mail address: brookspate@virginia.edu (B.H. Pate).

¹ Present address: Division of Natural Sciences, New College of Florida, 5800 Bay Shore Road, Sarasota, FL 34243, United States.

² Present address: Division de Ciencias e Ingenierias, Universidad de Guanajuato, Leon, Gto. 37150, Mexico.

of a broad-bandwidth spectrum more efficient through this multiplex approach. Additionally, due to the absence of a resonator, the relative transition intensities observed by CP-FTMW spectroscopy are accurate to within 20% across a large dynamic range [36], allowing for easier spectral assignment. Applications of CP-FTMW spectroscopy in the 7.0–18.5 GHz frequency range to this date have included many-conformer systems [37–42] and systems with complex nuclear quadrupole hyperfine structure [43–45].

To study larger systems by rotational spectroscopy, such as molecules of biological interest or containing heavier atoms (such as metals or large halides), it is often desirable to obtain spectra at lower frequencies. As a molecule's size increases, its Boltzmann intensity peak at molecular jet temperatures falls into the 2-8 GHz spectral region. This is illustrated in Fig. 1, where simulated rotational spectra of molecules of increasing size, at a typical pulsed-jet rotational temperature of 1 K, are compared. The rotational spectrum of the lowest-energy conformer (*trans*) of ethyl formate (panel A, five heavy atoms, mass 74.08 u) [46,47] has very little transition intensity in this region. For a larger molecule such as tryptophol (panel B, 12 heavy atoms, 161.20 u) [48], there is a great deal more intensity from 2-8 GHz, but a large number of strong transitions exist above 8 GHz as well. As molecular size increases further, however, spectrometers below 10 GHz become necessary. The calculated rotational spectrum of the tripeptide antioxidant glutathione (panel C, 20 heavy atoms, mass 307.32 u) has very little intensity above 10 GHz, and so a high-sensitivity rotational spectroscopy technique for the 2-8 GHz region is required for pulsed-jet microwave studies of systems of this size.

In a cavity FTMW spectrometer, sensitive operation below \sim 4 GHz is difficult, as diffraction sets the low-frequency limit of the spectrometer. The original cavity FTMW spectrometer design of Balle and Flygare contained mirrors with a diameter of 36 cm and achieved a lower-frequency limit of 4.5 GHz. One way to improve the low-frequency performance of a cavity FTMW spectrometer is to increase the size of the mirrors; one such spectrometer with mirrors 122 cm in diameter, operating down to 1 GHz, has been recently described [49]. Specially designed smaller spectrometers have also been able to achieve lower operating frequencies.



Fig. 1. Simulated rotational spectra (at a temperature of 1 K) of several molecules as a function of size. (A) Most stable conformer (*trans*) of ethyl formate, using experimental rotational constants (A = 17746.7 MHz, B = 2904.7 MHz, C = 2579.1 MHz) and dipole moments ($\mu_a = 1.85$ D, $\mu_b = 0.69$ D) from Refs. [46,47]. (B) Observed conformer of tryptophol, using experimental rotational constants (A = 1748.2 MHz, B = 678.0 MHz, C = 549.6 MHz) and calculated dipole moments ($\mu_a = 1.6$ D, $\mu_b = 1.9$ D, $\mu_c = 0.5$ D) from Refs. [48]. (C) One conformer of glutathione, using calculated rotational constants (A = 381.9 MHz, B = 140.6 MHz, C = 111.7 MHz) and dipole moments ($\mu_a = 1.3$ D, $\mu_b = 0.6$ D, $\mu_c = 1.9$ D).

Storm et al. [50] designed a cylindrical resonator that operated on the TE_{01q} mode, and could operate in the 1–4 GHz frequency region. Alternatively, Etchison et al. [51] developed a FTMW cavity spectrometer that could achieve operation in the same frequency range using hemispherical mirrors of radius 40 cm, observing molecular transitions below 1 GHz.

