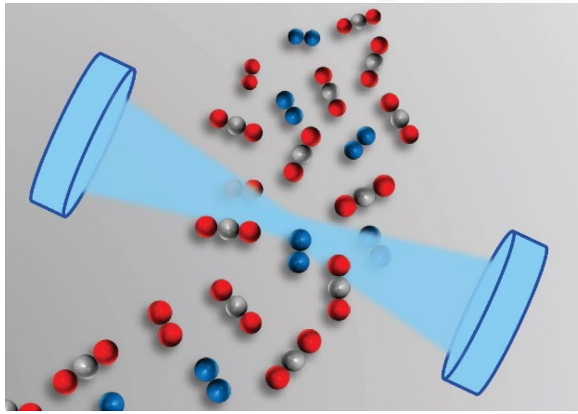
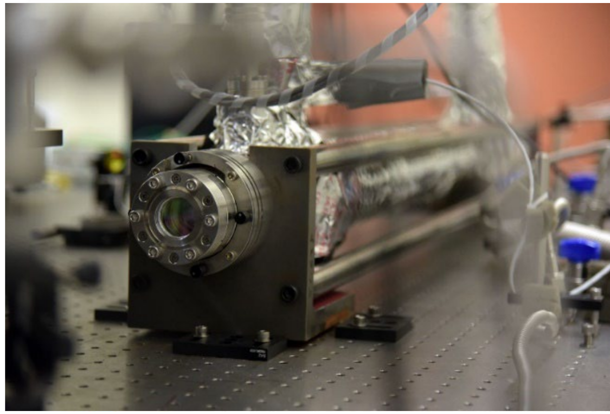




Accurate cavity-enhanced spectroscopy of molecules with coherent light

Adam J. Fleisher | CES Summer School | Lecco, Italy | 14 June 2022

National Institute of Standards and Technology
U.S. Department of Commerce

MATERIAL MEASUREMENT LABORATORY

National Institute of Standards and Technology (NIST)

Gaithersburg, MD: ~32 km northwest of Washington, DC

ATMOSPHERIC TRANSMITTANCE: EARTH AND BEYOND

With an accurate model for how light is absorbed by molecules in the Earth's atmosphere, researchers can measure gas column densities globally, over urban areas, wildfires, and regional carbon sources and sinks (e.g., forests, oceans, etc.).

Current and future probes and Great Observatories (NASA, ESA, etc.) monitor transmission and emission spectra from planets, moons, stars, exoplanets, and other astronomical bodies to better understand the chemical composition and dynamics of the Solar System and beyond.

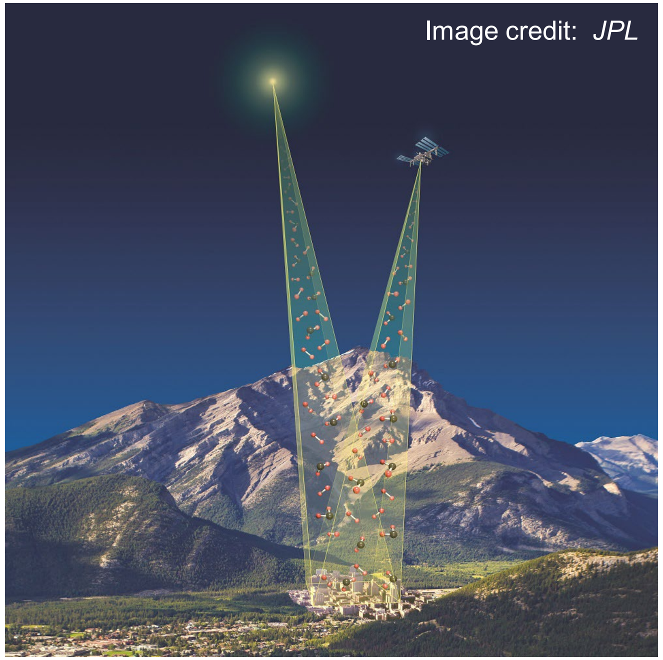


Image credit: *JPL*

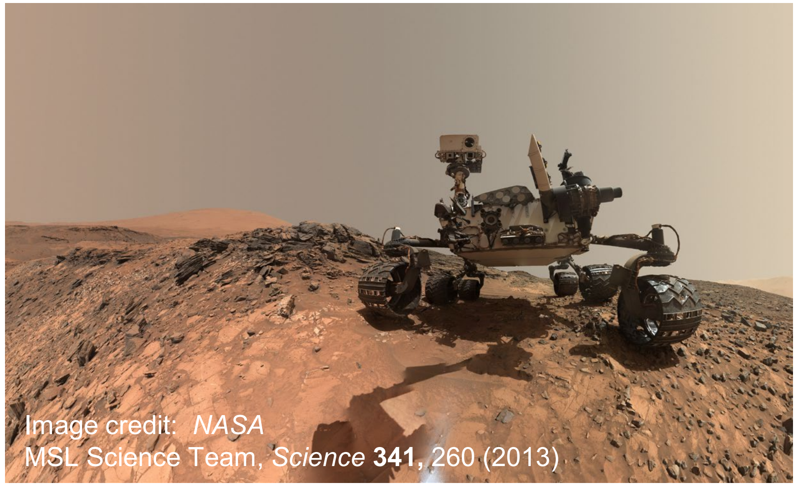
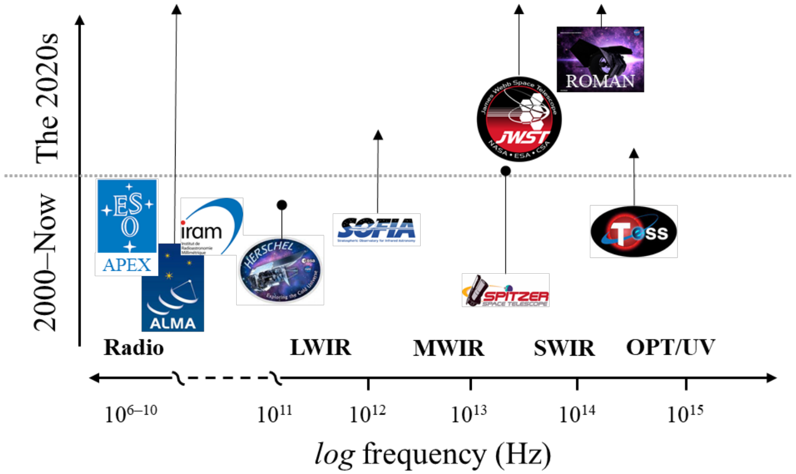
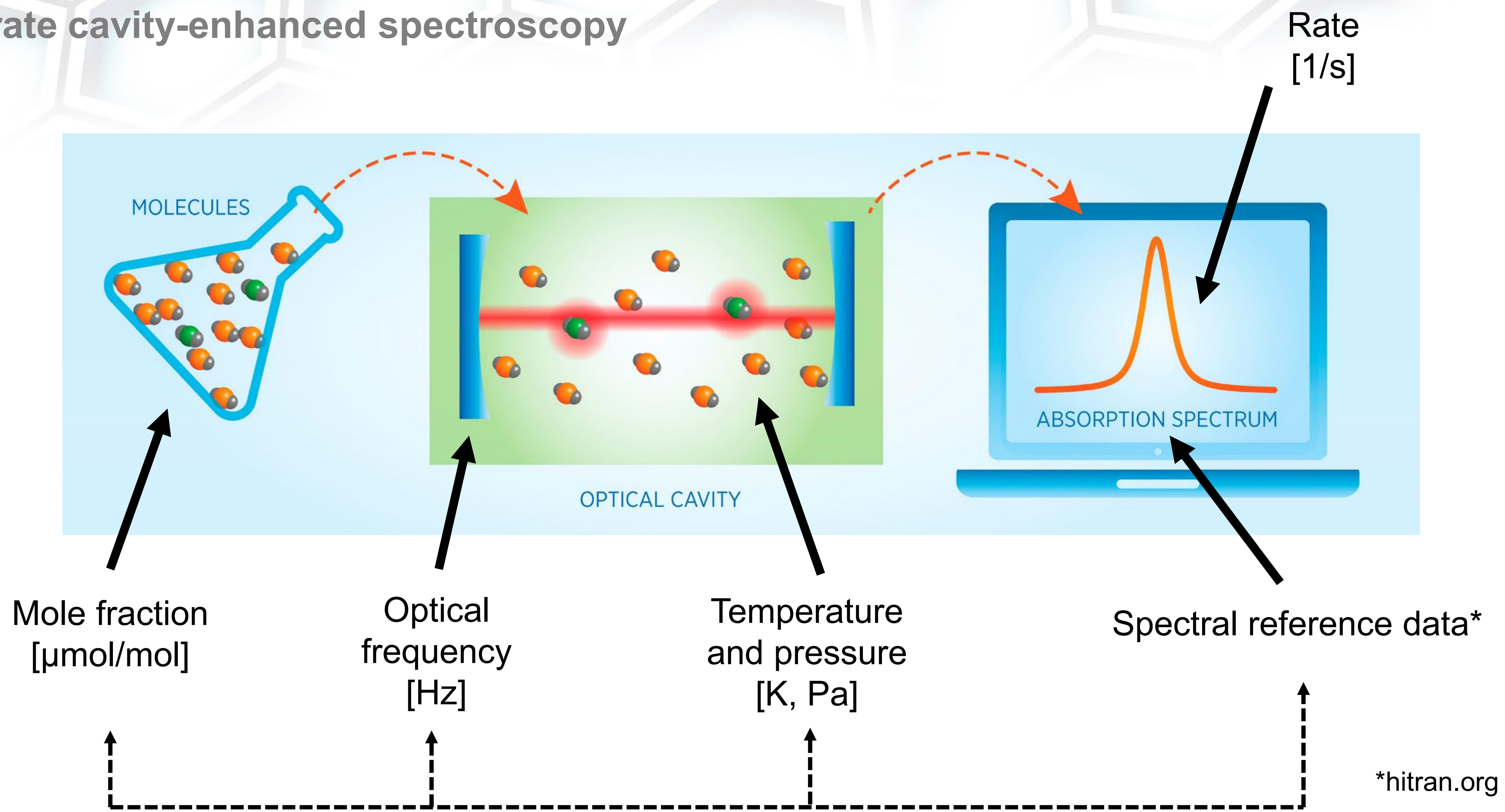


Image credit: *NASA*
MSL Science Team, *Science* **341**, 260 (2013)



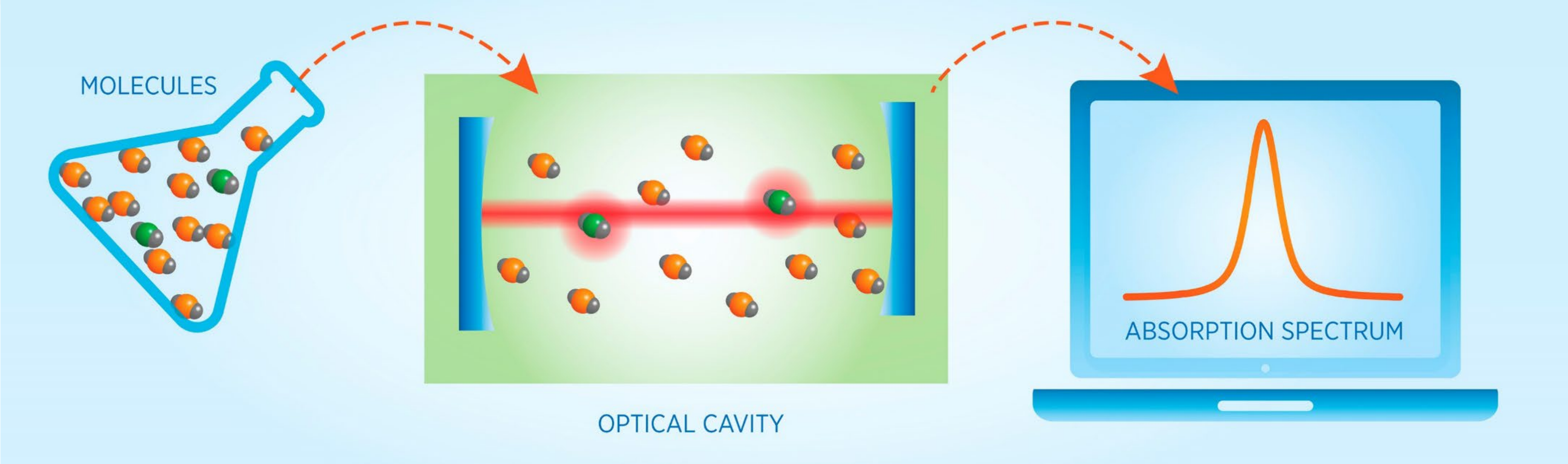
"Great observatories: The past and future of panchromatic astrophysics," arXiv:2104.00023 [astro-ph.IM]

Accurate cavity-enhanced spectroscopy



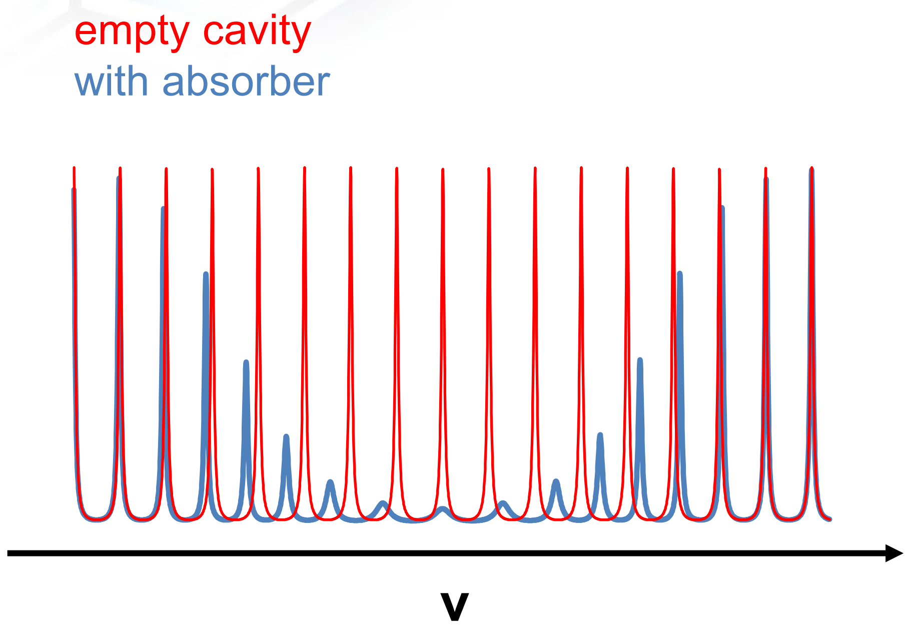
*hitran.org

Accurate cavity-enhanced spectroscopy



Long interaction pathlength (km’s in a compact physical footprint)
Stable frequency axis (relative stability better than 10^{-8})
Spatially coherent (well-defined beam shape / mode volume / mode cross-section)
High resolution (high quality factor / finesse)

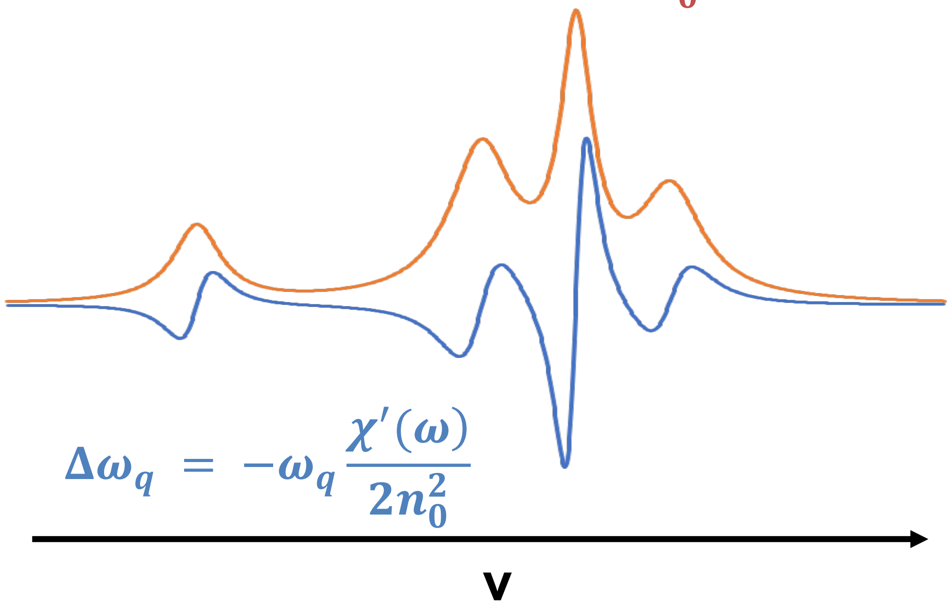
Cavity transmission spectrum



Lehmann and Romanini, *JCP* **105,** 10263 (1996)
Lehmann, Dispersion and Cavity-Ringdown Spectroscopy, in Cavity-Ringodwn Spectroscopy, eds. Bush and Bush (APS, 1999)
Cygan et al., *MST* **27,** 045501 (2016)
Cygan et al., *Commun. Phys.* **4,** 14 (2021)

