Chip-Scale Molecular Clock

Cheng Wang, Student Member, IEEE, Xiang Yi, Member, IEEE, James Mawdsley, Student Member, IEEE, Mina Kim, Student Member, IEEE, Zhi Hu, Student Member, IEEE, Yaqing Zhang, Bradford Perkins, and Ruonan Han, Member, IEEE

Abstract—An ultra-stable time-keeping device is presented, which locks its output clock frequency to the rotational-mode transition of polar gaseous molecules. Based on a high-precision spectrometer in the sub-THz range, our new clocking scheme realizes not only fully-electronic operation but also implementations using mainstream CMOS technology. Meanwhile, the small wavelength of probing wave and high absorption intensity of our adopted molecules (carbonyl sulfide, $^{10}$O/$^{12}$C/$^{34}$S) also enable miniaturization of the gas cell. All these result in an “atomic-clock-grade” frequency reference with small size, power and cost. This paper provides the architectural and chip-design details of the first proof-of-concept molecular clock using a 65-nm CMOS bulk technology. Using an 231.061-GHz PLL with FSK modulation and a sub-THz FET detector with integrated lock-in function, the chip probes the accurate transition frequency of OCS gas inside a single-mode waveguide, and accordingly adjusts the 80-MHz output of a crystal oscillator. The clock consumes only 66 mW of DC power and has a measured Allan deviation of $3.8 \times 10^{-16}$ at an averaging time of $\tau = 1000$ s.

Index Terms—molecular clock, rotational spectroscopy, OCS, Allan deviation, CMOS, frequency stability, navigation, GPS

I. INTRODUCTION

FREQUENCY and timing references with high stability are essential to electronic systems. At present, electronic oscillators using high-$Q$ quartz crystal and MEMS resonators are widely adopted [1]. They provide excellent phase noise, and are suitable for systems such as portable radio and radar transceivers, which only require frequency stability within a short term ($<1$ s). On the other hand, there is a vast application space where stability over a much longer time duration is needed. For example, positioning and navigation systems rely on their internal time stamps to determine the arrival time of satellite signals (in the case of GPS$^1$) or the double integral of acceleration (in the case of inertial navigators). They are especially critical in situations where broadcasting signals for time service are unavailable, such as indoor operations, battle fields with electromagnetic spectral jamming, and underground/underwater sensing. As an example, in undersea reflection seismology for oil explorations [2], [3], where a large hydrophone sensor array detecting artificial seismic pulses is placed on the ocean floor, the timing error over the entire deployment duration of $\sim 1$ year should ideally be kept within $1 \sim 10$ ms; that requires sensor-integrated clocks with a long-term stability, quantified as Allan deviation [1], at $10^{-11}$ (or 10 ppt) level.

The frequency of a quartz crystal/MEMS oscillator is determined by the geometry and material properties of the resonator, hence having large sample-to-sample variability and susceptibility to environmental (e.g. temperature and acceleration) changes. To minimize the large drift ($\sim 100$ ppm) of crystal oscillators over $\sim 100$°C temperature range, temperature-compensated crystal oscillators (TCXO) are extensively adopted [5], which incorporate temperature sensing and back-end frequency correction based on a pre-characterized temperature dependency. A TCXO typically consumes a few mW, but only reduces the drift to ppm level [6]. By enclosing the crystal in a temperature-stabilized oven chamber, an oven-controlled crystal oscillator (OCXO) further decreases the drift to ppb level [5]. This, however, comes at the expense of watt-level power consumption, a few minutes of warm-up time, and high cost ($\sim$100). Note that the above timing devices also suffer from significant aging effect.

The ideal approach to address the above stability problem is to reference the output frequency to a certain invariant physical constant. An atomic clock is based on such a principle by probing and locking to the hyperfine transition of electrons in, for example, cesium ($^{133}$Cs, $f_0=9.192631770$ GHz) and rubidium ($^{87}$Rb, $f_0=6.834682611$ GHz) atoms. Excellent stabilities at $10^{-11}$ to $10^{-18}$ levels are obtained from atomic clocks [4], [7]. Generally, these clocks are too bulky and costly for mainstream electronic systems; nevertheless, remarkable progress has been made in the miniaturization of atomic clocks over the past two decades. Utilizing a coherent-population trapping principle [8] and advanced packaging technologies [9]–[11], cm$^3$-level atomic clocks (i.e. chip-scale atomic clocks, CSACs) are demonstrated and deliver a
frequency stability at $10^{-11}$ level (over an integration time $\tau$ of 1000 s to one day) while consuming $\sim 0.12$ W of power [12]. A typical CSAC diagram is shown in Fig. 1a [4]: in addition to an voltage-controlled crystal oscillator (VCXO) and clock electronics, it also contains a VCSEL (vertical-cavity surface- emitting laser)-photodiode spectrometer (for the optically-assisted probing of the Cs transition) and a cesium vapor cell tightly integrated with heaters (for evaporation of alkali metal and mK-level temperature stabilization for VCSEL). Moreover, since the 9.192631770-GHz line of Cs has a large second-order Zeeman drift with the presence of an external magnetic field ($\Delta f=427$ Hz/Gauss$^2$ or $\sigma=4.6\times10^{-8}$/Gauss$^2$ [13], [14]), a magnetic shield is also normally used. Such a complicated implementation leads to high cost (> $1000) and degraded reliability [3], which have hindered the wide application of CSACs in mainstream, civil-grade systems.