In this report, we discuss the design of a CP-FTMW spectrometer operating in the 2-8 GHz frequency range, ideal for larger molecules. Because the technology exists to both directly generate and detect broadband microwave pulses in this frequency region, this spectrometer contains no frequency mixing or multiplication stages. In addition, the spectrometer uses small horn antennas and so there is no need for a large vacuum chamber or pumping system. The utility of this spectrometer has been demonstrated in a recent study of the rotational spectrum of bromoform [52]. Here the performance of this spectrometer is demonstrated by measuring the spectrum of iodobenzene. In addition to a remeasurement of its rotational spectrum, its four distinct singly-substituted ¹³C isotopologues have been detected, along with the van der Waals cluster of iodobenzene with a neon atom. In addition, the implementation of broadband microwave-microwave doubleresonance spectroscopy to facilitate spectral assignments is described.

2. Experimental and computational methods

2.1. 2-8 GHz CP-FTMW spectrometer

A schematic diagram of the 2–8 GHz CP-FTMW spectrometer is shown in Fig. 2. A linear frequency sweep, typically with a duration of 4 μ s, is created by an arbitrary waveform generator (AWG, Tektronix 7102B with Option 06) with sampling rate 20 GS/s. An 8.5 GHz 8-pole low-pass filter (K&L Microwave) is placed on the output of the AWG to improve pulse purity. The pulse is then input into a 200 W pulsed traveling wave tube amplifier (Amplifier Research, 200T2G8A). Fig. 3 shows a spectrogram of the excitation



Fig. 2. Schematic of the 2–8 GHz CP-FTMW spectrometer. The schematic is separated into three sections: (1) pulse generation and amplification; (2) molecular beam chamber; (3) FID amplification and detection. See the text for further description.



Fig. 3. Time-frequency analysis of the chirped-pulse output of the AWG (panel A) and of the pulse after TWT amplification (panel B).

pulse, both before and after the TWTA. Before TWTA amplification, the only detectable frequency component of the pulse other than the desired frequency output v(t) is due to mixing of the pulse with the 10 GHz clock inside the AWG. The amplifier introduces a few other spurious components, particularly 2v(t) and 3v(t). However, these spurious sweeps are low in intensity (-10-15 dB) relative to the primary sweep, and have not been observed to affect the relative intensity accuracy of molecular signals observed with this spectrometer, as will be demonstrated below.

The amplified chirped-pulse is broadcast into a molecular beam vacuum chamber by a WRD-250 (2.5–7.5 GHz) horn antenna (Advanced Technical Materials, part no. 250-441-C3) with 7–13 dBi gain (low to high-frequency) and dimensions (face height × face width × length) of $13 \times 10 \times 17$ cm. The horns were separated by 50 cm so that two pulsed nozzles, spaced by 20 cm and oriented perpendicular to the axis of microwave propagation, could be operated simultaneously; this leads to a factor of 4 saved in time and a factor of two lower sample consumption to reach the same sensitivity due to the *N*-emitter effect [36,53]. The horn separation distance is set by the directionality of the broadcast pulse and is less than that achieved in the higher frequency spectrometer (7.0–18.5 GHz).

To protect the detection electronics from the high-power TWTA pulse, a passive solid-state PIN diode limiter (Advanced Control Components, ACLM-4601-1 K, 1 kW peak power handling) and a solid-state single-pole single-throw (SPST) switch (Advanced Technical Materials, S1517D) are used in front of a high-gain, low-noise five-stage broadband amplifier (Miteq AFS5-00100800-14-10P-5, 40 dB gain, 1.4 dB noise figure). The molecular FID signal is directly digitized on a fast oscilloscope (Tektronix TDS6124C, 12 GHz hardware bandwidth) operating at a 20 GS/s sampling rate. The FID was acquired for 20 μ s to match the typical T_2 dephasing times of molecular transitions in this frequency range (~20–25 μ s at the low-frequency end, ~10–12 μ s at the high-frequency end). All frequency and trigger sources in the experiment, as well as the digital oscilloscope, are phase-locked to a 10 MHz rubidium-disciplined crystal oscillator to provide phase stability and frequency accuracy.