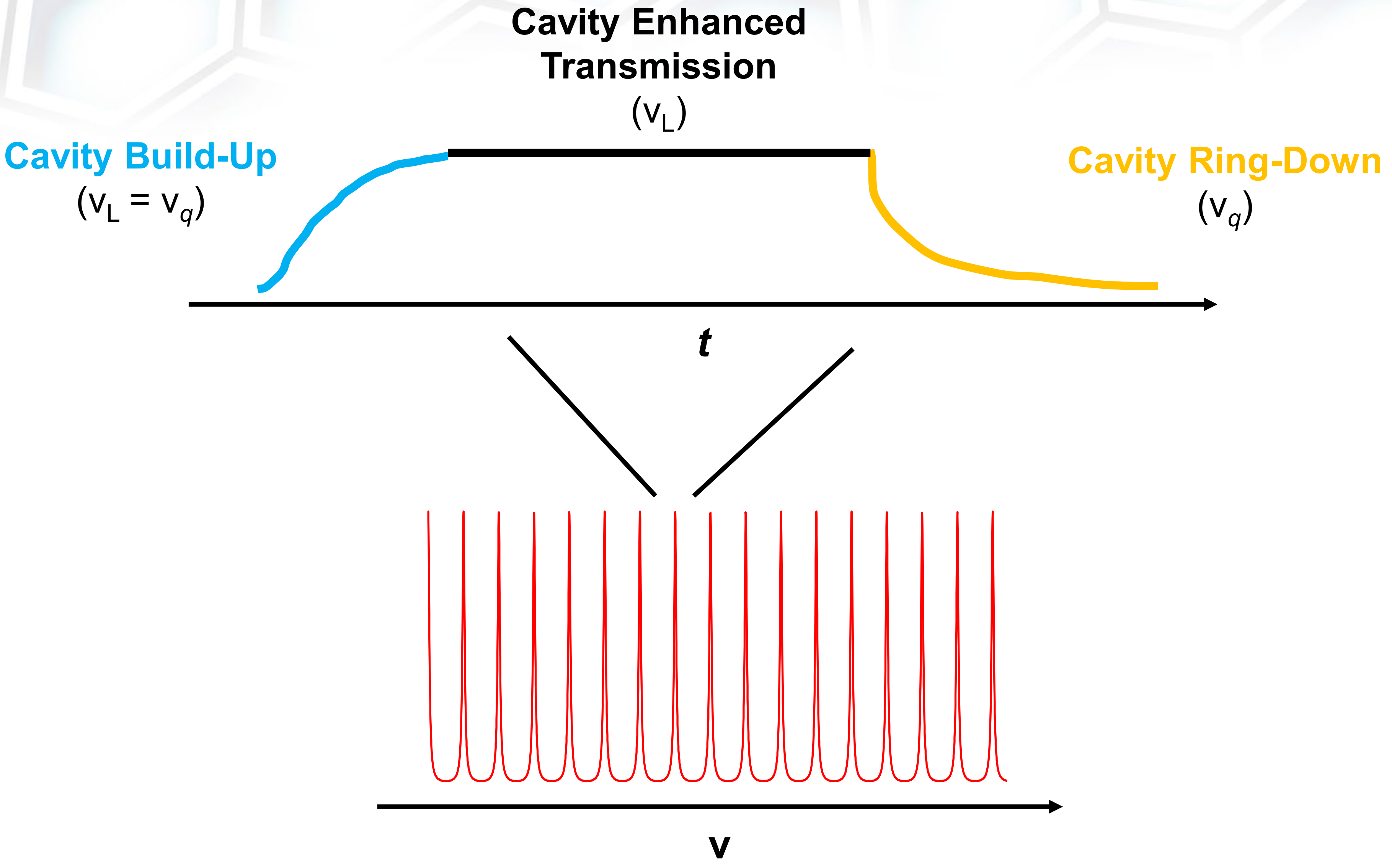
Molecular absorption and dispersion

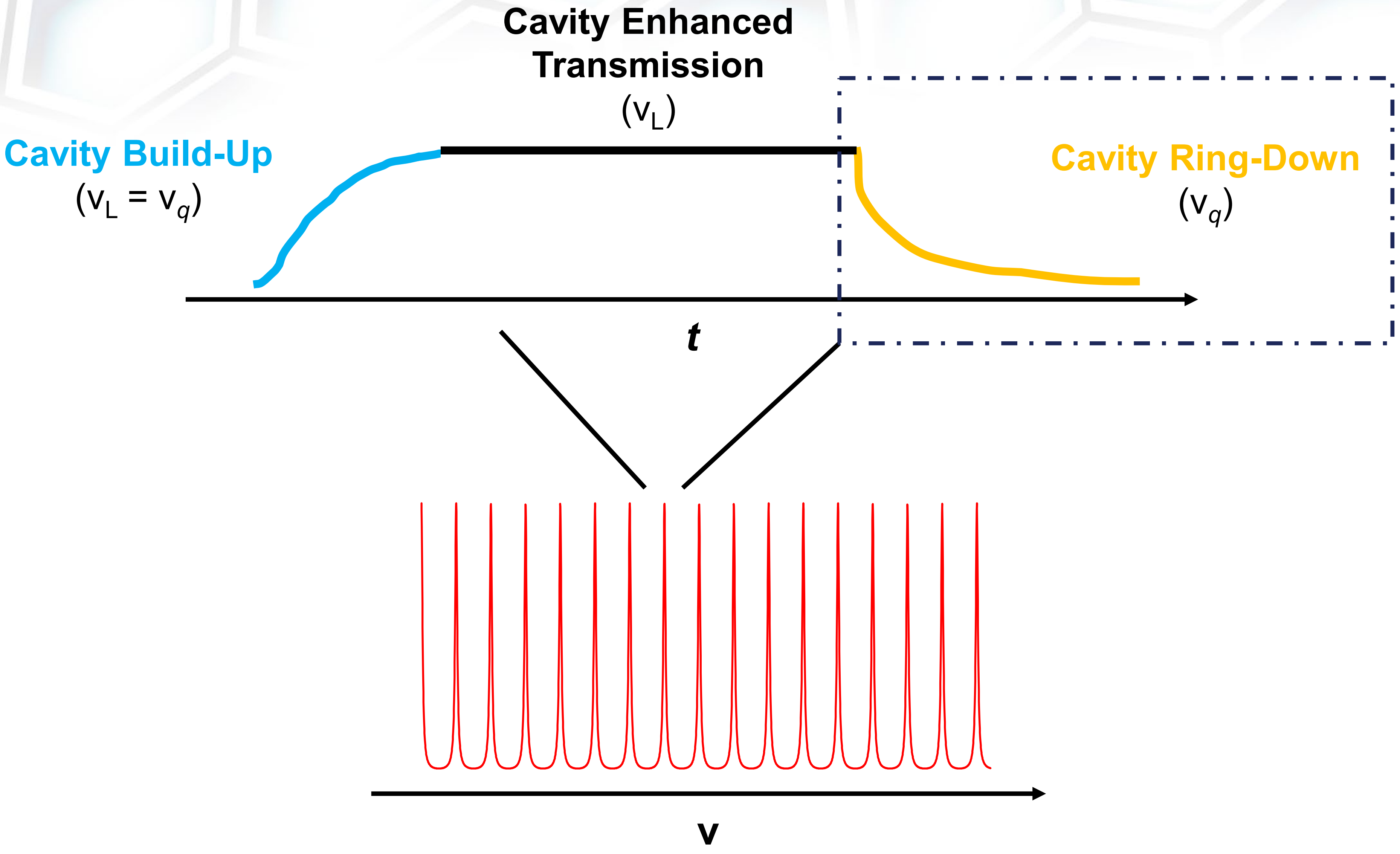
$$\alpha_q(t) = 2\Delta\Gamma_q/c = \omega_q \frac{\chi''(\omega)}{cn_0}$$



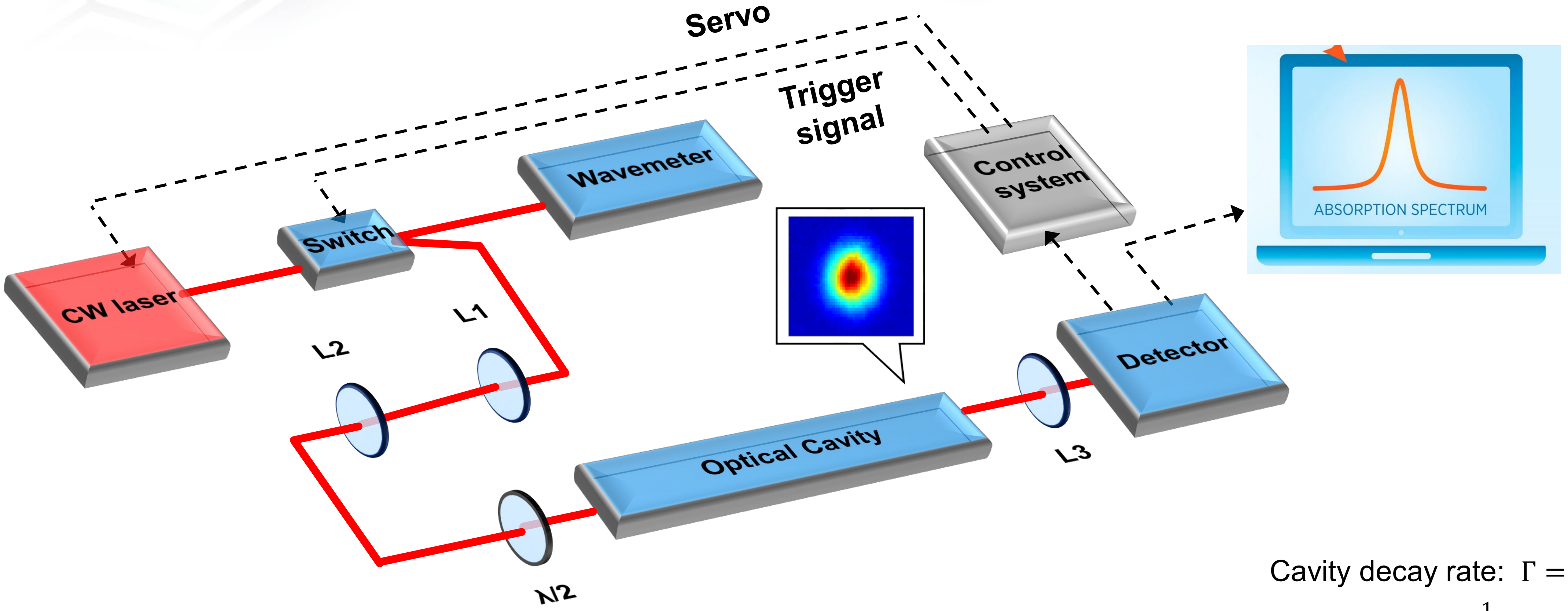
$$\Delta\omega_q = -\omega_q \frac{\chi'(\omega)}{2n_0^2}$$

$$\frac{\delta\omega_q}{\Delta\Gamma_q} = -\frac{\chi'}{n_0\chi''} = \frac{\mathrm{Im}\{\mathcal{L}(\omega_q - \omega_L)\}}{n_0\mathrm{Re}\{\mathcal{L}(\omega_q - \omega_L)\}}$$


Cavity Enhanced Transmission
(νL)
Cavity Build-Up
(νL = νq)
Cavity Ring-Down
(νq)
t
ν


Cavity Enhanced Transmission
(νL)
Cavity Build-Up
(νL = νq)
Cavity Ring-Down
(νq)
t
ν

CAVITY RING-DOWN SPECTROSCOPY



Cavity decay rate: $\Gamma = 1/\tau$

Losses: $L_{tot} = \frac{1}{c\tau} = \alpha + L_0$

Fleisher et al., *JPCL* **8,** 4550 (2017)

CAVITY RING-DOWN SPECTROSCOPY

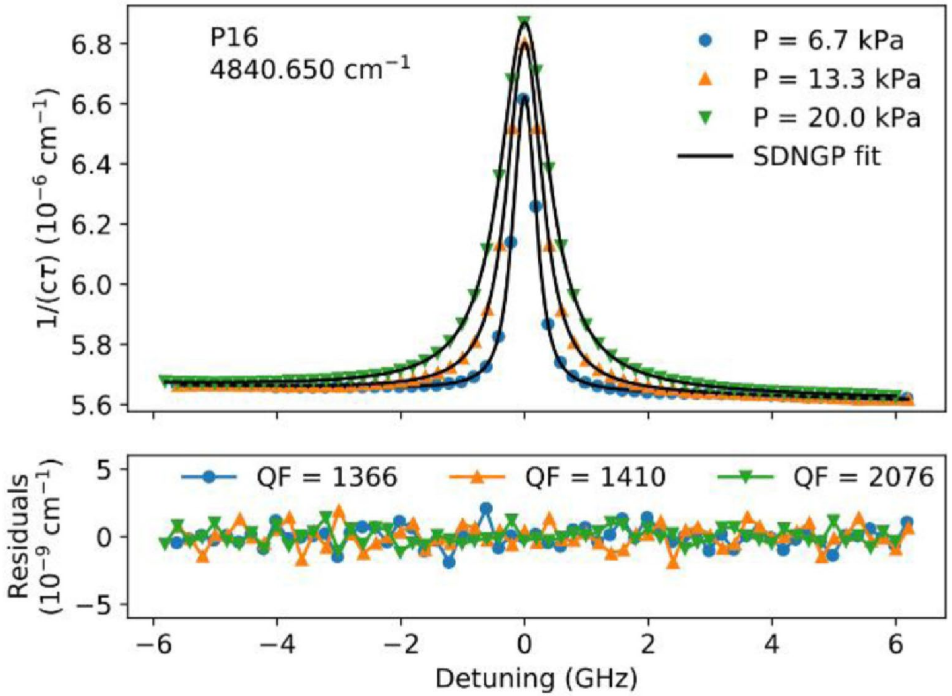
Cavity decay rate: $\Gamma = 1/\tau$

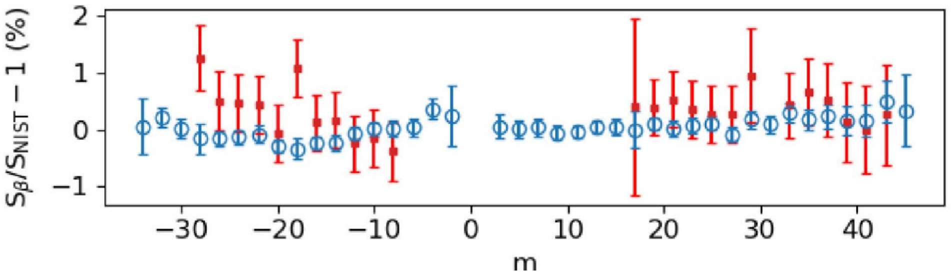
Losses: $L_{tot} = \frac{1}{c\tau} = \alpha + L_0$

Measure CRDS for many lines on a sample of CO_2 with mole fraction traceable to gravimetric and volumetric samples (NIST GMG)