This paper presents a new clock based on a fully-electronic spectrometer, of which the output frequency is locked to the rotational-mode transition of carbonyl sulfide ($^{16}$O$^{12}$C$^{32}$S) gas molecules in the sub-THz range. THz rotational spectroscopy was primarily used for molecular identification in astronomy [15] and is recently explored for bio-medical diagnosis [16]–[18]. By applying it in a clock encapsulating certain pure gas sample, the needs for heaters, VCSEL, and photodiode in CSAC are eliminated. More importantly, we note that significant progresses in CMOS/SiGe-based THz spectrometers are made recently [19]–[21]. That opens up opportunities in building miniature molecular clocks with very low cost, size and power. The diagram in Fig. 1b indicates not only a much simpler implementation of our chip-scale molecular clock, but also the potentials of integrating it monolithically (except the gas cell) into a System-on-Chip (SoC).

The physical principles of molecular clock, as well as the demonstration of a lab-scale prototype with $2.2\times10^{-11}$ stability ($\tau=1000$ s), were recently described in [22]. In this paper, we present design details of the first molecular-clock CMOS chip [23] and related experimental data. By probing a transition line of OCS molecules at 231.060983 GHz, the chip provides an Allan deviation of $3.8\times10^{-10}$ ($\tau=1000$ s) while consuming only 66 mW of DC power. These preliminary data of the molecular clock indicate clear advantages over OCXOs and also well compare with CSACs. The remainder of the paper is organized as follows. In Section II, an overview of rotational spectroscopy and the line properties is given. In Section III, the architecture of the clock chip is presented. In Section IV, we discuss the design details of each circuit block and the clock packaging. Then, the experimental results, including the characterizations of a few circuit blocks and the stability of the entire clock, are provided in Section V. In Section VI, we conclude the paper with a comparison with the other state-of-the-art time-keeping devices.

II. FREQUENCY BASE OF THE CLOCK: ROTATIONAL SPECTRUM OF POLAR MOLECULES

We select a rotational spectral line of gaseous polyatomic molecules with a linear structure (e.g. carbonyl sulfide) as the reference of our clock. Compared to molecules with symmetric/asymmetric-top structures, linear molecules possess less rotational-vibrational coupling and fewer spectral lines adjacent to the line of our interest [24]. Note that each spectral line has finite linewidth, and if the tails of adjacent lines extend into the line under probing, the measured line profile becomes asymmetric and the line center frequency drifts when the gas pressure/temperature changes.

Similar to other behaviors of microscopic particles, the rotation of linear molecules has quantized energy levels (Fig. 2). For certain angular-momentum quantum number $J$, the rotational energy $E_J$ follows a quadratic relationship [24]:

$$E_J = \frac{\hbar^2}{8\pi^2 I} (J + 1),$$

(1)

where $\hbar$ is Planck’s constant and $I$ is the molecular moment of inertia about axes perpendicular to the internuclear axis. For an incident wave to be absorbed by the molecule, its photon energy should match the energy difference of $E_J$. So the associated transition frequency $f_0$ is:

$$f_0 = f_{J+1\leftrightarrow J} = \frac{E_{J+1} - E_J}{\hbar} = \frac{\hbar}{4\pi^2 I} (J + 1),$$

(2)

which indicates that the absorption spectrum consists of a set of equally-spaced lines ($\Delta f=\hbar/(4\pi^2 I)$). For $^{16}$O$^{12}$C$^{32}$S, $\Delta f$ is about 12.16 GHz [26]. Next, the absorption coefficient $\alpha_{gas,J+1\leftrightarrow J}$ is affected by two factors: first, each $J$ angular momentum corresponds to $2J+1$ degenerated sub-levels due to different orientations with magnetic quantum number $m_J=-J, -(J-1), \ldots, 0, 1, \ldots, J-1, J$; thus, rotational transition at higher frequency involves more quantum states contributing to absorption. Second, governed by Boltzmann’s distribution, the probability of a molecule being at certain $J$ state decreases exponentially with $E_J$. Those factors lead to:

$$\alpha_{gas,J+1\leftrightarrow J} \propto (2J + 1) \cdot e^{-\frac{\hbar^2 (J+1)}{2kT(\pi I \hbar)^2}}.$$

(3)

OCS is chosen also for its large dipole moment ($\mu_{OCS}=0.7$ debye [25]), which leads to strong absorption $\alpha_{gas,J+1\leftrightarrow J}$. As shown in Fig. 2, the absorption of OCS firstly increases with frequency $f_0$, then peaks at $\sim 0.5$ THz and finally decreases as $f_0$ rises towards 1 THz. Compared with those at lower frequencies, a spectral line at low-THz range provides adequate absorption via a short spectroscopic path length. Meanwhile, the clock gas cell, when shrunk into its minimum possible
size, is a single-mode waveguide with a cross-sectional area proportional to $1/f_0^2$. As a result, higher $f_0$ enables gas cell miniaturization. In our work, the OCS transition line near 231.061 GHz ($J+1\leftarrow J = 19\leftarrow 18$) is chosen, of which the absorption is already 0.6–0.7× of its peak value at ~0.5 THz (Fig. 2). That achieves both small size of the gas cell and low power consumption of the CMOS electronics.