2.2. CP-FTMW-MW double-resonance spectroscopy

In order to perform CP-FTMW-single-frequency MW doubleresonance experiments, a single-frequency MW pulse must be generated that is spectrally pure so that "false positives" will not be observed. Because of its spurious frequency outputs and high noise power, a TWTA cannot be used to amplify the single-frequency pulse. Instead, for this pulse we use a 4 W, 2–8 GHz solid-state amplifier (SSA, Microwave Power Inc., L0208-36-T421) with a TTL driver internally installed. A schematic of the spectrometer in this configuration is shown in Fig. 4. The AWG creates the pulse sequence, in which the chirped-pulse is immediately followed by



Fig. 4. The 2–8 GHz CP-FTMW spectrometer as designed to perform microwavemicrowave double-resonance experiments.

the single-frequency MW pulse with a sinc intensity profile to provide a highly frequency-selective pulse. The single-frequency MW pulse typically has 4 µs duration. Using a single-pole double-throw (SPDT) switch, the chirped-pulse is directed to the TWTA as in the normal CP-FTMW experiment, but the single-frequency pulse is directed to the SSA. The outputs of the two amplifiers are then combined using a Wilkinson power combiner. To prevent damage to the SSA from TWTA power returned from the power divider, two 2–8 GHz isolators (DiTom Microwave, 10 dB isolation each) are placed on the output of the SSA. The combined pulse sequence is then broadcast into the vacuum chamber. The SPST detection switch is timed to protect the low-noise amplifier during both microwave pulses.

2.3. Chemical methods and electronic structure calculations

Iodobenzene (98% purity) was purchased from Aldrich and used without further purification. The sample was placed in a stainless steel reservoir at room-temperature and a backing gas consisting of approximately 70% neon and 30% helium ("first run neon") was flowed over it at a backing pressure of 0.5 atm. The mixture was then expanded into the chamber through the pulsed nozzles (General Valve Series 9, 0.9 mm diameter) with a pulse duration of 500 µs. A total of 210,000 FIDs were averaged together for the final spectrum. A Kaiser-Bessel digital frequency filter was applied to the FID before Fourier transformation.

Ab initio electronic structure calculations of iodobenzene and its neon complex were performed using Gaussian 09 Revision A.02 [54], at the MP2/6-311G(d,p) level of theory. This basis set for iodine was obtained from the EMSL Basis Set Exchange [55–57].

3. Results

3.1. CP-FTMW spectrum of iodobenzene and spectrometer performance

The rotational spectrum of iodobenzene has been measured and assigned previously, first in a room-temperature waveguide cell [58], then later in a low-frequency FTMW cavity [51], followed by further FTMW cavity and millimeter-wave measurements [59]. In addition, Stark effect measurements in a FTMW cavity were performed to determine its dipole moment, which is oriented along the *a* principal axis ($\mu_a = 1.6250(20)$ D) [59]. Its dense rotational spectrum, owing to the large nuclear quadrupole coupling constants of the iodine nucleus, makes it a good benchmark molecule to demonstrate the sensitivity and relative intensity accuracy of the 2–8 GHz CP-FTMW spectrometer.

In the panel (A) of Fig. 5, the 2–8 GHz CP-FTMW spectrum of iodobenzene is compared to a simulation using the fit Hamiltonian parameters from Ref. [59], at a rotational temperature of 1 K. All spectral fitting and simulation in this report was performed using SPFIT/SPCAT [60], and PIFORM [61] was used to reformat the results and determine standard errors for parameters. In panel (B), an expanded view shows the J = 4-3 region of the spectrum. The results of Watson Hamiltonian fits are presented in Table 1, showing the fit of the CP-FTMW data on its own as well as in conjunc-

Table 1

A-reduction Hamiltonian parameters of iodobenzene.