Compare with *ab initio* or spectroscopic model to yield band intensity

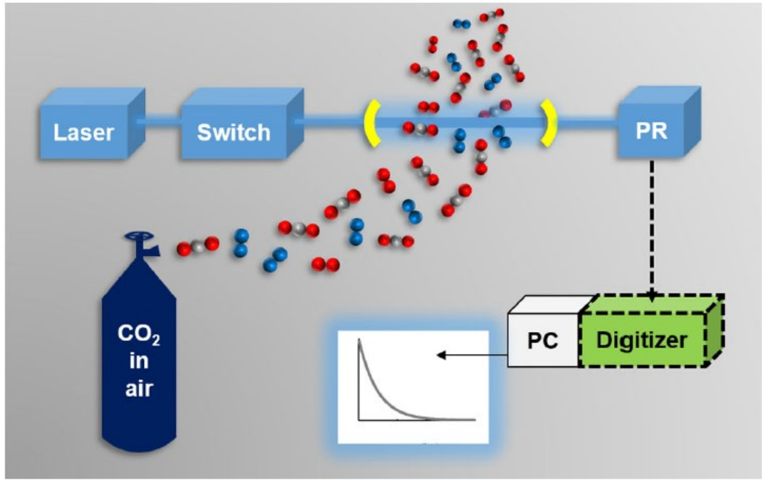
Apply to OCO missions, HITRAN2020

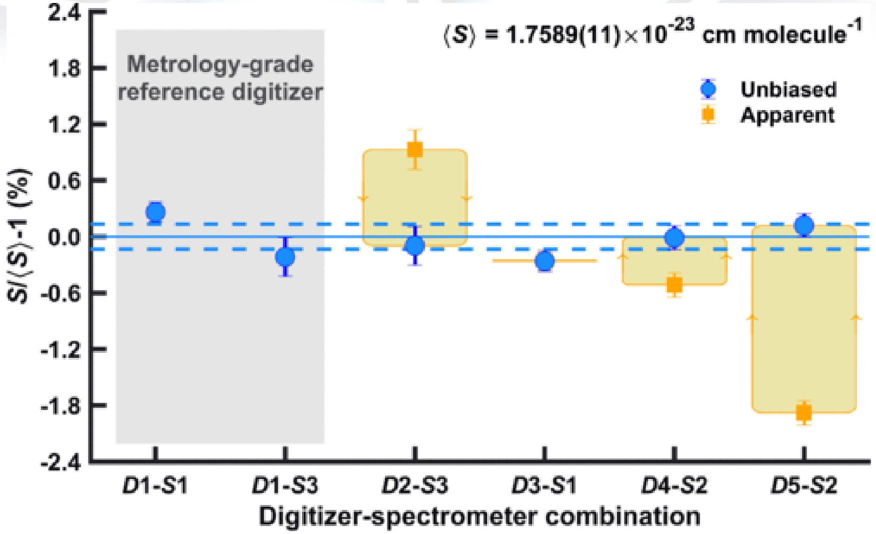




Fleurbaey et al., *JQSRT* **252,** 107104 (2020)

Uncertainty budget: Digitizer





Measure DC voltage linearity
Measure synthetic decay signals
Optimize fitting algorithm and regime*

PHYSICAL REVIEW LETTERS **123,** 043001 (2019)

Editors' Suggestion | Featured in Physics

Twenty-Five-Fold Reduction in Measurement Uncertainty for a Molecular Line Intensity

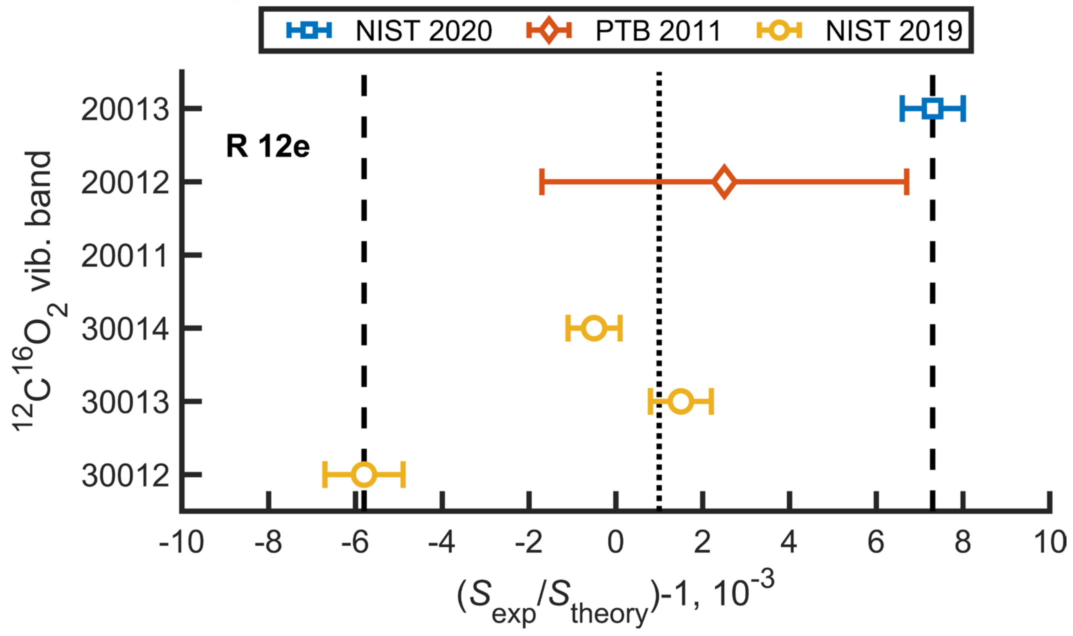
Adam J. Fleisher,* Erin M. Adkins, Zachary D. Reed, Hongming Yi, David A. Long, Hélène M. Fleurbaey, and Joseph T. Hodges†
National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899, USA

*Huang and Lehmann, *JPCA* **117,** 13399 (2013)
Fleisher et al., *PRL* **123,** 043001 (2019)

Agreement with an *ab initio* line list

Result: <0.5% agreement between CRDS and theory.

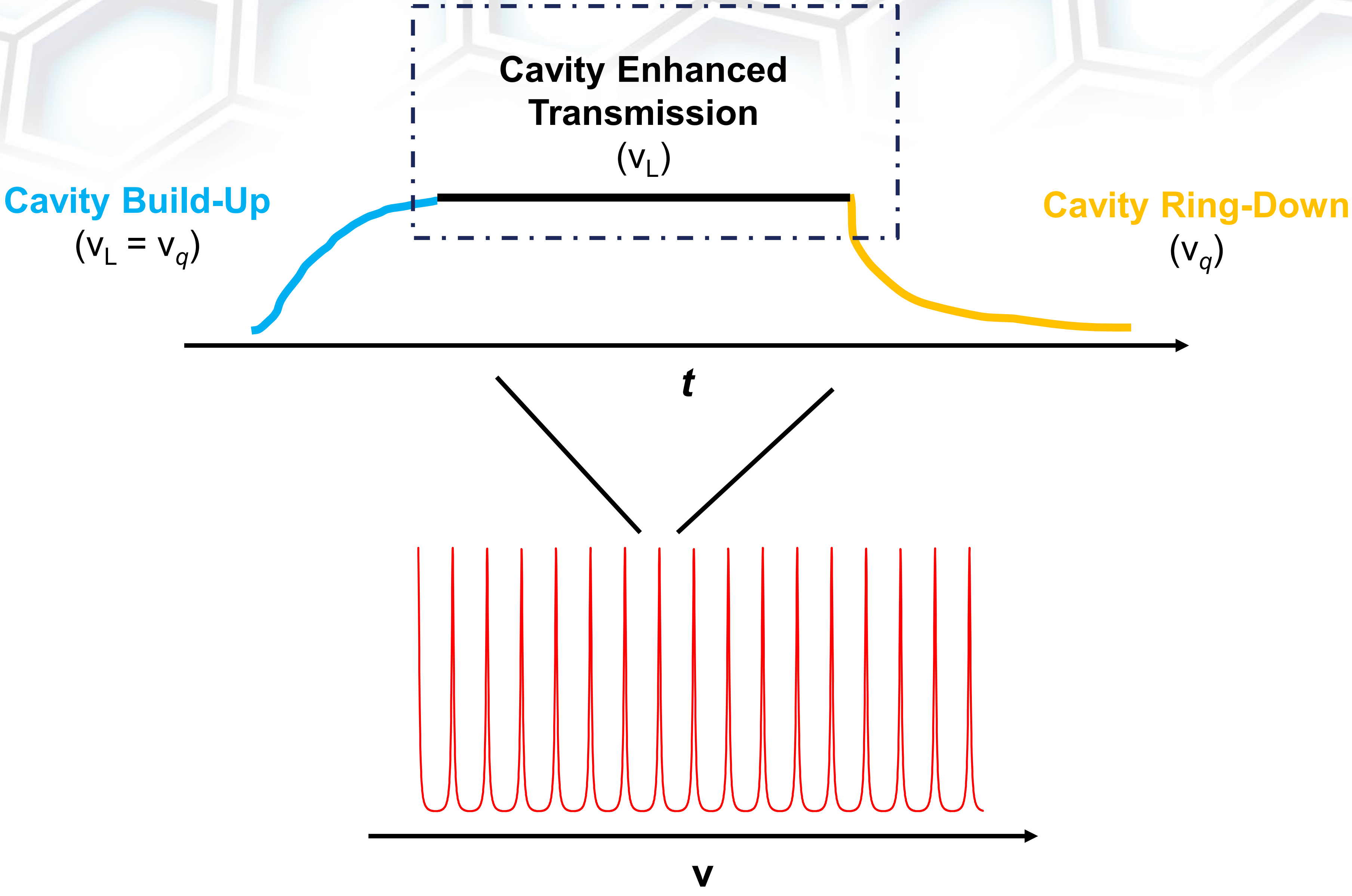
Limitations for CO_2: sampling, line profile + constraints



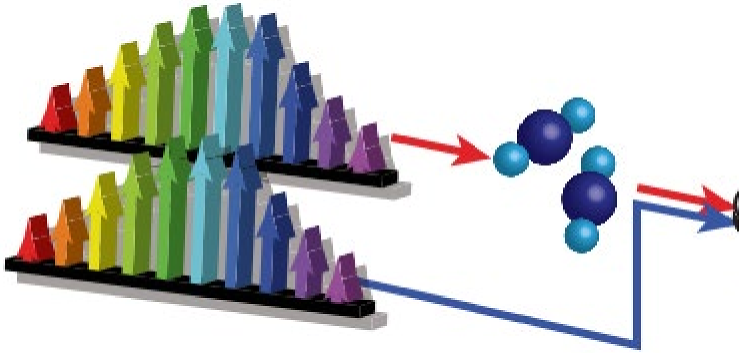
Uniform distribution

$u_r = (6.6 \times 10^{-3})/\sqrt{(3)} = 3.8 \times 10^{-3}$

Long et al., *GRL* **47,** e2019GL086344 (2019)
Wübbeler et al., *JCP* **135,** 204304 (2011)
Fleurbaey et al., *JQSRT* **252,** 107104 (2020)
Fleisher, Yi et al., *Nat. Phys.* **17,** 889 (2021)


Cavity Enhanced
Transmission
(ν$_L$)
Cavity Build-Up
(ν$_L$ = ν$_q$)
Cavity Ring-Down
(ν$_q$)
t
ν

CAVITY-ENHANCED SPECTROSCOPY

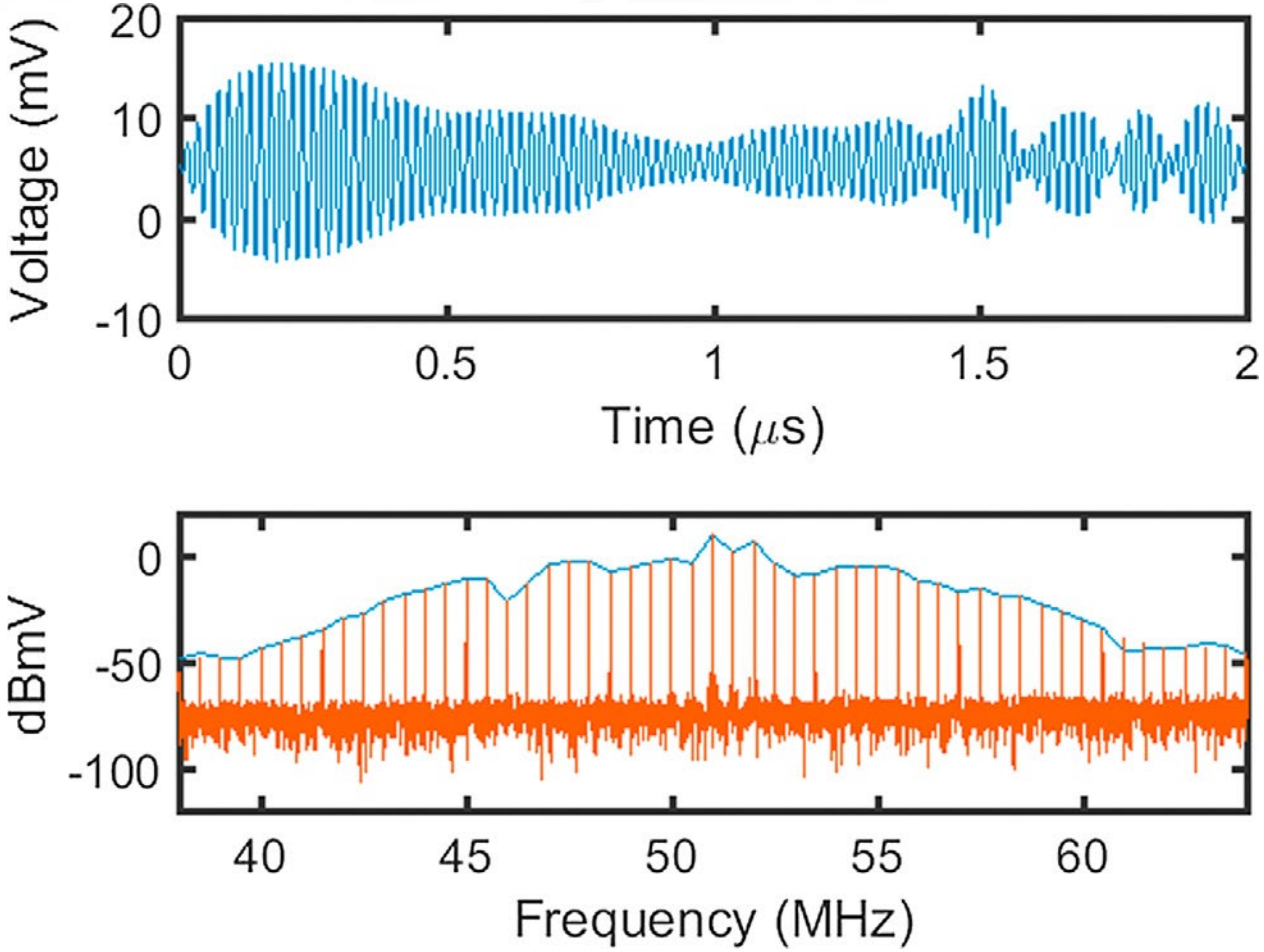


Dual-comb interferogram

Coherent averaging

Fourier transform

Cavity transmission intensity spectrum as sampled by an electro-optic comb



Coddington et al., *Optica* **3,** 414 (2016)
Long et al, *Opt Lett.* **39,** 2688 (2014)
Fleisher et al., *Opt. Express* **24,** 10424 (2016)
Fleisher et al., *J. Mol. Spectrosc.* **352,** 26 (2018)