A gas cell based on a WR-4.3 rectangular waveguide is implemented (Fig. 3a). The waveguide has a cross-sectional area of $1.092 \times 10^{-4} \text{m}^2$ and a length of 140 mm – a value that maximizes the signal-to-noise ratio ($SNR$) [18]. RF-transparent epoxy is used to seal OCS gas with a volume of 83 mm³. A meandering shape of waveguide is adopted for gas cell miniaturization, which results in a clock volume limit of ~1 cm³. Shown in Fig. 3b, the measured loss of the gas cell without OCS is 7.3 dB. Next, with OCS gas filling, a measured spectral line at 231.060983 GHz is shown in Fig. 3c. With a gas pressure of 1 Pascal, the Doppler-limited full width at half maximum (FWHM) is 0.65 MHz ($Q=3.6 \times 10^5$), and the peak absorption intensity is 7%. With a pressure of 10 Pascal, the FWHM is 1.47 MHz ($Q=1.6 \times 10^5$) and is dominated by pressure broadening; the peak absorption intensity is 33%. For our clock, the pressure of 10 Pascal is selected to optimize the $Q$-$SNR$ product in (8).

III. DYNAMIC FREQUENCY COMPENSATION SCHEME AND CLOCK STABILITY

Similar to CSACs (Fig. 1a), the molecular clock performs closed-loop dynamic frequency correction to an off-chip voltage-controlled crystal oscillator (VCXO). A simplified schematic is shown in Fig. 4a. A THz phase-locked loop (PLL) referenced to the VCXO generates a probing signal with center frequency $f_p$. To detect the frequency error between $f_p$ and the spectral line center $f_0$, frequency-shift keying (FSK) is adopted, with modulation frequency $f_m$ and frequency deviation $\Delta f$. As a result, the instantaneous frequency of probing signal is periodically toggled between $f_p + \Delta f$ and $f_p - \Delta f$. If $f_p \neq f_0$, the gas absorption is different between the two half duty cycles, as shown in Fig. 4b. A square-law detector then extracts the envelope fluctuation $V_{BB}$ of THz probing signal, and the amplitude and phase of $V_{BB}$ correspond to the instantaneous offset $f_p - f_0$. Eventually, an error signal $V_{\text{error}}$ derived from a lock-in detection (Fig. 4a) is used to adjust the frequency $f_{\text{XO}}$ of VCXO. The loop settles when $V_{\text{error}}$ is zero, and $f_{\text{XO}}$, which locks to $f_0$ (through a preset frequency division ratio), is used as the clock output.

The switch $S_0$ is on for normal clock operations. If the switch $S_0$ in Fig. 4a is off, a spectroscopic dispersion curve (Fig. 5a) is obtained by recording $V_{\text{error}}$ while scanning the center frequency $f_p$ of the FSK-modulated probing signal. The zero-crossing point ($f_p-f_0=0$) of the dispersion curve aligns with the spectral line center. Thus, when the feedback loop settles, the clock locks at that zero-crossing point. Note that in order to reduce the frequency error $f_p-f_0$, sufficiently large

Note that the modulation frequency $f_m$ is much smaller than $\Delta f$, in order to concentrate the probing power within the spectral width of the transition line.
Finally, we define the quality factor $Q$ and the $SNR_{c/o}$ of a spectral line as

$$\frac{Q}{SNR_{c/o}} = \frac{f_0}{f_{FWHM}}$$

and

$$SNR = \frac{V_{error,max}}{V_n} \approx 0.23 \cdot K_r \cdot f_{FWHM},$$

respectively. Using (6) and (7), the Allan deviation of molecular clock in (5) can be re-expressed based on the $Q$-$SNR$ product of the dispersion curve:

$$\sigma_y(\tau) \approx \frac{V_n}{Q \cdot SNR \cdot \sqrt{2\pi}}.$$  

Note that (8) is valid only if the frequency deviation of the FSK-modulated probing signal is set to $\Delta f_{opt}$ and $\Delta f_{opt} \gg f_m$. Lastly, we point out that for the feedback control loop of the clock to converge correctly, the slope of the spectrometer-probed dispersion curve should be positive at any moment. That means the initial offset of the probing frequency $f_p$ should be within $\pm f_{e,peak}$ (Fig. 5a), where $f_{e,peak}$ is the frequency at which the dispersion curve reaches its peak value, and is derived to be 0.38 $f_{FWHM}$ (see (16) in Appendix). For the OCS line shown in Fig. 3c, that is related to a frequency tolerance of $\pm 2.4$ ppm. This is achievable with either a TCXO or a start-up process involving a rough search of the zero-crossing point followed by the setting of the initial frequency of a VCXO.

IV. MOLECULAR CLOCK ON CMOS

A pair of CMOS transmitter (TX) and receiver (RX) chips, with an architecture shown in Fig. 6, is implemented to realize the above frequency regulations to an 80-MHz VCXO. The separation of the TX and RX is to facilitate the packaging of this first prototype and to avoid any undesired coupling of sub-THz signal through the silicon substrate. The latter may cause large tilting of the spectroscopic baseline and output frequency drift [22]. Nevertheless, a single-chip implementation of molecular clock is still possible in the future.

A. Clock Transmitter: Generation of Sub-THz Probing Signal

On the TX chip, the 231.061-GHz probing signal is generated by a sub-THz front-end, which consists of a 57.8-GHz harmonic voltage-controlled oscillator (VCO), two cascaded frequency doublers, and inter-stage amplifiers. The 28.9-GHz fundamental oscillation of the harmonic VCO is also divided down to establish a fractional-$N$ phase-locked loop (PLL), which locks to an 80-MHz VCXO. The PLL contains a 5-bit multi-modulus divider, which is modulated by a 40-bit, third-order multi-stage noise shaping (MASH) 1-1-1 modulator. This modulator enables a frequency-tuning resolution of $10^{-12}$ ($\sim 0.2$ Hz at 231 GHz and $\sim 0.1$ mHz at 80 MHz), which is used for high-accuracy calibration of the output frequency.