	Ref. [59]	Global Fit ^a	CP-FTMW Fit
$A (MHz)$ $B (MHz)$ $C (MHz)$ $\Delta_J (kHz)$ $\Delta_{J\kappa} (kHz)$ $\Delta_{K} (kHz)$ $\delta_{\delta} (kHz)$	5669.126(15) 750.414323(52) 662.636162(44) 0.0195479(14) 0.891(52) 0.00253098(65) 0.15554(32)	5669.131(14) 750.414293(43) 662.636146(38) 0.0195470(14) 0.164636(67) 0.908(50) 0.00253065(63) 0.15551(32)	$\begin{array}{c} 5669.252(78)\\ 750.41443(10)\\ 662.63646(10)\\ 0.02794(97)\\ 0.126(12)\\ 0.908^{\rm b}\\ 0.00253065^{\rm b}\\ 0.15551^{\rm b} \end{array}$
$\Phi_{JK} (Hz)$ $\Phi_{KJ} (Hz)$ $\chi_{aa} (MHz)$ $\chi_{bb}-\chi_{cc} (MHz)$ $M_{aa} (KHz)$ $M_{bb} = M_{cc} (kHz)$ No of lines σ_{w} rms error (kHz) ((kH(kHz))	0.0000609(13) -0.000337(16) -1892.0398(46) 65.593(12) -1.67(86) -2.60(13) 296 0.793	0.0000607(13) -0.000378(16) -1892.0395(22) 65.5872(76) -1.42(36) -2.499(52) 606 0.799	-1892.0395(28) 65.5856(68) -2.338(70) 310 3.7

^a Combined fit of the transitions in Ref. [59] and measured in this study.
 ^b Assumed value.

tion with all previously measured transitions. Frequencies of the transitions of iodobenzene measured in this study can be found in the Supplementary Information.

In addition, due to the sensitivity of this spectrum, the four distinct carbon-13 isotopomers of iodobenzene are observed in natural abundance. Panels (C) and (D) of Fig. 5 show expanded views of the CP-FTMW spectrum, with transitions due to these carbon-13 isotopologues indicated. Isolated spectra of these isotopologues are shown in Fig. 6, compared to simulated spectra. The intensities of these simulations have been scaled from those of the normal species in Fig. 5 by the known relative abundances of the two carbon isotopes, with those of carbons 2 and 3 doubled due to symmetry. This demonstrates the accuracy of the relative transition



Fig. 5. The 2–8 GHz CP-FTMW spectrum of iodobenzene after 210,000 FID averages. (A) Comparison of the experimental spectrum (positive-going) to its simulated spectrum at a rotational temperature of 1 K (negative-going). (B) An expanded view of the J = 4-3 region is shown to demonstrate the relative intensity accuracy of the spectrometer. (C) An expanded view to show the dynamic range and resolution at baseline of the instrument. The labeled peaks are from the ¹³C-2 isotopomer, and the off-scale peaks are normal species transitions. (D) A further expanded view of the spectrum, showing the noise level of the spectrum. Labeled peaks are from the ¹³C-1 isotopomer and the ²⁰Ne and ²²Ne clusters. The off-scale peak near 5.634 GHz is from the ¹³C-2 isotopomer, and the off-scale peak near 5.639 GHz is from the normal species of iodobenzene.



Fig. 6. Isolated rotational spectra of the four distinct singly-substituted 13 C isotopologues of iodobenzene, compared to their simulated spectra. These isolated spectra were obtained by removing all transitions not associated with the species of interest from the spectrum. The simulated spectra are scaled from that in Fig. 5 by the isotopic abundance of 13 C, with those of C₂ and C₃ doubled due to symmetry.

intensities of this spectrometer across a large dynamic range. The fit Hamiltonian parameters of these species are found in Table 2, while lists of all observed transitions are located in the Supplementary Information. It should be noted that although the linewidths obtained in this spectrometer (~120 kHz FWHM) are larger than those obtained on a Balle–Flygare-type spectrometer with a pulsed nozzle parallel to the axis of microwave propagation, the frequency accuracy of the CP-FTMW spectrometer is better than 4 kHz for lines with high signal-to-noise, and 5–7 kHz for weaker transitions.