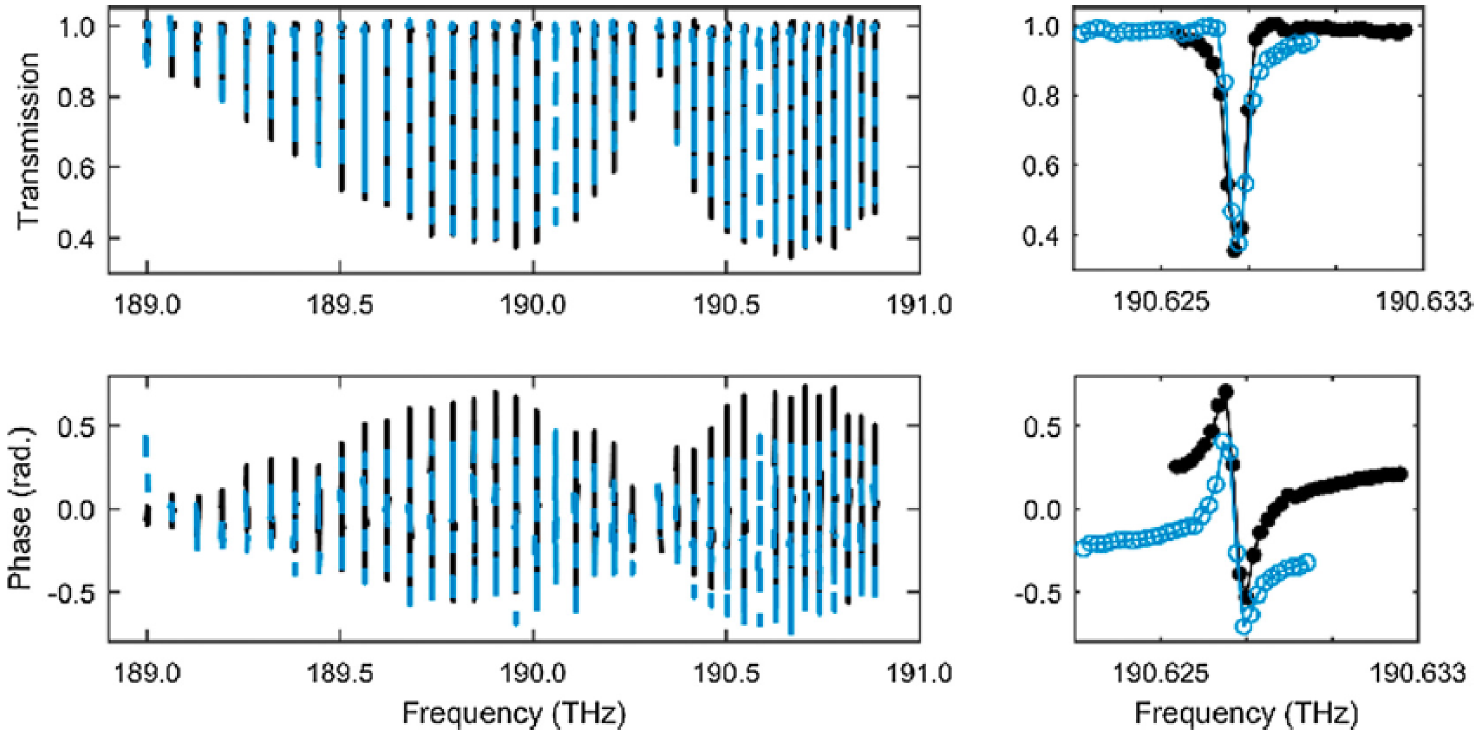
CAVITY-ENHANCED SPECTROSCOPY

Model the complex-valued cavity transmission electric field with a local oscillator EO comb for DCS

Includes molecular dispersion and absorption, mirror dispersion, etc.

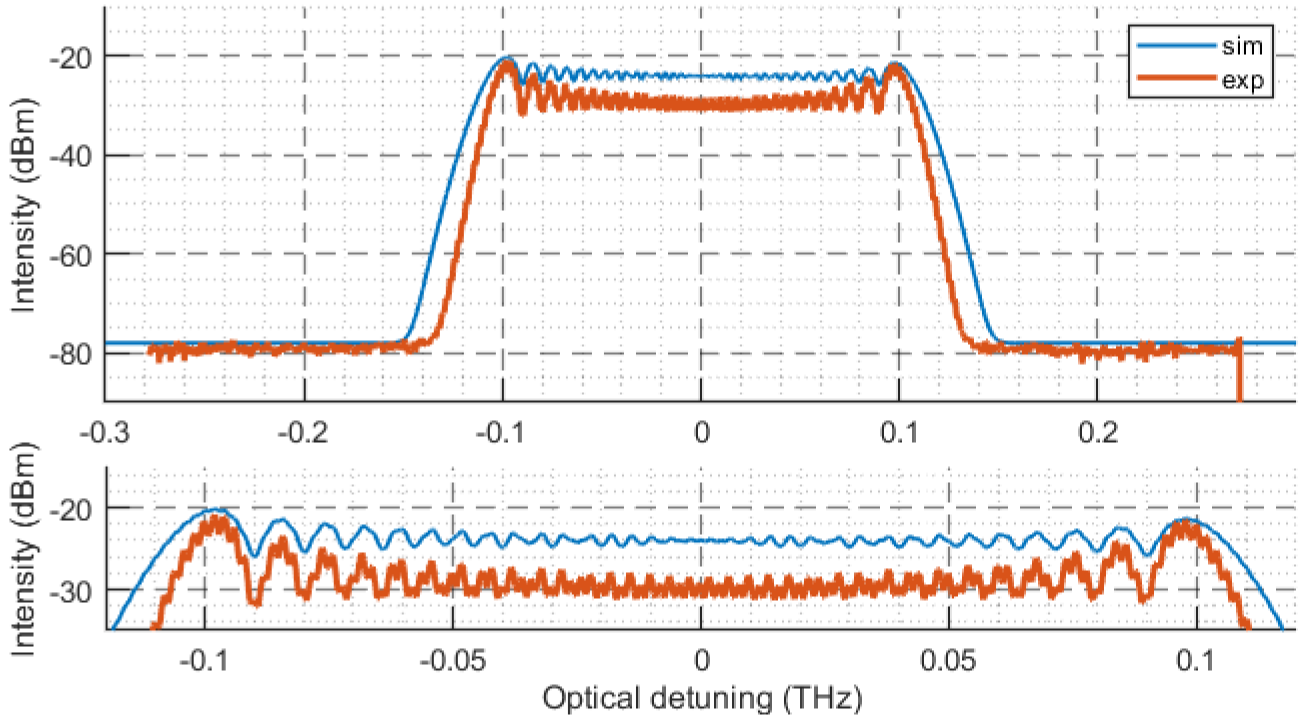
Changing the PDH lock point changes the observed cavity transmission electric field and EO-DC spectrum

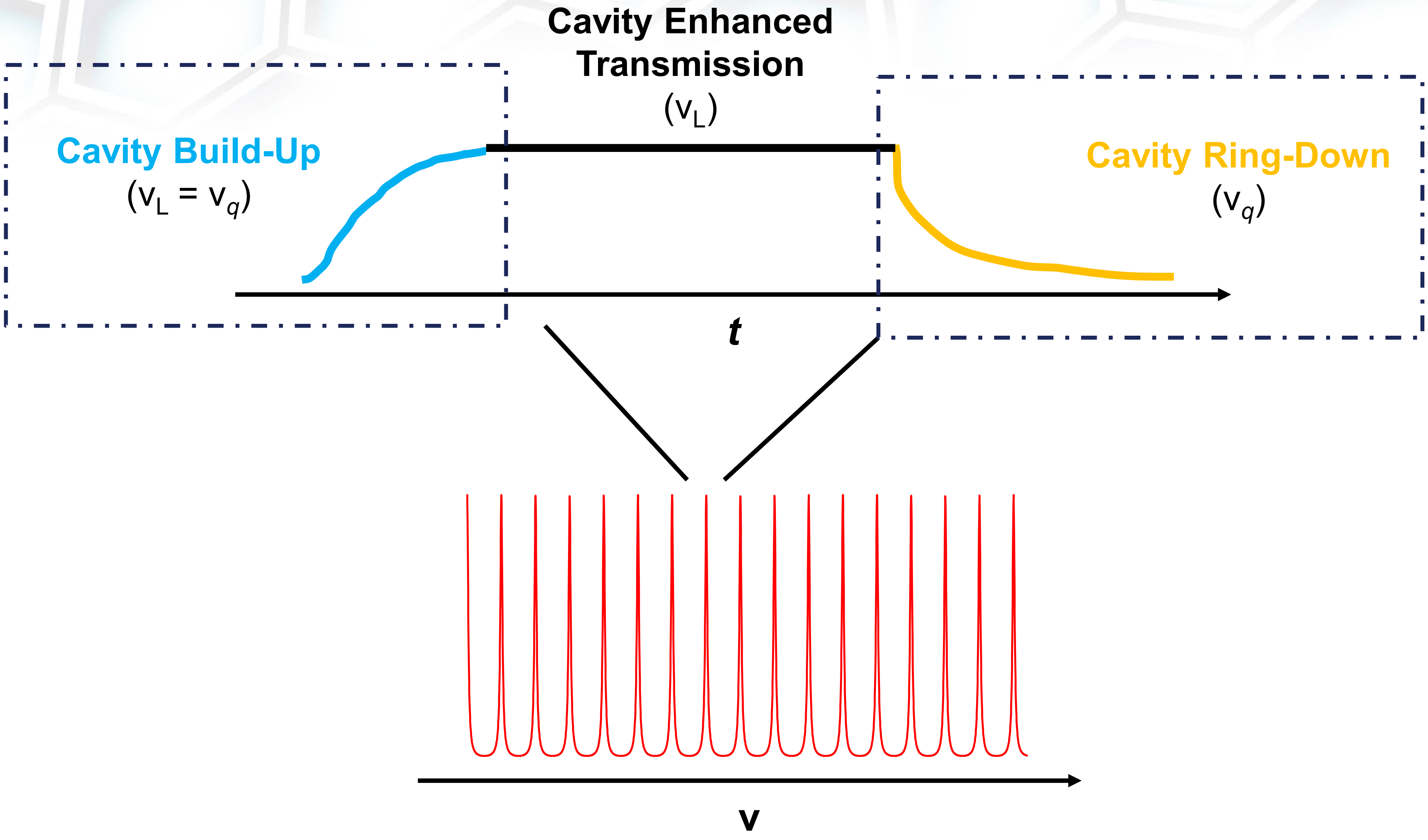
The transmission spectrum still requires normalization by the probe comb power spectrum



Foltynowicz et al., *APB* **110,** 163 (2013)
Fleisher et al., *J. Mol. Spectrosc.* **352,** 26 (2018)

Optically flat, broader band EO combs




Cavity Enhanced
Transmission
(vL)
Cavity Build-Up
(vL = vq)
Cavity Ring-Down
(vq)
t
v

BUILD-UP AND RING-DOWN HYBRID: HETERODYNE-DETECTED CRDS

RAPID COMMUNICATIONS

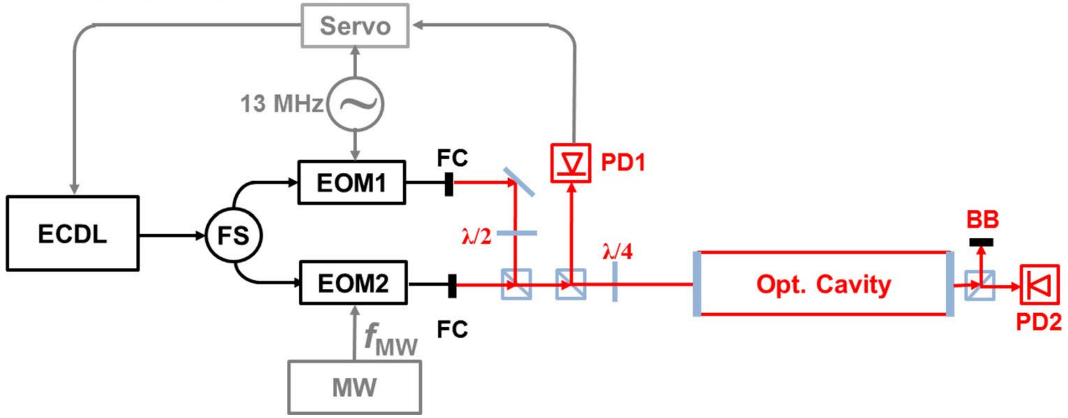
PHYSICAL REVIEW A, VOLUME 61, 061802(R)

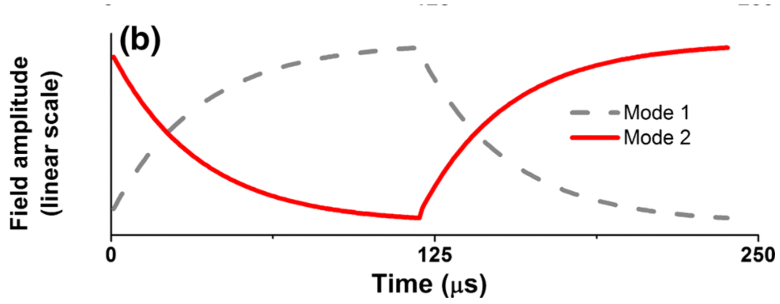
Cavity ringdown heterodyne spectroscopy: High sensitivity with microwatt light power

Jun Ye* and John L. Hall

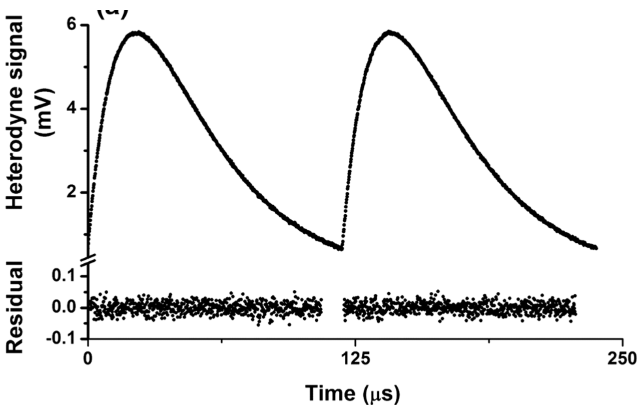
JILA, National Institute of Standards and Technology and University of Colorado, Boulder, Colorado 80309-0440

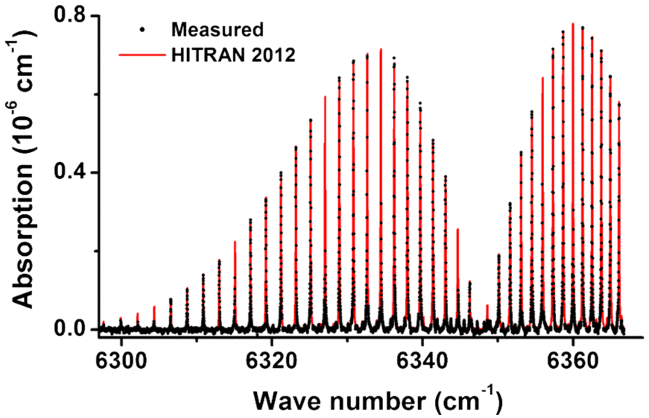
(Received 11 January 2000; published 17 May 2000)



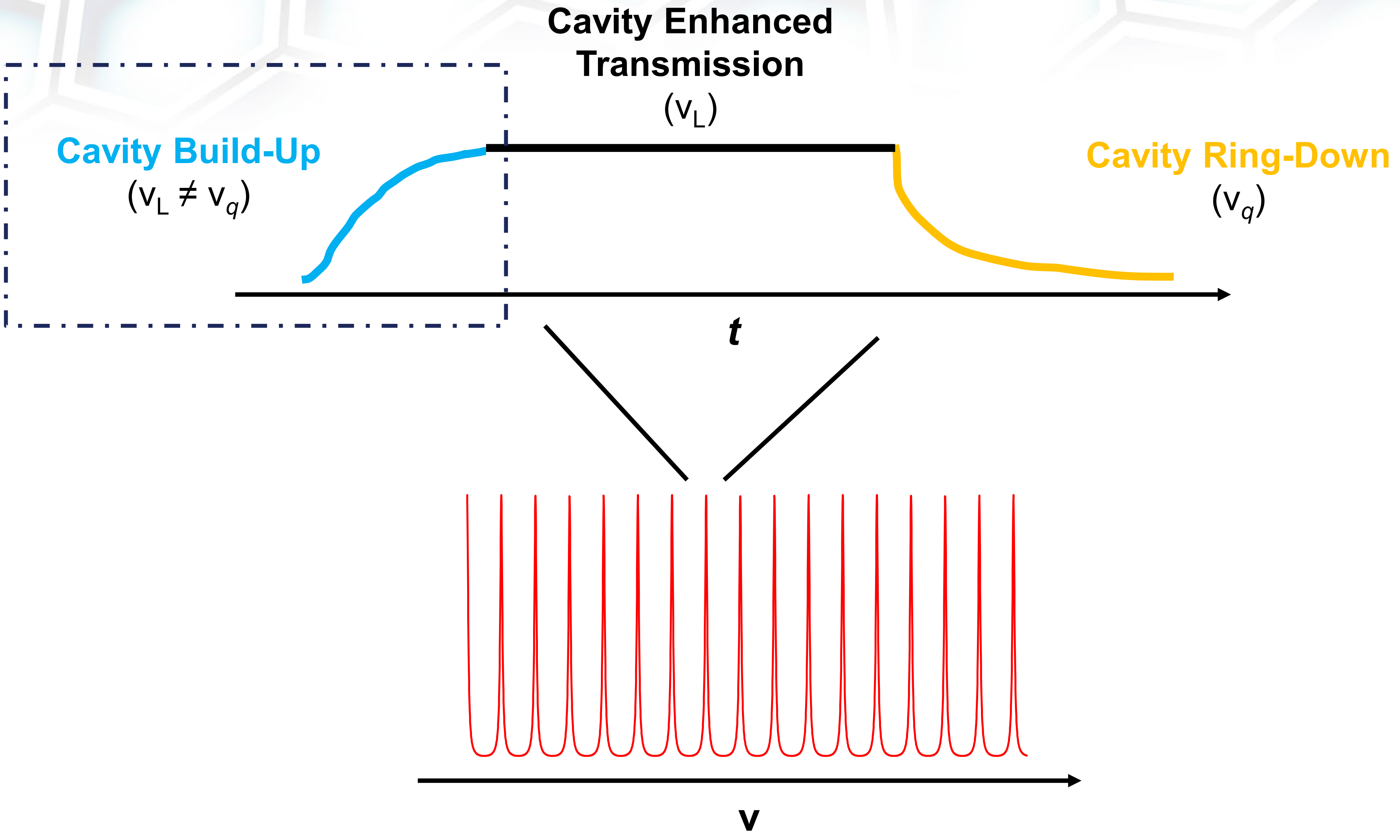


Quantum-noise-limited sensitivity in the near-IR with NEA = 6×10^{-14} cm^{-1} $Hz^{-1/2}$