Note that previous experimental works [30], [31] were only able to determine the OCS transition frequency with kHz-level accuracy. Therefore, the exact PLL division ratio needed for an 80-MHz clock output with $<10^{-9}$ accuracy can only be derived during our testing.
The fractional divisor $K/F$ of $\Delta - \Sigma$ is periodically reset by an on-chip digital counter to implement the FSK modulation. The loop-bandwidth of the 40-bit fractional-N PLL and the modulation frequency are selected to be 250 kHz and 16 kHz, respectively. According to our experiments, these two parameter values maximize the SNR of the measured spectral line and the short-term stability of clock. Note that low $f_m$ leads to excessive flicker noise in the THz detector, and high $f_m$ leads to shorter length and less randomness of the control code for the multi-modulus divider in the PLL during FSK modulation (hence larger frequency error). Meanwhile, the PLL loop bandwidth should be sufficiently high to support the FSK modulation. The integer divisor $I$, fractional divisor $K/F$ (40-bit), FSK modulation frequency $f_m$ (3-bit), frequency deviation $\Delta f$ (3-bit) and a FM enabler (1-bit) are set externally through a serial-to-parallel data interface (SPI).

Fig. 7 shows the 3D structure and detailed schematic of the 231-GHz transmitter front-end. Note that, in contrast to prior THz gas sensing setups [19]–[21], the waveguide gas cell used in our clock highly confines the THz power, which may cause power saturation of OCS molecules and broaden the spectral line [24]. Our study [22] indicated that an injected probing power of $\sim 50$ $\mu$W leads to the highest $Q$-SNR product. Such a power level is feasible for low-power operation using mainstream CMOS technologies. We use a millimeter-wave VCO cascaded with a sub-THz multiplier chain, instead of a sub-THz VCO plus a sub-THz divider chain, due to the following advantages of former scheme: (1) lower total power consumption, which dominates the DC power of the entire clock; (2) reduced amplitude (AM) noise due to the voltage-clipping effects of the multipliers, which are heavily driven into saturation; (3) wide VCO tuning range $\Delta f_T$ to cover the target spectral line; $\Delta f_T$ should be larger than the 12.16-GHz frequency spacing of OCS spectrum (Fig. 2). The VCO adopts a cross-coupled structure and oscillates at 28.88-GHz fundamental frequency. The common-mode $2^nd$ harmonic signal at 57.8 GHz is then extracted from the top of VCO. The two cascaded frequency doublers with output frequency at 116 GHz and 231 GHz, respectively, are realized using NMOS transistors biased close to the threshold voltage. Two resonators ($L_5$ and $C_4$, $L_7$ and $C_6$) reject the backward propagation of the $2^nd$ harmonic signals generated from the drains of transistor and leaked through their $C_{gd}$. No feedback structure [32] is adopted here for power saving. Two interstage buffers with common-source NMOS are implemented to provide sufficient driving power. The simulation of the sub-THz front-end shows a peak output power of $-9.1$ dBm at 231.9 GHz with a 3-dB bandwidth of 18.6 GHz (Fig. 11a).

**B. Sub-THz Receiver with Integrated Lock-In Detection**

Fig. 8 presents the schematic of the RX chip. The envelope fluctuation of probing signal induced by the OCS absorption (Fig. 4b) is obtained by a 231-GHz pseudo-differential square-law detector based on a NMOS transistor. The input signal applied at the gate and drain (through $C_{gd}$) of the device undergoes a self-mixing process. The NMOS is biased in the sub-threshold regime for the reduction of flicker noise. The simulated detector responsivity is 5.0 kV/W and the noise equivalent power (NEP) is 48 pW/Hz$^{0.5}$ at a baseband frequency of 16 kHz. The extracted baseband signal $V_{BB}$ is then amplified by a differential low-noise amplifier. Using a single-stage folded-cascade topology, the amplifier has a simulated gain of 55 dB. At the baseband frequency of 16 kHz, the amplifier has an input-referred noise of 20 nV/Hz$^{0.5}$, which
Fig. 7: 2<sup>nd</sup>-harmonic VCO and frequency multiplier chain of the TX: (top) 3D structure, and (bottom) circuit schematic.

Fig. 8: Schematic of the molecular clock receiver (RX).

is much lower than the 228-nV/Hz<sup>0.5</sup> output noise of the preceding square-law detector.

Next, the demodulation of the baseband signal is achieved by an integrated lock-in detector. The reference clock of the lock-in detector (FSK and FSK in Fig. 8) comes from the phase-aligned digital signal of the TX chip at the modulation frequency (f<sub>m</sub>=16 kHz, see Fig. 6). Based on a bank of transmission gates feeding to an amplifier and a low-pass filter [33], the lock-in detector performs a narrow-band (hence low noise) down-conversion of the envelope fluctuation V<sub>BB</sub> into a DC error signal V<sub>error</sub>. As described in Section III, V<sub>error</sub> represents the frequency difference between the instantaneous probing frequency f<sub>p</sub> and the spectral line center f<sub>0</sub>. V<sub>error</sub> is eventually used to control the 80-MHz VCXO; hence a dynamic frequency-compensation loop is established.