From the moments of inertia of the ¹³C-monosubstituted isotopologues, a semi-experimental structure of iodobenzene can be derived. In Table 3, the Kraitchman substitution coordinates of the carbon atoms of iodobenzene are compared to those from its ab initio calculated structure. These coordinates were determined using the KRA program of Kisiel [61], with the error estimated by Costain's formula. It can be seen that carbons 1 and 4 have determined non-zero values for b and c; this is also reflected in the fact that the A rotational constant decreases slightly in these isotopically substituted species, as seen in Table 2. This is attributed to zero-point vibrational effects, as the three lowest-frequency vibrational modes of iodobenzene (the iodine-phenyl in-plane and out-ofplane bends, as well as the C-I stretch) all have frequencies below 300 cm^{-1} [59]. As the considerable errors that can arise in determining the coordinates of atoms near principal axes are well known [62,63], an effective least-squares fit of internal coordinates

Table 3Carbon substitution coordinates of iodobenzene.

Carbon	Experiment			Ab initio		
	a (Å)	b (Å)	c (Å)	a (Å)	b (Å)	c (Å)
$C_1 \\ C_2/C_6 \\ C_3/C_5 \\ C_4$	0.734(3) 1.4469(13) 2.8468(8) 3.5470(6)	0.05(4) 1.2143(15) 1.2078(19) 0.06(3)	0.087(27) [0] ^a [0] ^a 0.077(27)	-0.776 -1.466 -2.865 3.568	0.000 ±1.218 ±1.209 0.000	0.000 0.000 0.000 0.000

^a Value constrained to zero.

to the moments of inertia of iodobenzene and its isotopomers was also performed, using the STRFIT program of Kisiel [61,64]; the results of this fit are presented in Table 4.

As discussed in Ref. [52], interference from wireless communication signals is present near 2.5 GHz, and so the spectrometer's performance is poor in this region. Attempts to isolate the detection electronics, particularly the low-noise, high-gain amplifier, by placing them inside the vacuum chamber, did not successfully eliminate this interference.

3.2. CP-FTMW-MW double-resonance spectroscopy

Double-resonance techniques that aid in spectral assignment are of tremendous utility in parsing dense rotational spectra, in

Table 2

Fit Hamiltonian parameters of singly-substituted carbon isotopologues of iodobenzene.

	Normal species	¹³ C-1 ^a	¹³ C-2 ^a	¹³ C-3 ^a	¹³ C-4 ^a
A (MHz) B (MHz) C (MHz) $\chi_{\alpha\alpha}$ (MHz) $\chi_{bb}-\chi_{cc}$ (MHz) No of lines rms error (kHz)	$\begin{array}{c} 5669.131(14)\\ 750.414293(43)\\ 662.636146(38)\\ -1892.0395(22)\\ 65.5872(76)\\ 606 \end{array}$	$5668.48(46) \\749.80640(31) \\662.16646(28) \\-1892.306(38) \\65.54(14) \\64 \\6.6$	$5577.33(25) \\748.08728(25) \\659.55540(21) \\-1891.955(26) \\65.596(52) \\76 \\5.6$	5579.13(43) 741.48220(45) 654.44323(39) -1891.927(43) 65.68(16) 76 6.1	5668.54(34) 736.66714(27) 651.89770(23) -1892.008(35) 67.50(14) 59 5.5

^a All parameters not listed here were fixed to their normal species values from Table 1.