Ye and Hall, *PRA* **61,** 061802(R) (2000)
Long et al., *APB* **115,** 149 (2014)


Cavity Enhanced
Transmission
(νL)
Cavity Build-Up
(νL ≠ νq)
Cavity Ring-Down
(νq)
t
ν

CAVITY BUILD-UP SPECTROSCOPY

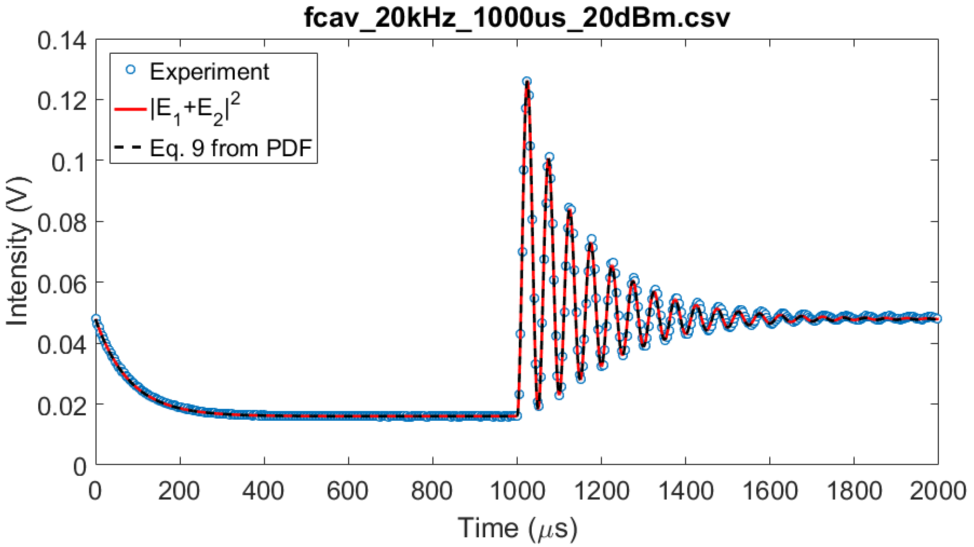
Frequency-locked CW-laser

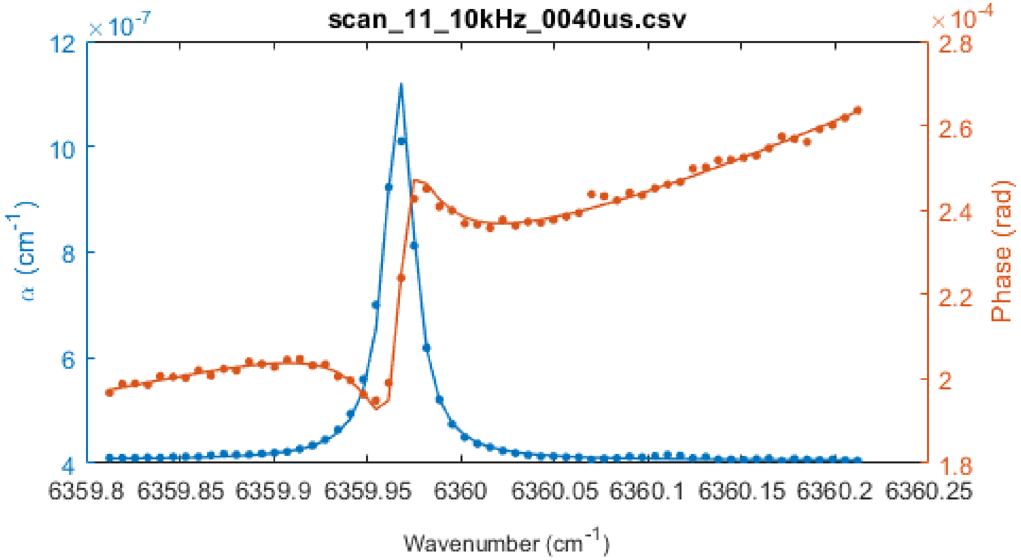
Electro-optic modulator to generate sideband and act as a fast optical switch

Probe a cavity mode with a detuned sideband

Measure cavity build-up, model, fit

Retrieve complex-valued molecular absorption spectrum





Truong et al., *Nat. Photon.* **7,** 532 (2013)
Cygan et al., *Commun. Phys.* **4,** 14 (2021)
Lisak et al., *Sci. Rep.* **12,** 2377 (2022)
Fleisher et al., US Patent No. 11209314B2.

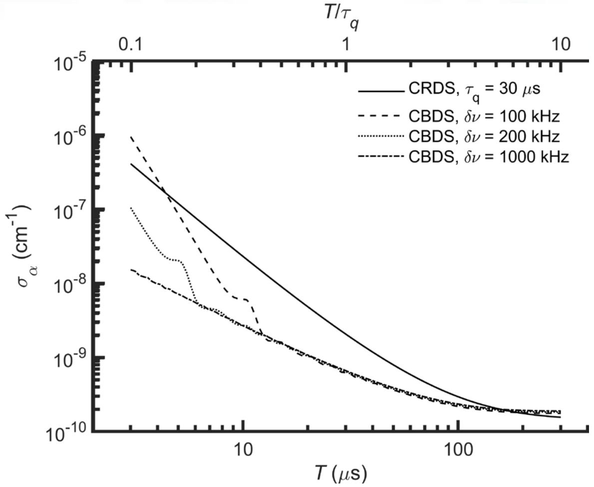
CAVITY BUILD-UP SPECTROSCOPY

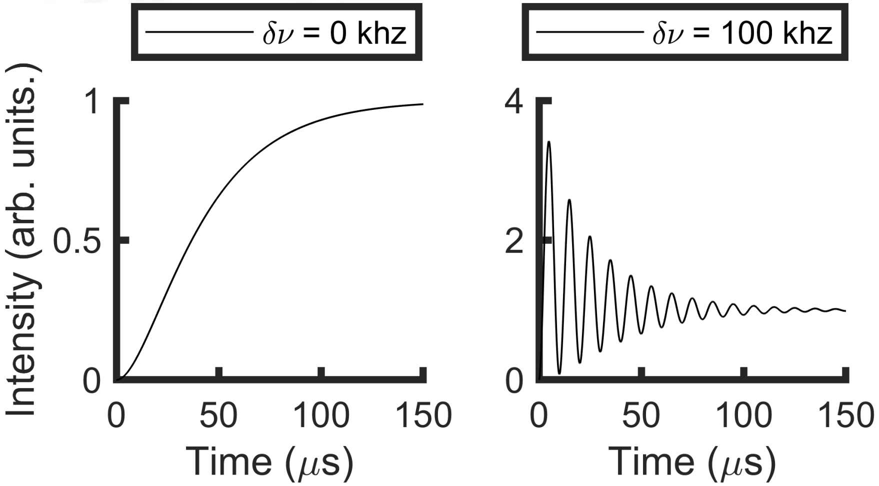
Analytical model for performance

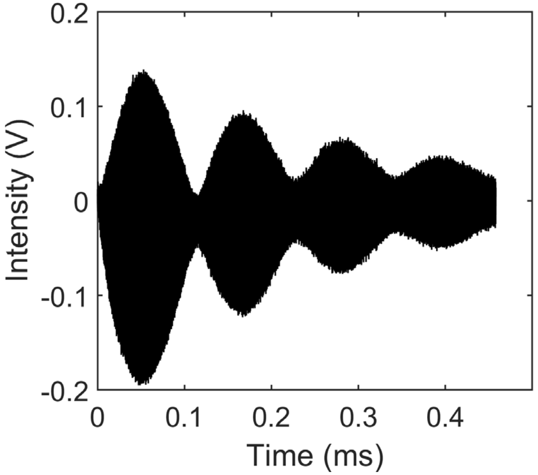
Now, heterodyne-detected CRDS can be seen as a special case of CBUS where $v_L = v_q$

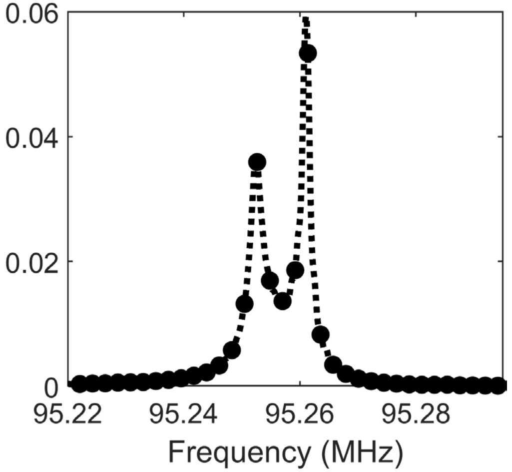
Detuning from the cavity FSR—which occurs naturally near resonant absorption—can be readily modeled

Move CRDS to higher frequencies



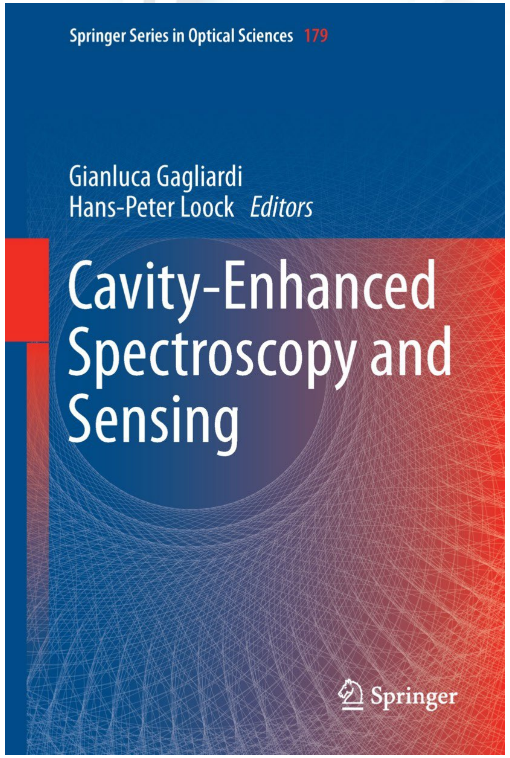






Cygan et al., *Commun. Phys.* **4,** 14 (2021)
Fleisher et al., US Patent No. 11209314B2

Transient behavior



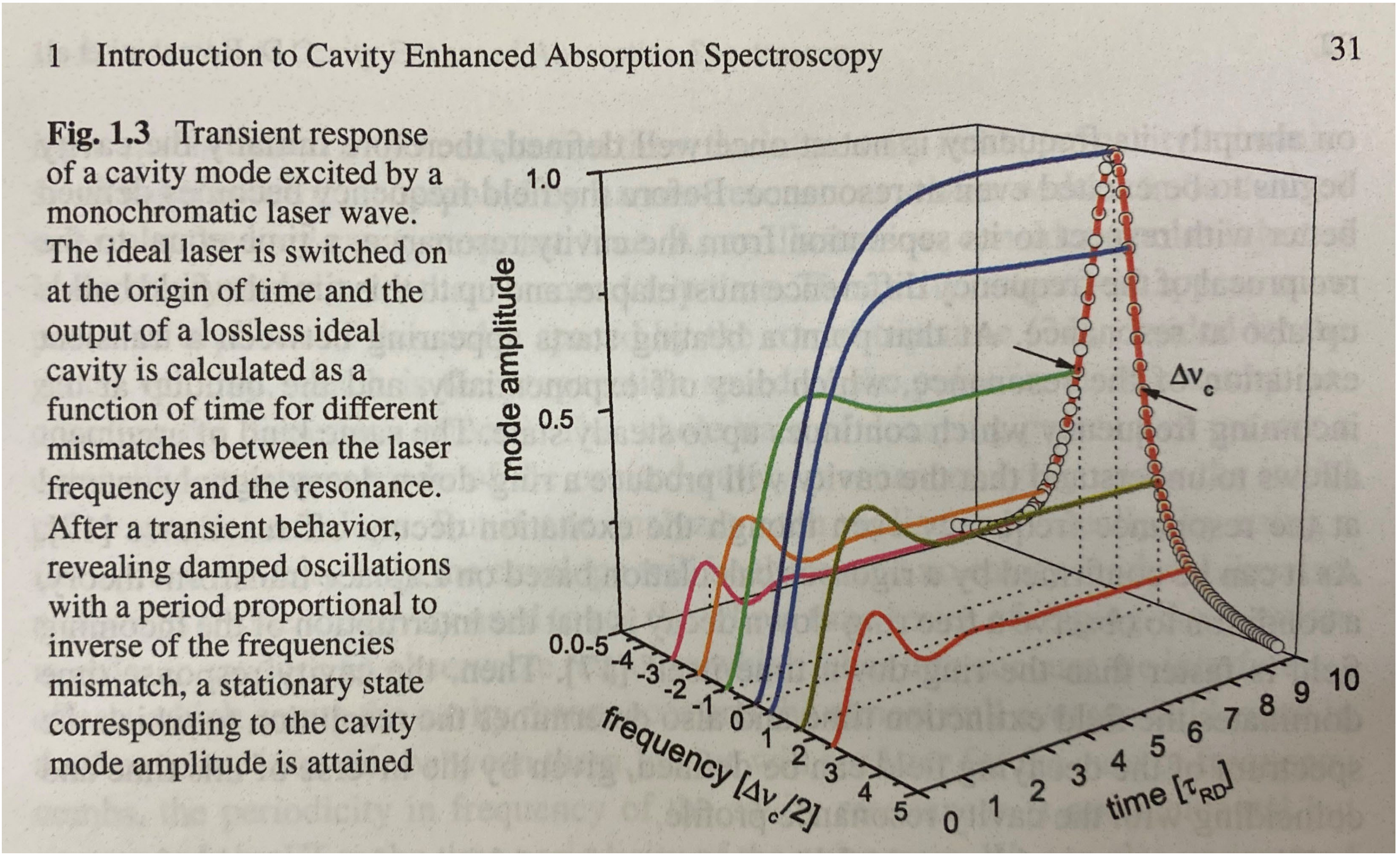


Fig. 1.3 Transient response of a cavity mode excited by a monochromatic laser wave. The ideal laser is switched on at the origin of time and the output of a lossless ideal cavity is calculated as a function of time for different mismatches between the laser frequency and the resonance. After a transient behavior, revealing damped oscillations with a period proportional to inverse of the frequencies mismatch, a stationary state corresponding to the cavity mode amplitude is attained