It is noteworthy that heterodyne detection scheme is not adopted by the clock receiver. In a radio or radar system, heterodyne detection is typically much more sensitive than direct detection, because the input RF power of receiver is much smaller than the local-oscillation (LO) power; so a heterodyne mixing leads to an output signal much larger than that from the self-mixing in a square-law detector. In a spectroscopic system, however, the receiver input power is much larger, hence heterodyne detection is less effective in SNR enhancement. In addition, direct detection does not require LO signal and is therefore much more power efficient.

Fig. 9: Design of the 231 GHz chip-to-waveguide coupler: (a) 3D structure for electromagnetic simulations and (b) simulated S-parameters.
C. Chip-to-Waveguide Signal Coupling

Two chip-to-waveguide couplers are implemented to establish the THz signal connections between the CMOS TX/RX chips and the WR-4.3 waveguide gas cell. As shown in Fig. 9a, the coupler is based on a microstrip line to waveguide probe structure [34]. The probe is fabricated on a fused quartz substrate with a thickness of 50 µm and a relative dielectric constant of 3.8. Based on 3.5-µm-thick gold, the metal pattern turns the quasi-TEM signal at the microstrip side into a TE-mode wave at its extension into the vertical waveguide. Three bond wires forming a ground-signal-ground transmission line are used to connect the chip with the quartz probe. Impedance matching using a step-impedance stripline is designed to further reduce the reflection due to the inductance of the bond wires. The simulated S-parameters of the coupler is shown in Fig. 9b, which indicates an insertion loss of ~1.0 dB at 231 GHz and a 3-dB bandwidth over 30 GHz.

V. CHIP PROTOTYPE AND EXPERIMENTAL RESULTS

The clock chipset is fabricated using a TSMC 65-nm CMOS low-power (LP) technology $f_{\text{max}} \approx 220$ GHz. Fig. 10 shows the micrographs of the chips, as well as the packaging of the molecular clock module. The module consists of (1) an atmospheric-pressure metal cavity, which houses the TX/RX chips and PCB, and (2) a bottle-cap-sized metal chamber, which houses the waveguide gas cell. The chamber is also connected to a vacuum pumping system via a KF-10 flange for low-pressure (~10 Pascal) OCS gas injection. As is shown in Fig. 3a and 10c, the above two parts of the clock module are separated by RF-transparent epoxy filled inside two short (~1 mm) sections of the waveguide near the chips.

A. Measurement Results of CMOS TX/RX Chips

A custom-designed VCXO on PCB provides the 80 MHz reference for the PLL in TX. After phase-locking, the power of the sub-THz output from the TX is measured by a VDI Erickson PM-5 power meter connected to the WR-4.3 waveguide flange of the packaged molecular clock module. As shown in Fig. 11a, the output power reaches -20.2 dBm with a 18-GHz tunable bandwidth. Note that these data include the loss of the chip-to-waveguide coupler. Next, a VDI even-harmonic mixer (EHM), driven by a LO signal at 14.424 GHz ($16^{th}$-harmonic mixing), is utilized to down-convert the TX signal at $f_0=231.06983$ GHz to an inter-mediate (IF) frequency of 279 MHz. Fig. 11b shows the measured IF spectrum using a spectrum analyzer (Keysight N9020A). The two sideband spurs are from the 80-MHz VCXO clock signal. The phase noise of the 231.061-GHz TX output is -68.4 dBc/Hz at 1-MHz frequency offset (Fig. 11c). It refers to a phase noise of
< -138 dBc/Hz at 1-MHz offset of the 80-MHz clock output. This is \(~10\times\) higher than other PLLs in similar frequency range [35], [36]; but note that the DC power budget assigned for our clock transmitter is also \(~10\times\) lower than the above. We also note that, the phase noise of the sub-THz signal may increase baseband noise via a PM-to-AM noise conversion, due to the steep slope of the transition line [18]. The expected \(SNR\), if it is only limited by the above mechanism, is evaluated by the following equation (from [18]):

\[
SNR_{PN} = \frac{f_{\text{FWHM}}}{f_m \times PN(f_m)},
\]

where \(f_{\text{FWHM}}=1.47\) MHz is the full width at half maximum of rotational spectral line, \(f_m=16\) kHz is the modulation frequency, \(PN(f_m)=53.6\) dBc/Hz@16kHz is the phase noise at the modulation frequency \(f_m\). The calculated \(SNR_{PN}\) is 93 dB, which is much higher than the measured \(SNR\) to be shown next. Hence, the short-term stability of our clock chip is currently not limited by the phase noise.

Next, an amplitude-modulated sub-THz signal generated by a VDI frequency extender is injected into the RX chip. The injected power is calibrated by the PM-5 power meter. A lock-in amplifier (Stanford Research Systems SR865A) measures the responsivity \(R_v\) (unit: V/W) of RX, including the waveguide-to-chip coupler, sub-THz square-law detector, and on-chip LNA. Meanwhile, the output noise spectral density \(V_n\) (unit: V/Hz\(^{0.5}\)) of RX is also measured, which then gives the noise equivalent power (NEP) as \(\text{NEP}=V_n/R_v\). At the baseband frequency of 16 kHz, the measured responsivity is \(1.8\times10^5\) V/W (Fig. 12a) and the measured NEP is 501 pW/Hz\(^{0.5}\) (Fig. 12b). Due to the dominance of the flicker noise from the NMOS detector, higher baseband frequency (i.e. FSK modulation frequency \(f_m\)) is preferable. However, as mentioned earlier, \(f_m\) is selected to be 16 kHz considering the tradeoff between the flicker noise in RX and the accuracy of FSK modulation in TX.