Table 4

Internal coordinates of iodobenzene, as determined by an effective least-squares fit, compared to ab initio values.^a

Internal coordinate	r ₀	Ab initio
r(C2–C1) (Å)	1.412(15)	1.400
r(C3-C2)	1.400(10)	1.399
r(C4–C3)	1.39(4)	1.399
r(I-C1)	2.063(21)	2.112
((C3–C2–C1) (deg)	119.9(10)	119.2
((C2–C1–C6)	119.0(15)	120.9
((C4–C3–C2)	120.5(12)	120.5
((I-C1-C2)	121.1(13)	119.5

^a All internal coordinates not listed in this table were held fixed to their *ab initio* values.

which several species are present. The relative intensity accuracy and stability of the CP-FTMW spectrometer makes CP-FTMW-MW spectroscopy a powerful tool. A 4 μs single-frequency MW pulse, amplified by a 4 W SSA, following the chirped-pulse destroys



Fig. 7. Demonstration of microwave-microwave double-resonance spectroscopy on a 2–8 GHz CP-FTMW spectrometer. Top panel: fractional modulation of iodobenzene transitions upon excitation with a 4 W, 4 μ s single-frequency pulse at the frequency of the 4₀₄ 11/2–3₀₃ 9/2 transition. The asterisk indicates the pumped transition. The six transitions modulated by more than 50% are the only six transitions which share a quantum state with the pumped transition. Middle and bottom panel: expanded views comparing the spectra with the single-frequency pulse on and off, showing the selective modulation of connected transitions.

the rotational coherence of any rotational transition that shares a quantum state with the transition being pumped, reducing its intensity significantly. Transitions not connected to the pump transitions, meanwhile, are unaffected by the double-resonance pulse. Using the CP-FTMW spectrometer for microwave-microwave double-resonance spectroscopy allows all of the transitions that share a quantum state with the pump transition to be detected simultaneously.

In Fig. 7, a demonstration of the CP-FTMW-MW double-resonance technique is presented. The $J'_{Ka'KC'}F-J''_{Ka'KC'}F'' = 4_{04} 11/2-3_{03}$ 9/2 transition of iodobenzene is chosen as the double-resonance pump transition. In the top panel, the fractional modulation of each rotational transition in the spectrum is shown. A total of six transitions are reduced in intensity by at least 50%, and each of these transitions, and no others, share a quantum state with the pumped transition. Expanded spectra in the bottom two panels show that connected transitions are modulated selectively.

3.3. Spectrum and structure of the iodobenzene-neon complex

After the spectra of iodobenzene and its singly-substituted ¹³C isotopologues were removed from the 2–8 GHz CP-FTMW spectrum, a large number of transitions remained, showing a spacing pattern characteristic of an *a*-type spectrum with a single iodine nucleus present. From these transitions the spectrum of the complex of iodobenzene with a single neon atom was assigned. Two spectra, identified as the ²⁰Ne and ²²Ne isotopologues of the cluster, were fit. The fit Hamiltonian parameters of these two species are presented in Table 5 and compared to parameters from *ab initio* calculations. All observed transitions of these complexes can be found in the Supplementary Information.

The assignment of these two clusters as different isotopologues of the neon-iodobenzene complex is confirmed by the nuclear quadrupole hyperfine tensors of the two species and a comparison

Table 5

Fit A-reduction Hamiltonian parameters of the neon-iodobenzene complex.

	Iodobenzene- ²⁰ Ne r Experiment <i>Ab initio</i>		Iodobenzene-22Ne		
Parameter			Experiment	Ab initio	
A (MHz)	1818.674(20)	2005.59	1731.58(4)	1911.08	
B (MHz)	605.6455(12)	592.13	598.7810(16)	585.51	
C (MHz)	537.5551(11)	545.38	524.3010(12)	532.67	
$\Delta_I (kHz)$	1.192(7)	1.192(7)			
Δ_{lK} (kHz)	18.30(4)	18.30(4) 15.68(7)			
Δ_K (kHz)	16.7(28)		10(5)		
δ_I (kHz)	0.294(5)		0.356(8)		
δ_{K} (kHz)	13.0(3)		12.7(4)		
χ_{aa} (MHz)	-1779.38(4)	-1711.36 -1755.14(8) -169		-1692.84	
$\chi_{bb} - \chi_{cc}$ (MHz)	-177.06(17) -135.72 544.26(6) 483.89		-201.28(22)	-154.24	
χ_{ab} (MHz)			598.24(11) 529.23		
No of lines	123		72		
rms error (kHz)	9.8		7.8		