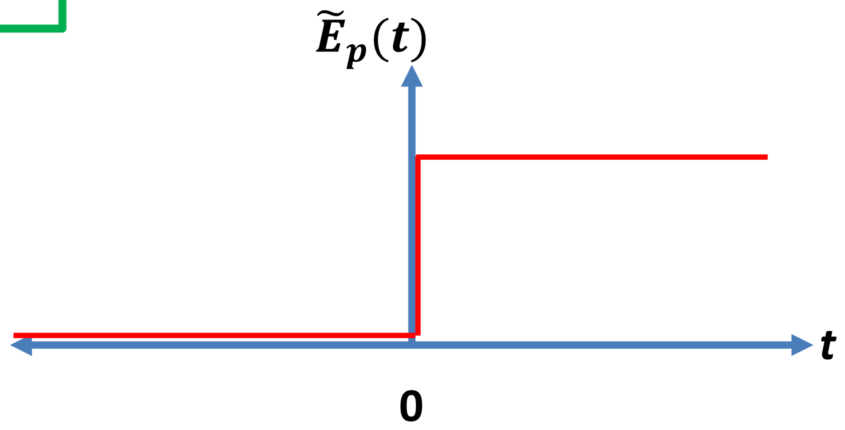
Romanini et al., Introduction to Cavity Enhanced Absorption Spectroscopy. In *Cavity-Enhanced Spectroscopy and Sensing*, eds. Gagliardi and Loock (Springer 2014)

Linear response of an optical cavity mode

$$\tilde{E}_q(t) = \int \tilde{G}_q(t-t')\,\tilde{E}_p(t')dt'$$

$t < 0 \qquad \tilde{E}_p(t) = 0$

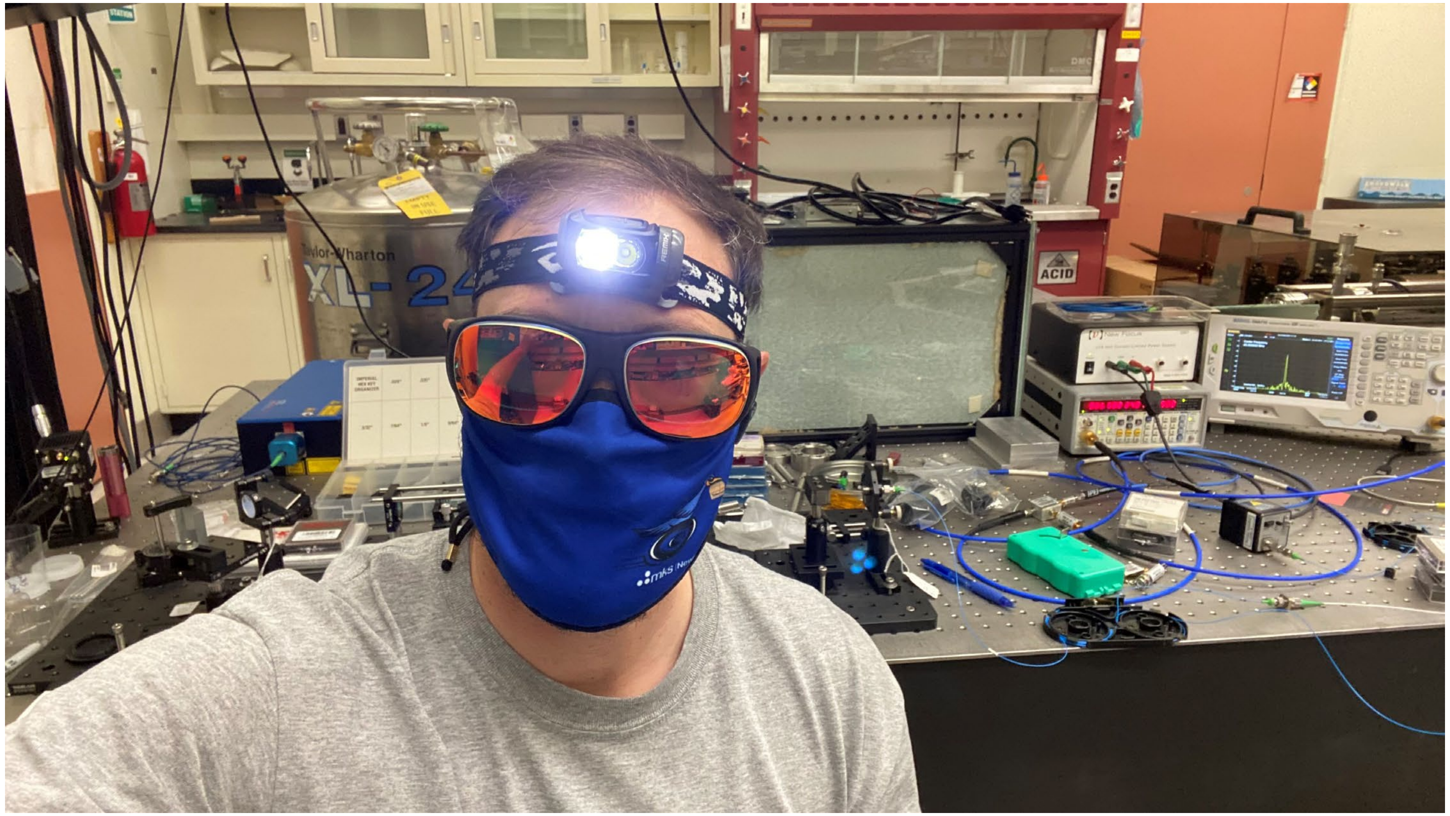
$t \geq 0 \qquad \tilde{E}_p(t) = E_0 e^{i\omega_p t}$



$$\tilde{E}_{\text{out}}(t) = E_0 \frac{Te^{-\alpha L/2}}{t_r R e^{-\alpha L}} \frac{1}{i(\omega_p - \omega_q) + \Gamma_q} \left[e^{i\omega_p t} - e^{i(\omega_q - \Gamma_q)t}\right]$$

Lehmann and Romanini, *JCP* **105,** 10263 (1996)
Cygan et al., *Commun. Phys.* **4,** 14 (2021).

CES applications



STABLE AND RADIOACTIVE ISOTOPES, ISOTOPIC COMPOSITION

Tracers in the environment, medicine

Climate Science

Forensics

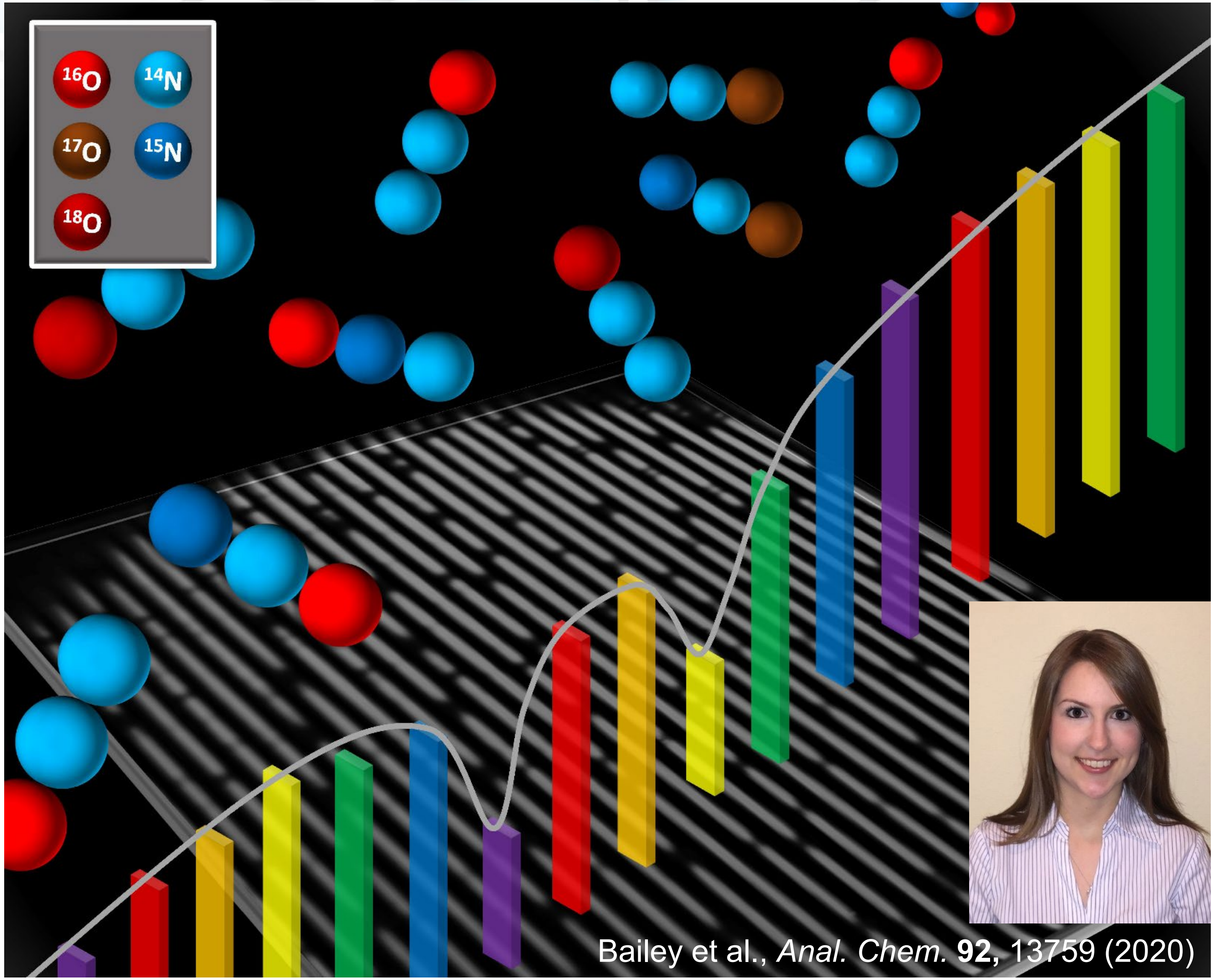
Archeology

Geophysics

Solar System formation, dynamics

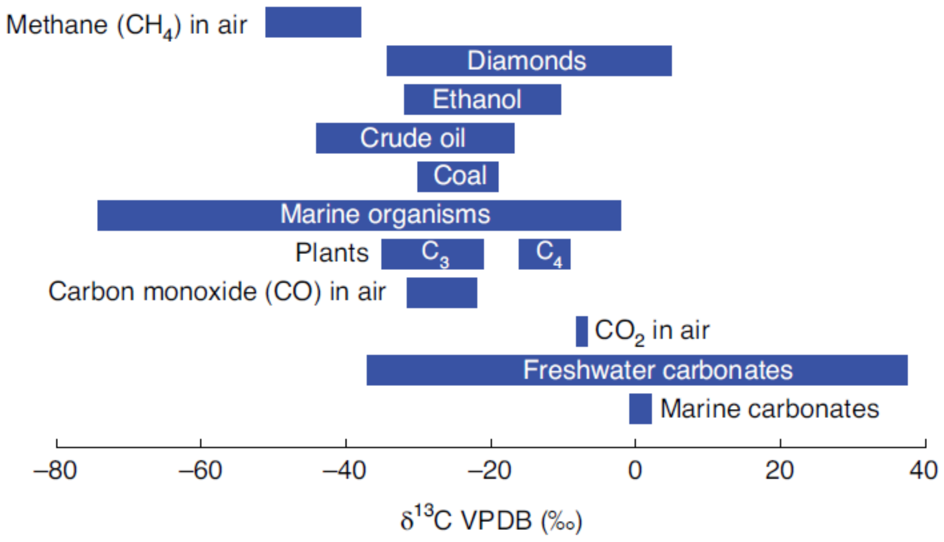
Paleoclimatology

Food webs



Bailey et al., *Anal. Chem.* **92,** 13759 (2020)

VALUE-ASSIGNMENTS FOR ISOTOPIC REFERENCE MATERIALS: VPDB $\delta^{13}C$



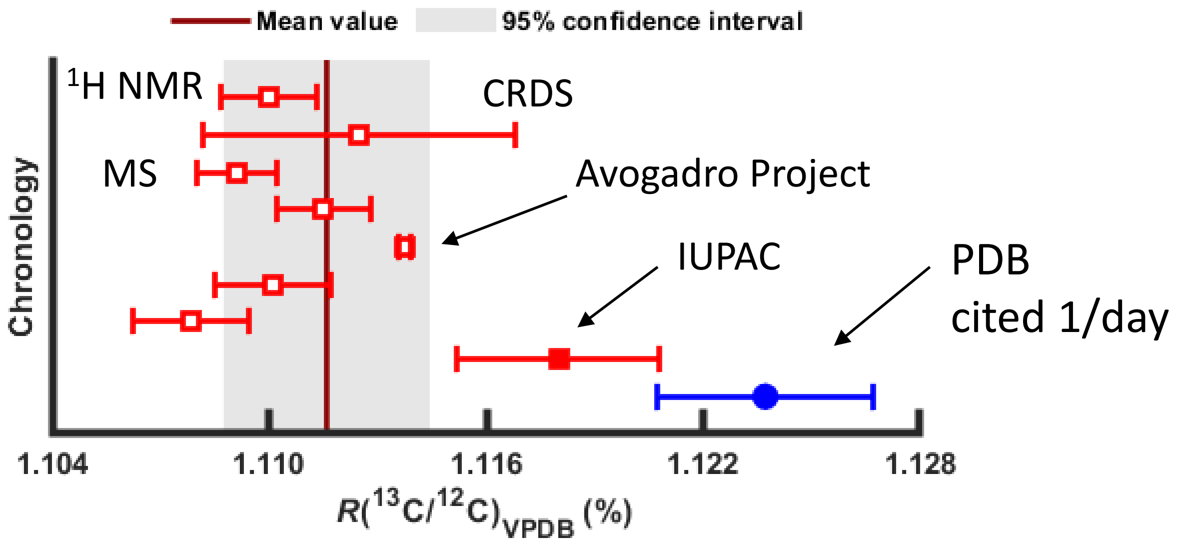
Dual-color CRDS instrument to simultaneously probe $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ in air

Fleisher, Yi et al., *Nat. Phys.* **17,** 889 (2021)

VALUE-ASSIGNMENTS FOR ISOTOPIC REFERENCE MATERIALS: VPDB $\delta^{13}C$

Instead of having artifacts define scales ...

Can we instead use accurate infrared spectroscopy (and other methods) to value-assign artifacts with traceability to the SI?

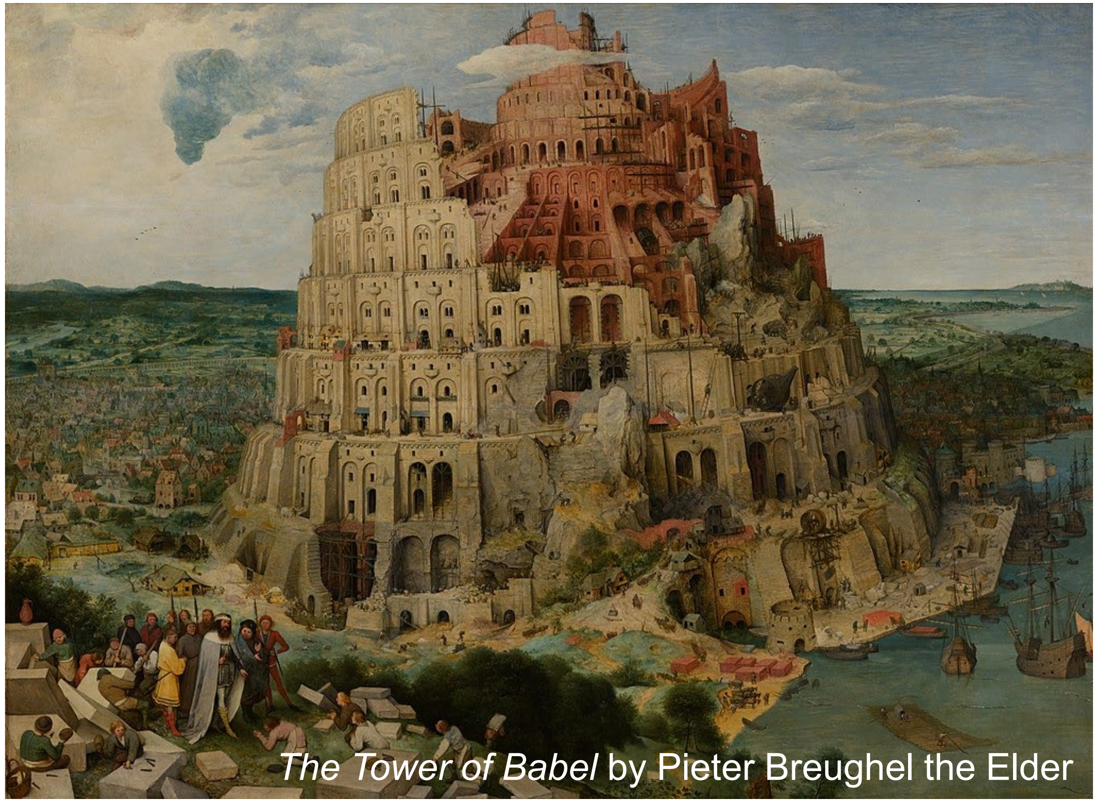


Fleisher, Yi et al., *Nat. Phys.* **17,** 889 (2021)
Hoffman and Rasmussen, *Anal. Chem.* **94,** 5240 (2022)

What could go wrong with artifacts?