According to the simulation-measurement comparisons in Fig. 11a and 12b, we suspect that an excessive insertion loss of \(~10\) dB exists in each chip-to-waveguide coupler at 231 GHz. That may due to the overlength of the bond wires, as well as the wave absorption into the thick (\(~300\) \(\mu\)m) silicon substrate exposed to the coupler. The problem will be further investigated and addressed in the future. Lastly, the total power consumption of TX and RX chip is 66 mW, 70% of which comes from the 2\textsuperscript{nd}-harmonic VCO and sub-THz multiplier chain (Fig. 13). The RX chip only consumes 3 mW of power.

### B. Performance Characterization of CMOS Molecular Clock

With OCS gas injected into the WR-4.3 gas cell, the dispersion curve of the transition line is measured as the first step of clock performance characterization. This is achieved by (1) performing FSK modulation and scanning of probing frequency \(f_p\) on the TX chip, and (2) feeding the output of the folded-cascode LNA on the RX chip to a lock-amplifier (SR865A), which references to the 16 kHz FSK modulation signal from the TX. From this open-loop configuration of the clock chipset, the lock-in amplifier reading \(V_{\text{LID}}\) as a function of \(f_p\) is obtained (Fig. 14). The measured \(SNR\) of the dispersion curve, under an OCS pressure of 10 Pascal, is 445 in voltage or 53 dB in power.

Next, to ensure initial locking, the output frequency of VCXO with the control terminal grounded is measured by a Keysight 53230A frequency counter referenced to a Stanford Research Systems rubidium atomic clock PRS10\(^4\). Then, the 40-bit control code of the fractional-N PLL is calculated so that the probing signal lands near the center of the OCS spectral line. Note that in our testing, we are concerned more about the clock stability than its accuracy; any output frequency offset (i.e. inaccuracy) can be easily calibrated later by changing the static control code of PLL after clock locking.

Finally, the CMOS molecular clock is configured with a closed loop: the output signal \(V_{\text{LID}}\) of the RX, which

\(^4\)The same setup is also used later for the clock stability characterization, as is shown in Fig. 6. The PRS10 reference has an Allan deviation below \(10^{-12}\) at \(\tau=1000\) s, which is sufficiently low to measure our molecular clock.
is demodulated by the on-chip lock-in detector in Fig. 8, is fed into a low-pass filter ($R_0=50$ kΩ, $C_0=10$ μF, see Fig. 6), and then connected to the control terminal of VCXO. Fig. 15a gives the measured overlapping Allan deviation $\sigma_y$ [29] when OCS pressure is 10 Pascal. With an averaging time of 1000 s, $\sigma_y$ reaches $3.8\times10^{-10}$. Comparing with the free-running VCXO, it enhances the long-term stability by $15\times$. This factor is expected to be larger with a greater change of environmental temperature. Note that the prediction in Fig. 15a, which is based on (8), shows excellent agreement with the measurement in the short-term ($\tau<10$ s). Also note that due to the degraded SNR of the measured OCS line, the clock exhibits higher fluctuation than the VCXO when $\tau<6$ s. This is expected to be improved in the future. For example, Fig. 15a gives the measured Allan deviation if the loss of each chip-to-waveguide coupler is reduced from 10 dB to 1 dB (the simulated value): the expected short-term $\sigma_y$ at $\tau=1$ s improves to $4\times10^{-11}$ – this is the minimum short-term instability of the clock based on the presented CMOS chipset. Lastly, Fig. 15b shows the measured instantaneous frequency of the CMOS molecular clock over 4000 s. It is obvious that the molecular clock feedback prevents the long-term VCXO frequency from drifting.

In addition, Fig. 16a presents the measured Allan deviations under different pressure of the OCS sample. Although OCS sample at 1 Pascal has narrower linewidth compared with that at 10 Pascal ($Q_{1\text{ Pascal}}=3.6\times10^5$ versus $Q_{10\text{ Pascal}}=1.6\times10^5$, see Fig. 3c), in our measurements, the latter provides $3\times$ better short-term stability ($\tau<10$ s) due to the enhanced $Q$-SNR product. Furthermore, the measured pressure-induced frequency drift is shown in Fig. 16b. At pressure of 10 Pascal, the clock exhibits a pressure dependency of $6.6\times10^{-8}$ Pascal$^{-1}$. In our current prototype, the vacuum system exhibits a leakage rate <0.1 Pascal/hour, which leads to the long-term frequency drift in Fig. 15a. This issue can be solved by using a hermetic gas cell, which is disconnected from the vacuum pump.

According to the gas law, the pressure change over temperature is $3.3\times10^{-2}$ Pascal/K (under 10-Pascal pressure and 300-K temperature), which then leads to a clock temperature coefficient of $2.2\times10^{-9}$ K$^{-1}$. This temperature dependency, however, is mainly due to the non-flat spectroscopic baseline of the packaged clock module [22], rather than the intrinsic temperature-induced drift of OCS transition frequency; the latter is $\sim1\times10^{-11}$ K$^{-1}$ or below [22], [37]. The temperature induced frequency drift is due to the variation of mean free time of inter-molecular collision under pressure change and velocity dependency of the collision cross-section. Hence, assuming a temperature variation rate of $\Delta T/\Delta t=1$ K/10$^3$s, a long-term stability of $1\times10^{-11}$ with $\tau=10^3$ s is expected, as shown in Fig. 15a. In addition, Fig. 16a shows that the pressure-induced drift is more severe at lower pressure; because the impact of the baseline tilting is more predominant when OCS absorption is weak. Note that such impacts (hence the temperature dependency) can be effectively reduced by probing high-order dispersion curves in the clock-feedback loop, which was demonstrated in the lab-scale clock in [22].