Table 6

Principal nuclear quadrupole coupling tensors of iodobenzene and its neon complexes.

Parameter	Iodobenzene	Iodobenzene-20Ne	Iodobenzene-22Ne
$\chi_{zz} (MHz)^a$	-1892.039(5)	-1889.48(5)	-1889.38(8)
χ_{xx} (MHz)	978.816(6)	978.22(9)	978.21(10)
χ_{yy} (MHz)	913.222(6)	911.25(9)	911.16(10)
θ_{az} (deg) expt.	0	11.4355(14)	12.6461(19)
θ_{az} (deg) ab initio	0	10.531	11.578

^a The *z*-axis is collinear with the C–I bond, and the *a* principal axis of iodobenzene, and the *x*-axis is in the plane with the benzene ring, the *b* principal axis of iodobenzene. to electronic structure calculations. In the bare iodobenzene molecule, the *a* principal axis falls along the I–C₁ bond; however, upon complexation with a neon atom, the principal axis system is rotated, and this bond is in the *a*-*b* principal axis plane. By diagonalization of the quadrupole coupling tensor, as shown in Table 6, it can be seen that the eigenvalues of the quadrupole tensors of the two neon complexes differ from those of iodobenzene by less than 0.3%, indicating that the electric field gradient at the iodine nucleus is nearly identical between the monomer and its neon complexes, as would be expected. Also, the angle between the I–C₁ bond and the *a* principal axis is shown to be ~10% larger in the ²²Ne complex than in the ²⁰Ne complex, in excellent agreement with *ab initio* calculations. If the weaker species were instead a vibrationally excited state of ²⁰Ne–iodobenzene, this angle would be expected to be nearly the same between the two clusters.

In Fig. 8 the isolated spectra of these two clusters are compared to simulations, using the fit Hamiltonian parameters in Table 5. It can be seen that the ²⁰Ne–iodobenzene/²²Ne–iodobenzene signal intensity ratio is approximately 3.5:1, compared to the natural relative abundance ratio of 9.8:1. This anomalous relative intensity in these isotopes of neon in weakly bound clusters has been previously observed and commented on by several research groups. It has been attributed to the slightly lower zero-point vibrational energy, and hence higher dissociation energy, of clusters with the heavier ²²Ne isotope, leading to preferential stabilization of these clusters in the supersonic expansion [65–67].

The structure of this cluster can be determined using the method described by Suenram et al. for the argon–formamide cluster [68] and implemented in the RGDFIT program [61,69]. The structure of the iodobenzene molecule is assumed to be unchanged upon complexation, and so there are only three variable structural parameters in the structure of the iodobenzene–neon cluster, defining the position of the neon atom. These parameters are presented in Table 7 for the ²⁰Ne and ²²Ne clusters. In Table 8, the angle between the *a* principal axis of the iodobenzene–neon cluster and the I—C bond as derived by diagonalization of the quadrupole coupling tensor is compared to that of this derived structure. The two methods for determining this angle yield very similar results (within 3%).