*"… there is the considerable **Babylonic confusion** within the measurement community, which often perpetuates years after [a] new reference sample is introduced or a new zero point is assigned to the isotope delta scale (e.g. VPDB instead of PDB, …"*

P. D. P. Taylor, P. De Bièvre & S. Valkiers, in *Handbook of Stable Isotope Analytical Techniques*, Volume 1 (Elsevier, Amsterdam, 2004).

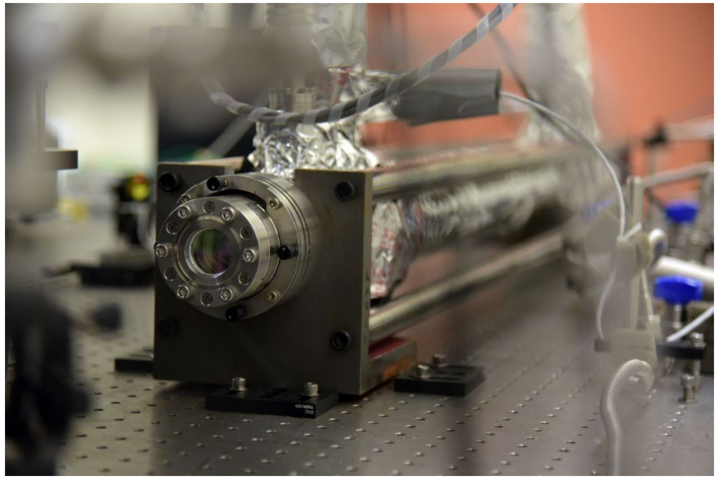


The Tower of Babel by Pieter Breughel the Elder

ISOTOPIC COMPOSITION: RADIOCARBON DIOXIDE ($^{14}CO_2$)

Create the measurement technology to enable honest brokering of emerging carbon markets.

Applications in nuclear forensics, fugitive emissions monitoring, green technologies, and carbon dating.



Fleisher et al. *J. Phys. Chem. Lett.* **8,** 455 (2017);

In *The Future of Atmospheric Boundary Layer Observing, Understanding, and Modeling*. NASEM Workshop, 2018.

Fleisher, *Nat. Phys.* **17,** 1432 (2021)

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Latest News
Web Date: October 3, 2017

1 6
Email Print

An easier way to tell fossil fuels from biofuels

Prototype laser absorption spectrometer could make radiocarbon analysis less expensive

By ***Deirdre Lockwood***

measure for measure

Check for updates

Radiocarbon age is just a number

The idea of radiocarbon existing at equilibrium within Earth's atmosphere has established radiocarbon dating. Adam Fleisher takes a look at its beginnings, achievements and limitations.

Once a living thing stops taking up carbon, what remains will act as a radioactive version of one of those beeping clocks from the most dramatic scene in an action movie and begin to tick down. Every clock ticks at its own rate. For radionuclides like ^{14}C, this rate is inversely proportional to the half-life. As recommended by the Decay Data Evaluation Project, an international collaboration of metrologists, the radiocarbon half-life is (5700 ± 30) years[1]. When the half-life and the background radiation levels are known

Credit: Adam Eastland / Alamy

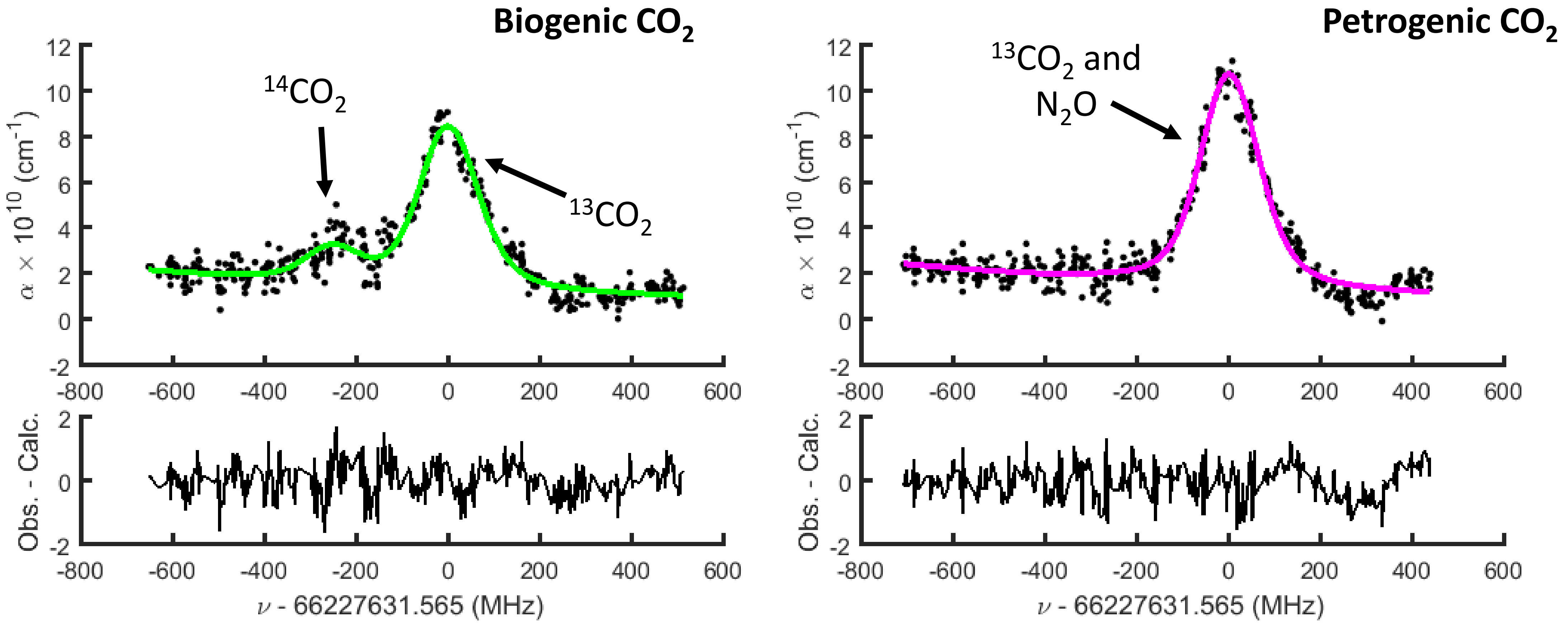
between ^{14}C ages and calendar ages are indicative of physics-based changes in Earth's radiocarbon equilibrium. Accurate estimates of these deviations against a modern baseline are therefore valuable.

Libby himself recognized the need to use different measurement approaches to establish half-life accuracy[3]. Early on, these included solid, liquid and gas decay-counting methods and mass spectrometry atom-counting methods. In the last decade, highly sensitive optical spectroscopy methods have also been

Results

Fleisher et al., *JPCL* **8,** 4550 (2017)

Differentiate fossil-fuel CO_2 from biofuel CO_2 with high degree of confidence



686 Vol. 8, No. 5 / May 2021 / Optica Research Article

optica

Mid-infrared interference coatings with excess optical loss below 10 ppm

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Doppler-free two-photon cavity ring-down spectroscopy of a nitrous oxide (N_2O) vibrational overtone transition

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Frequency stabilization of a quantum cascade laser by weak resonant feedback from a Fabry–Perot cavity

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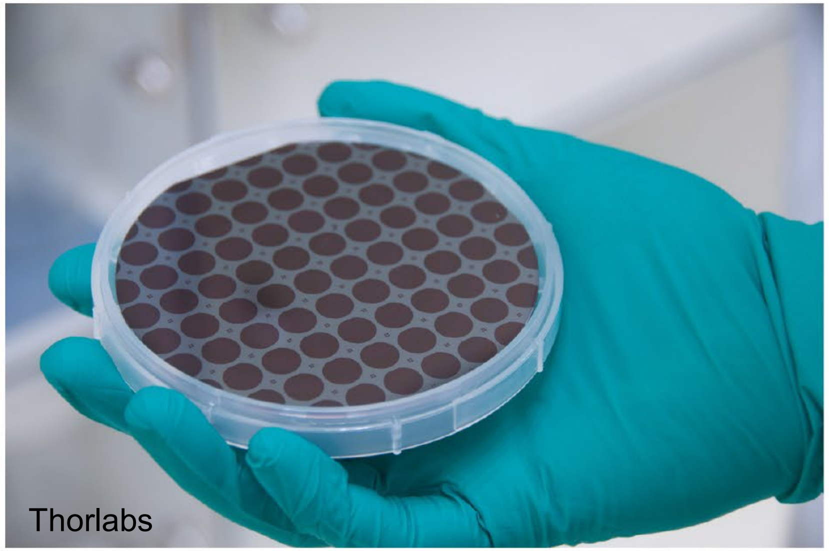
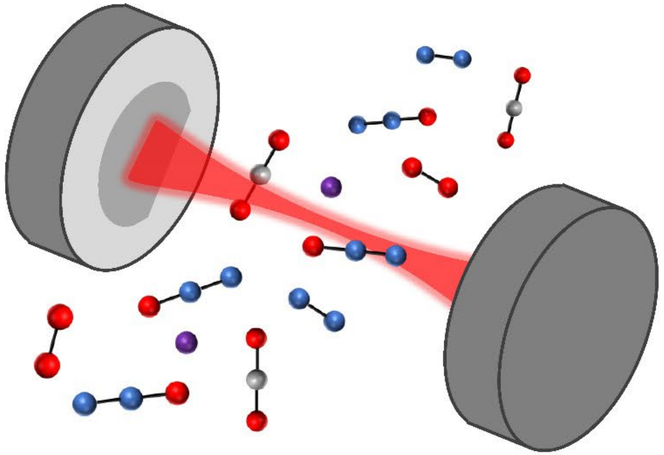
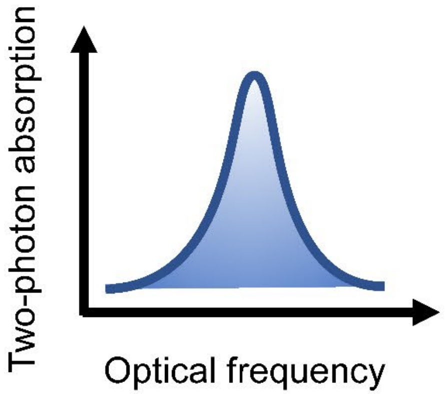




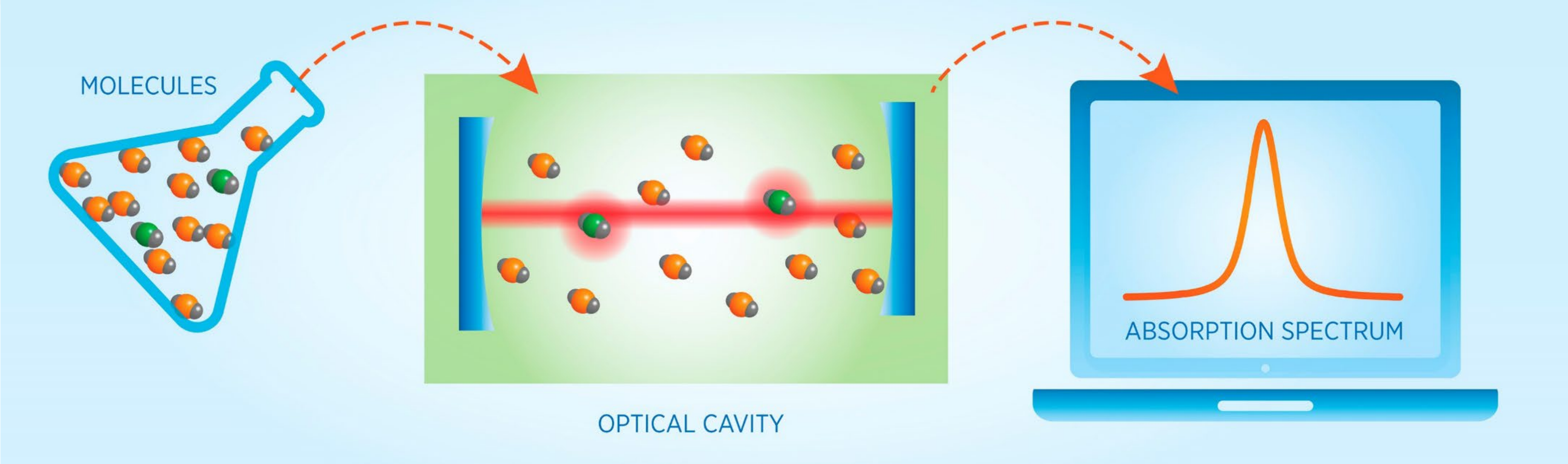


NEW MIRROR TECHNOLOGY, NEW SPECTROSCOPIC METHODS

The same crystalline interference coatings designed for LIGO are now used in our laser instruments.

New spectroscopic methods are more sensitive, more selective, and background free – enabling new molecular and isotopic sensing opportunities.