Besides temperature/pressure dependency, there are also
other factors leading to long-term frequency drift, such as: (1) drift of free-running VCXO, which can be suppressed by sufficiently high clock loop gain; (2) Zeeman effect, which refers to \( \sigma \)-component doublet splitting caused by magnetic field. The magnetic-induced shift is about \( 1 \times 10^{-10} \) G\(^{-1} \) for the 231.061 GHz spectral line. Thus, a magnetic field shielding structure such as that used in CSACs is unnecessary; (3) Stark effect, which refers to asymmetric frequency shifts of the sublevels due to the existence of external electrical field. Note that 10% fluctuation of RF power only causes a relative drift of \( 1 \times 10^{-13} \). Further information about the long-term stability can be found in [22], [24] and [26].

VI. Conclusion

In this paper, an “atomic-clock-grade” miniaturized clock based on a mainstream 65-nm CMOS technology is described. It is realized by referencing the electronic clock oscillation to the rotational-mode transition of OCS molecules at sub-THz band. Table I compares this work with the other relevant publications. Compared with ammonia clock utilizing inversion spectrum at K-band [39], the chip-scale molecular gas will be hermetically sealed inside the waveguide, so that no metal chamber nor connections to the vacuum system, shown in Fig. 10c, are needed. In addition, efficient sub-THz waveguides can also be manufactured using low-cost silicon micromachined technology [40]. Such progresses will further reduce the volume of the clock to <1 cm\(^3\). In conclusion, the presented chip-scale molecular clock has great potentials to be a highly-stable frequency reference with small cost, size and power, which is ideal for portable devices used in networked sensing, navigation and communication, and operations under GPS denial.

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APPENDIX: Optimal Frequency Deviation of the FSK-Modulated Probing Signal

In this section, we find the optimal frequency deviation \( \Delta f \) of the FSK-modulated probing signal, in order to maximize \( K_r \) in (5) (hence the short-term stability). First, when the FSK modulation is off, the baseband signal \( V_{BB} \) is written as:

\[
V_{BB}(f_p) = R_r P_0 e^{-\alpha_0 L} L, \tag{10}
\]

where \( R_r \) is the responsivity of receiver, \( P_0 \) is the power of probing signal, \( \alpha_0 \) is the loss of gas cell (without gas) per unit length, \( \alpha_{gas,J+1=J} \) is the absorption coefficient of spectral line per unit length, and \( L \) is the length of gas cell. Here, we assume \( \alpha_{gas,J+1=J} \cdot L \ll 1 \). Next, under pressure broadening, the absorption coefficient \( \alpha_{gas,J+1=J} \) of spectral line has a Lorentzian profile [24]:

\[
\alpha_{gas,J+1=J}(f_p) \approx \frac{\beta}{4(f_p - f_0)^2 + f_{FWHM}^2}, \tag{11}
\]

where

\[
\beta = \frac{16\pi N_m f_L \mu_{J,J+1}^2 f_{FWHM}^2}{3ckT}.
\]

In (12), \( N_m \) is the total number of molecules per unit volume, \( f_L \) is the fraction of molecules on the lower state of rotational transition, \( \mu_{J,J+1} \) is the dipole moment for the transition from state \( J \) to state \( J+1 \), \( c \) is the speed of light, \( k \) is Boltzmann’s constant, and \( T \) is the temperature. Therefore, after performing FSK modulation on the TX side and phase-aligned lock-in detection on the RX side, the induced error signal \( V_{error}(f_e) \) is expressed as:

\[
V_{error}(f_e) = V_{BB}(f_p + \Delta f) - V_{BB}(f_p - \Delta f) = R_r P_0 e^{-\alpha_0 L} \beta \left[ \frac{1}{4(f_e - \Delta f)^2 + f_{FWHM}^2} - \frac{1}{4(f_e + \Delta f)^2 + f_{FWHM}^2} \right], \tag{13}
\]

where we define \( f_e = f_p e^{-\gamma} \). Note that (13) describes the dispersion curve shown in Fig. 5a. Its zero-crossing slope \( K_r \) is then calculated as:

\[
K_r = V_{error}'|_{f_e=0} = R_r P_0 e^{-\alpha_0 L} \beta \cdot \frac{16 \Delta f}{(4 \Delta f^2 + f_{FWHM}^2)^2}. \tag{14}
\]

As a result, by setting \( dK_r / d\Delta f = 0 \), the optimum frequency deviation \( \Delta f \) that maximizes \( K_r \) is found to be:

\[
\Delta f_{opt} = \frac{f_{FWHM}}{2 \sqrt{3}} \approx 0.29 \cdot f_{FWHM}. \tag{15}
\]

Inserting \( \Delta f_{opt} \) into (13), we also obtain the frequency offset \( f_{peak} \) at which \( V_{error}(f_e) \) reaches its peak value:

\[
f_{peak} = \sqrt{\frac{2 \cdot (\sqrt{13} - 1)}{6}} f_{FWHM} \approx 0.38 \cdot f_{FWHM}. \tag{16}
\]

At this frequency point, the value of \( V_{error}(f_e) \) is:

\[
V_{error, max} \approx 0.23 \cdot K_r \cdot f_{FWHM}. \tag{17}
\]
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This Work

OCS Molecular Clock ($f_{0,Cs}=231.069938$ GHz) | $3 \times 10^{-10}$ ($\tau=1000$ s) | <1 | 662 | 65-nm CMOS Chip + Sub-THz Waveguide |

¹The power of the VCXO is not included. ²The power of off-chip heater, laser, and other components is not included.