This analysis, however, does not determine the sign of the coordinates of the neon atom, and so it could be located in any octant; due to the symmetry of iodobenzene, this results in two possible structures for the complex, which are presented in panel (A) of Fig. 9. In structure (a), the neon atom is located over the phenyl ring, while in structure (b), it is located above the iodine atom. Both structures accurately reproduce the observed rotational constants of the iodobenzene-neon cluster. However, only structure (a) corresponds to an *ab initio* optimized structure; structure (b) minimizes to a different structure upon geometry optimization. In addition, structure (a) corresponds closely to the experimentally derived structures of the fluorobenzene-neon [70] and chlorobenzene-neon [71] complexes, which are shown in panels (B) and (C) of Fig. 9. The structures of these complexes were confirmed through isotopic substitution measurements in other positions of the molecule. Additionally, the van der Waals radii of iodine and neon serve as further confirmation of the assignment of the iodobenzene-neon complex as structure (a). From the tabulations of Bondi [72], the sum of the radii of iodine and neon is 3.52 Å, while in structure (b), the I–Ne distance is only 3.42 Å, which is quite unlikely for a van der Waals complex.

As seen in Table 7, in the RGDFIT-derived structure of iodobenzene, the neon atom is not located in the a-c symmetry plane of iodobenzene, instead having a x coordinate of 0.46 Å for the ²⁰Ne complex, and 0.49 Å for the ²²Ne complex. A similar effect is also

Table 8

Angle (in degrees) between the a principal axis of the iodobenzene-neon cluster and the I–C₁ bond.

Method	Iodobenzene- ²⁰ Ne	Iodobenzene-22Ne
Quadrupole tensor	11.4355(14)	12.6461(19)
Structure fit	11.173	12.372
Ab initio	10.531	11.578



Fig. 8. Isolated rotational spectra of the two assigned isotopic species of the iodobenzene-neon complex, compared to simulated spectra with fit Hamiltonian parameters. An intensity rolloff is observed above 7.5 GHz due to lower TWTA power output and reduced horn transmission efficiency.

Table '	7
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Experimentally derived geometry of the iodobenzene-neon complex.

Species	Spherical coord	Spherical coordinates ^a		Cartesian coor	linates ^b	,b	
	R	θ	φ	<i>z</i>	<i>x</i>	y	
lodobenzene- ²⁰ Ne lodobenzene- ²² Ne	3.805 3.804	27.93 28.12	15.27 15.90	1.719 1.724	0.469 0.491	3.362 3.355	

^a *R* is the distance (in angstroms) between the neon atom and the center of mass of iodobenzene; θ is the angle between a vector along *R* and the *c* principal axis of iodobenzene, and φ is the angle between the projection of a vector along *R* into the *a*-*b* principal axis plane and the *a* principal axis of iodobenzene.

^b Coordinates (in angstroms) in the principal axis system of the iodobenzene monomer, with *z* as the *a*-axis, *x* as the *b*-axis, and *y* as the *c*-axis.



Fig. 9. Experimentally derived structures of halobenzene-neon complexes. Panel (A) shows the two possible structures of the iodobenzene-neon complex as derived from the structural analysis in the text. In panels (B) and (C) the structures of fluorobenzene-neon and chlorobenzene-neon, as derived from data in Refs. [70,71], respectively, are shown. The structural parameters R, θ , and ϕ from Table 7 are illustrated. The x-, y-, and z-axes signify the a, b, and c principal axes, respectively, of the halobenzene monomer.

observed in the chlorobenzene-neon and fluorobenzene-neon clusters, and is due to the large-amplitude zero-point motions of these floppy clusters, making a precise structure determination difficult [62,63,73].

4. Conclusion

In this report, the design and performance of a direct digital 2-8 GHz chirped-pulse FTMW spectrometer is discussed. A measurement of the rotational spectrum of iodobenzene demonstrates the sensitivity and relative intensity accuracy of this spectrometer, and from this spectrum the structure of iodobenzene and its neon complex is derived. In addition, a method for performing microwavemicrowave double-resonance experiments is presented. This spectrometer design has favorable characteristics for the study of the structure and dynamics of large molecules and clusters.

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Appendix A. Supplementary material

Supplementary data for this article are available on ScienceDirect (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.2011.04.016.

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