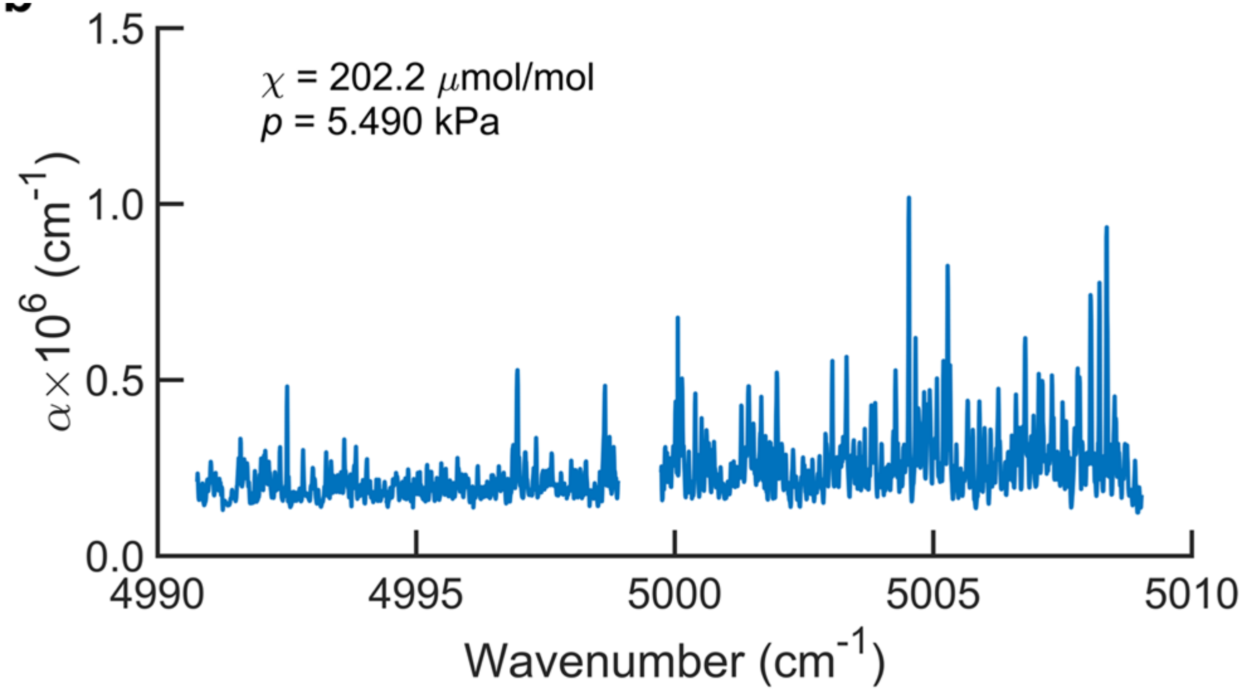
Accurate cavity-enhanced spectroscopy

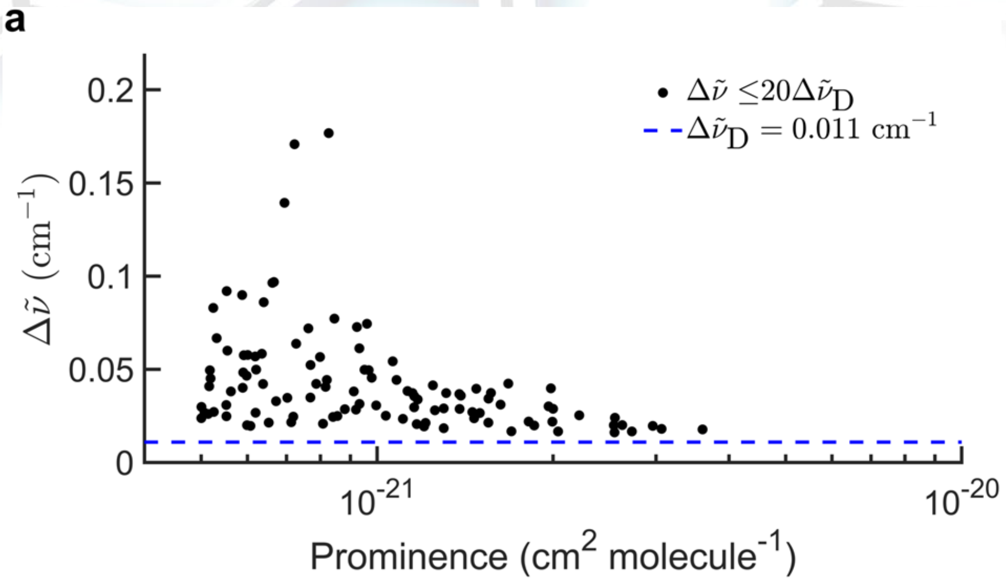


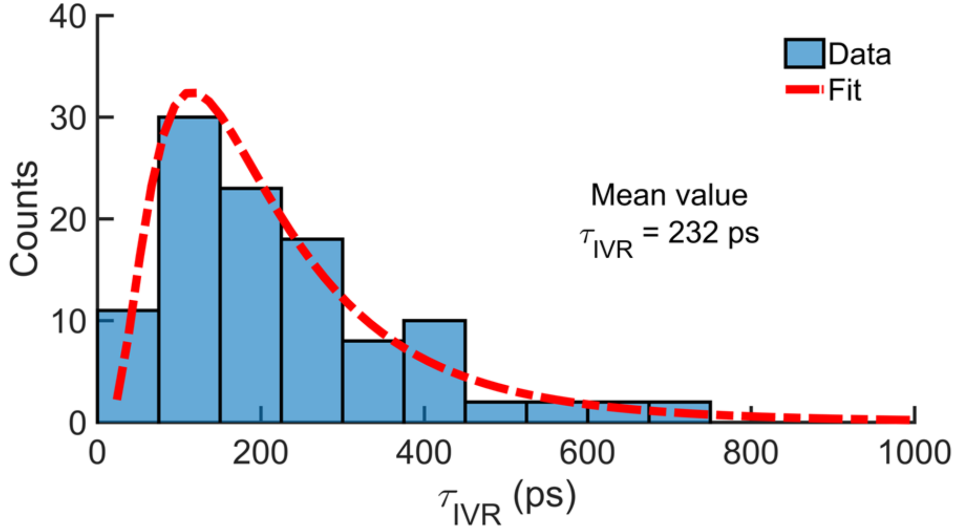
Long interaction pathlength (km's in a compact physical footprint)
Stable frequency axis (relative stability better than 10^{-8})
Spatially coherent (well-defined beam shape / mode volume / mode cross-section)
High resolution (high quality factor / finesse)

HIGH RESOLUTION CRDS AND CHEMICAL DYNAMICS: METHANOL

$\nu_1 + \nu_6$ combination band near λ = 2 µm
OH-stretch + OH-bend







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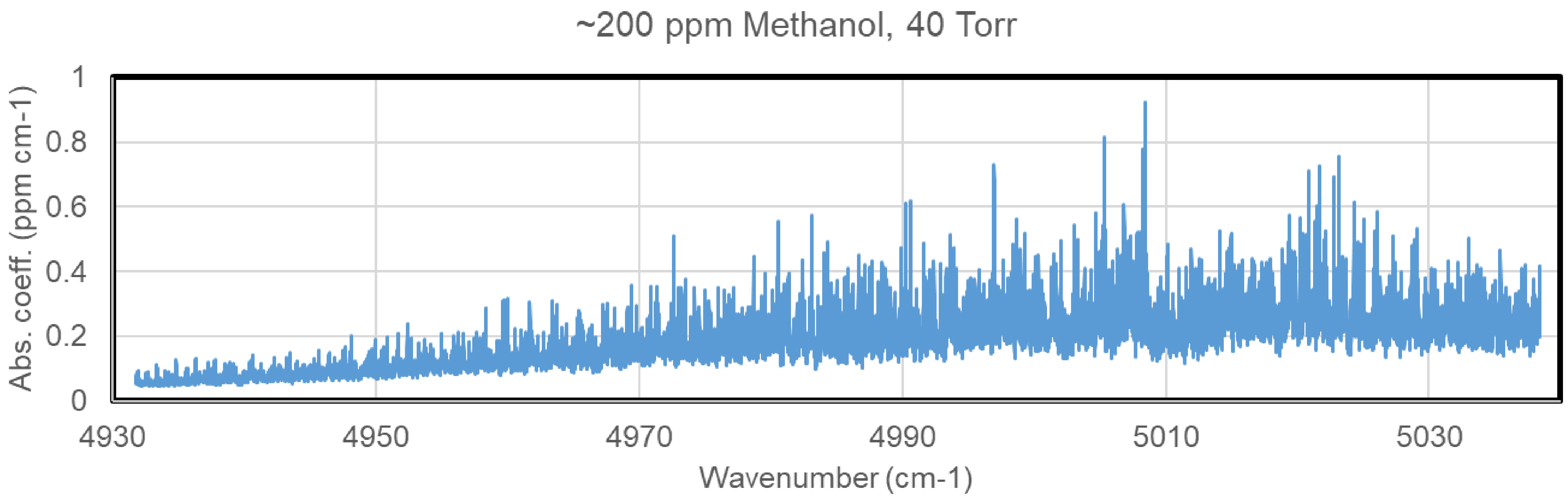
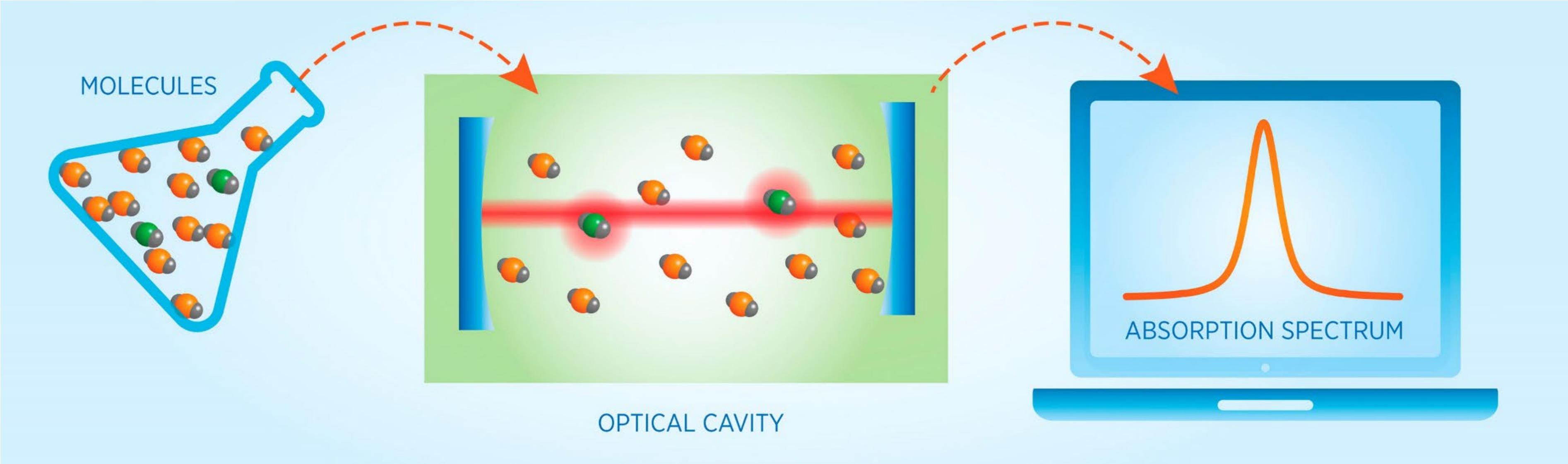
Continuous scanning

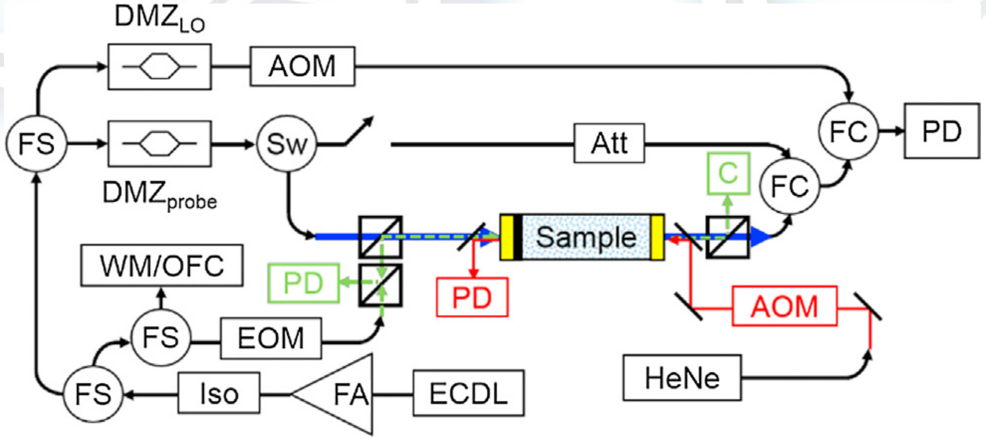


Hélène Fleurbaey
Hongming Yi, Michelle Bailey, Erin Adkins

Accurate cavity-enhanced spectroscopy



The experiments really look something like this ...



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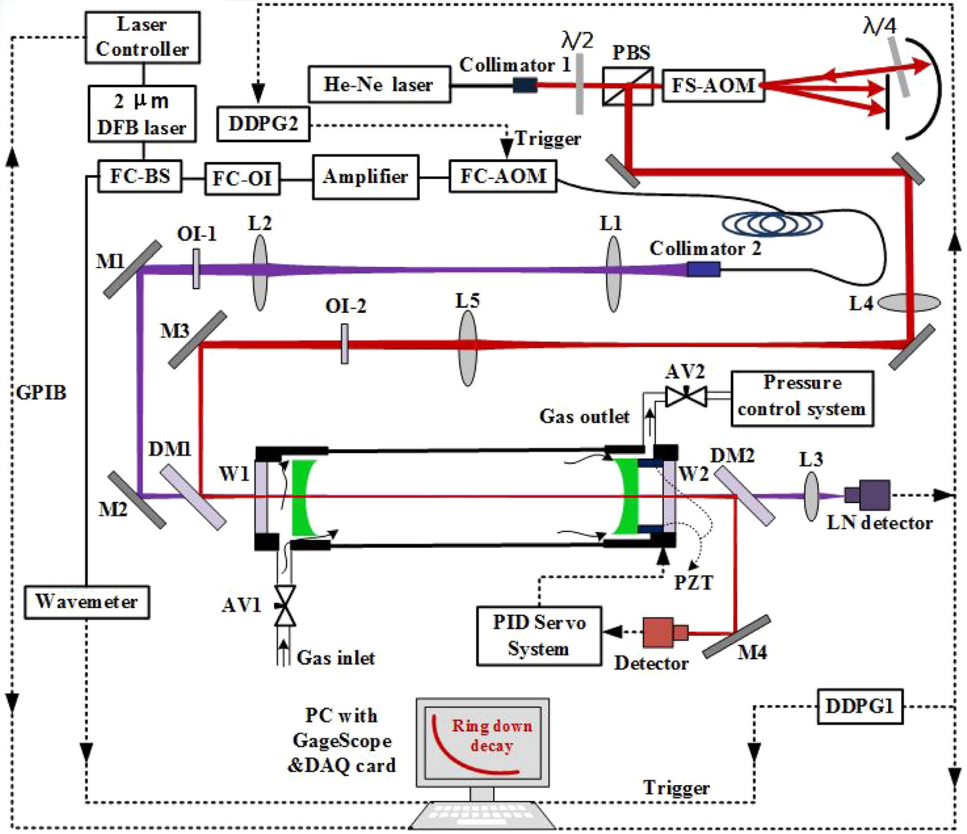

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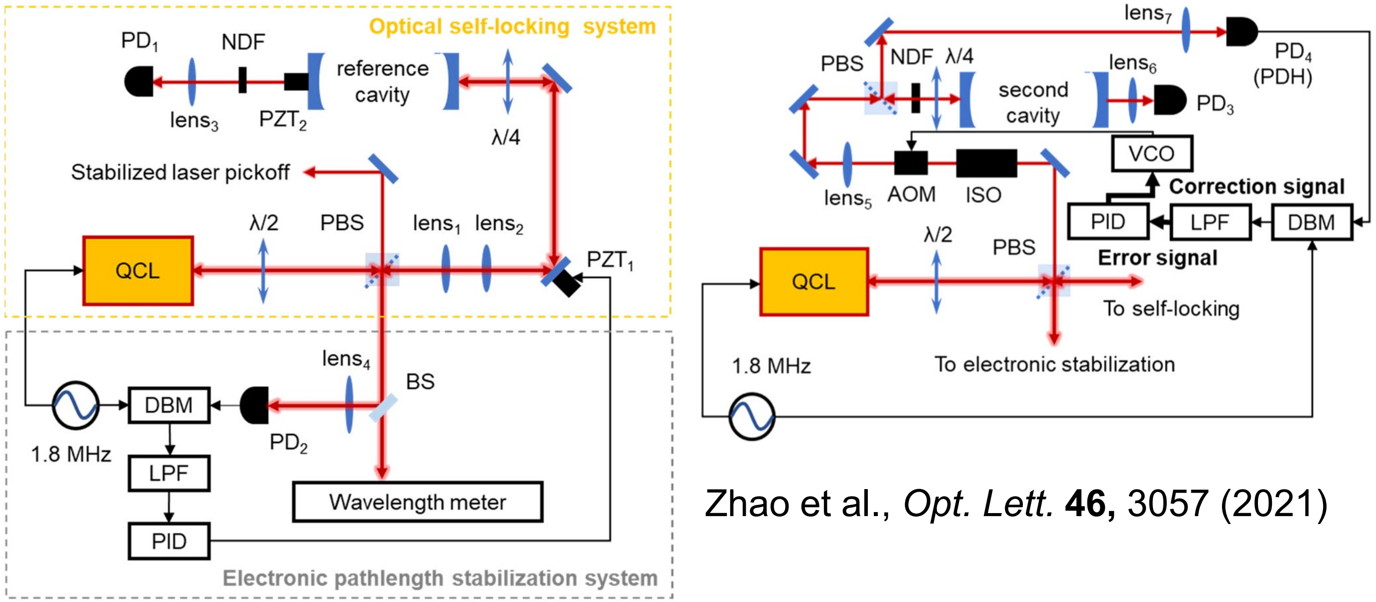

Zhao et al., *Opt. Lett.* **46,** 3057 (2021)

Postdoc opportunities!
Visitors welcome!
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University of Vienna (Heckl)
Thorlabs (Cole)
University of Virginia (Lehmann)
Laval University (Genest)
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University College London (Tennyson, Polyansky)
Harvard Center for Astrophysics (Gordon)
JPL, Caltech (Drouin, Okumura)
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NIST Greenhouse Gas and Climate Science Program
NASA OCO Missions, APRA (Laboratory Astrophysics)