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Cheng Wang received the B.E. degree in engineering physics from Tsinghua University, Beijing, China, in 2008, a M.S. degree in radio physics from China Academy of Engineering Physics, Mianyang, China, in 2011 and a M.S. degree in electrical engineering and computer science (EECS) from Massachusetts Institute of Technology (MIT), Cambridge, US, in 2018. He joined the Institute of Electronic Engineering, Mianyang, China as an assistant research fellow from 2011 to 2015. Currently, he is pursuing his Ph.D. degree at the Department of electrical engineering and computer science, MIT. In 2016, he received the Analog Device Inc. Outstanding Student Designee Award. In 2017, he received the IEEE Microwave Theory and Techniques Society Boston Chapter Scholarship. His research covers topics of millimeter/terahertz-wave gas spectroscopy, high-precision clock generation, wireless communication and automotive radar.

Xiang Yi (S’11M’13) received the B.E. degree, M.S. degree and Ph.D. degree from Huazhong University of Science and Technology (HUST) in 2006, South China University of Technology (SCUT) in 2009 and Nanyang Technological University (NTU) in 2014, respectively. He is currently working as a Postdoctoral Fellow in Massachusetts Institute of Technology (MIT). He was a Research Fellow in NTU from 2014 to 2017. His research interests include radio frequency (RF), millimetre-wave (mmwave), and terahertz (THz) frequency synthesizers and transceiver systems. Dr. Yi was the recipient of the IEEE ISSCC Silroad Award and SSCS Travel Grant Award in 2013. He is a technical reviewer for several IEEE journals and conferences.

Mina Kim received the B.S. degree and M.S. degree in electrical engineering from Ulsan National Institute of Science and Technology, Korea, in 2013 and 2016, respectively. She is currently pursuing the Ph.D. degree at the Massachusetts Institute of Technology, Cambridge, MA, USA. Her research interests include clock generation and millimeter/terahertz-wave integrated circuit design. She is a recipient of the MIT EECS graduate Alumni Fellowship, and the Kwanjeong scholarship for the graduate study in 2017.

Zhi Hu (S’15) received the B.S. degree in microelectronics from Fudan University in 2015. Currently as a graduate student at MIT he is exploring novel architectures of terahertz circuits. He was awarded the SCSK Scholarship in 2013, the KLA-Tencor Scholarship in 2014, and is the recipient of the Best Student Paper Award (2nd place) of the IEEE Radio-Frequency Integrated Circuits Symposium 2017.

Yaqing Zhang received the B.E. degree in Optoelectronics from Nankai University, Tianjin, China, in 2012. Currently he is pursuing his Ph.D. degree at the Department of Chemistry, Massachusetts Institute of Technology, under the supervision of Professor Keith A. Nelson. His research topic covers linear and nonlinear terahertz spectroscopy, gas phase rotational spectroscopy, and multi-dimensional terahertz spectroscopy.

Bradford Perkins received a B.A. degree in chemistry from Dartmouth College, Hanover, NH in 2001 and a Ph.D. degree in chemical physics from JILA at the University of Colorado, Boulder in 2009 for studies that investigated dynamics at the gas-liquid interface. He was awarded a National Science Foundation Postdoctoral Fellowship in 2010 to work in the chemistry department at MIT where he studied ultrafast processes in crystals and superconductors with THz spectroscopy. Dr. Perkins is currently Technical Staff member in the Chemical, Microsystems, and Nanoscale Technologies group at MIT Lincoln Laboratory in Lexington, MA. His current research interests involve chemical and biological material sensing, aerosol chemistry, and novel laser-based spectroscopic techniques.

James (Jimmy) Mawdsley will receive the S.B. degree in electrical engineering and M.Eng degree in electrical engineering from the Massachusetts Institute of Technology (MIT) in 2018 and 2019, respectively. He is currently engaged in research into terahertz integrated circuit design. During the fall of 2017, he worked at SpaceX in Irvine, CA, where he designed RFICs for satellite communications.
Ruonan Han (S’10-M’14) received the B.Sc. degree in microelectronics from Fudan University, China, in 2007, the M.Sc. degree in electrical engineering from the University of Florida, Gainesville, FL, USA, in 2009, and the Ph.D. degree in electrical and computer engineering from Cornell University, Ithaca, NY, USA, in 2014. In 2012, he was an Intern with Rambus Inc., Sunnyvale, CA. He is currently an associate professor with the Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA, USA. His current research interests include microelectronic circuits and systems operating at millimeter-wave and terahertz frequencies.

Dr. Han is a member of the IEEE Solid-State Circuits Society and the IEEE Microwave Theory and Techniques Society. He was a recipient of the Cornell ECE Directors Ph.D. Thesis Research Award, Cornell ECE Innovation Award, and two Best Student Paper Awards of the IEEE Radio-Frequency Integrated Circuits Symposium (2012 and 2017). He was also recipient of the IEEE Microwave Theory and Technique Society Graduate Fellowship Award, and the IEEE Solid-State Circuits Society Predoctoral Achievement Award. He is an associate editor of IEEE Transactions on Very-Large-Scale Integration (VLSI) System and also serves on the Technical Program Committee (TPC) of IEEE RFIC Symposium and the Steering Committee of 2019 IEEE International Microwave Symposium (IMS). He held MIT E. E. Landsman (1958) Career Development Chair Professorship, and was the winner of the National Science Foundation (NSF) CAREER Award in 2017.