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# COMMENT ON "INVALIDATION OF THE INTRACAVITY OPTO-GALVANIC METHOD FOR RADIOCARBON DETECTION" BY CANTWELL G CARSON, MARTIN STUTE, YINGHUANG JI, ROSELINE POLLE, ARTHUR REBOUL, AND KLAUS S LACKNER

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**ABSTRACT.** Carson et al. (2016) have measured the optogalvanic *response* of an intracavity cell discharge containing carbon dioxide enriched in radiocarbon in a $^{14}CO_2$ laser, and compared same to an unenriched sample. The measurement was carried out by modulating the laser wavelength while slowly tuning through the laser gain profile. The results of the measurements are claimed to "invalidate the optogalvanic method for radiocarbon detection." A broadband linear absorption model is presented in support of this hypothesis. In fact, the experimental design was such as to minimize any possibility for $^{14}C$ detection, and the model presented is not relevant to their experiment. Crucial control measurements were not carried out and the model used did not differentiate between broadband absorption spectroscopy and intracavity optogalvanic spectroscopy (ICOGS) with a narrow-band single-mode $CO_2$ laser.

**KEYWORDS:** intracavity optogalvanic spectroscopy, ICOGS, laser spectroscopy, radiocarbon.

## BACKGROUND

In 2008, a new intracavity laser spectroscopy, given the acronym ICOGS, was introduced (Murnick et al. 2008). Though the basic physics of the technique was described, the experiments were complex and required a thorough understanding of gas laser and glow discharge physics to properly carry out. Due to gaps in a full theoretical understanding, it was noted at the time that many variables must be carefully controlled both with respect to the laser and the sample discharge cell in order to obtain consistent results. In particular, measurements with an external reference discharge cell were crucial for control and stabilization of laser and system variables.

Typically, if one is to claim that a particular experiment is incorrect it is necessary to provide either a valid theoretical basis for that claim and/or to demonstrate unequivocally that the reported results could not be reproduced under identical conditions. Carson et al. (2016) as well as the references they cite to buttress their conclusions (Persson et al. 2013; Paul and Meijer 2015) do neither. In Carson et al., unlike the 2008 ICOGS work, the authors eliminate the crucial reference cell, do not stabilize their laser, and make measurements under conditions that appear to be designed to minimize sensitivity to $^{14}C$. They justify their conclusions with a model of linear absorption in a neutral gas by a continuously tunable narrow-band laser—a model totally inapplicable to the experiment they report or to any ICOGS experiment.

## THE MODEL

Carson et al. present a broadband linear absorption model for a tunable laser with a Lorentzian linewidth assumed to be 300 kHz. The calculations presented use the HITRAN database for spectral information in the region of the laser tuning range. Though useful for specific spectral data, the HITRAN database is for neutral atmospheric gases, not for glow discharges where populations of specific states depend on discharge conditions. They also claim that "The optogalvanic response as function of laser frequency has been shown to have the same form as the absorbance profile" based on a reference to Bachor et al. (1982). The actual reference, however, belies their claim. The paper cited discusses visible atomic optogalvanic spectra in an inert gas in an external cell, not infrared molecular transitions in an intracavity configuration, and even for the case studied shows widely varying optogalvanic lineshapes

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depending on discharge conditions (see especially Figure 4 of Bachor 1982). Contrary to Carson et al., Bachor states "The magnitude of the optogalvanic signal is not independent of the transition or the properties of the plasma under investigation and is not linearly related to the oscillator strengths of the transition."

The case of $CO_2$ is even more complicated than the system studied by Bachor. The optogalvanic effect for $CO_2$ is primarily a thermal effect on the electron energy distribution function, not direct ionization. Relevant references for $CO_2$ optogalvanic physics include the seminal papers of Moffatt and Smith (1984) where important time dependences, not considered by Carson et al., are discussed, and the modeling work of Tachikawa and Shimizu (1991). Intracavity effects are also ignored in the model presented by Carson et al. The use of an intracavity cell with high laser power means that a linear interaction model is insufficient near resonance due to saturation effects for $^{14}CO_2$ that are different from those for the off resonance background transitions.

The absorbance model presented, however, is reasonable for the case of a low-power tunable narrow-band laser absorption measurement of a low-pressure neutral gas such as described in Galli et al. (2011a, 2011b). In that work, the necessity for use of a narrow-band broadly tunable laser with careful laser metrology in order to resolve a dilute species is made explicit. The recent work of Genoud et al. (2015) is similar, where a less narrow-band laser yielded lower sensitivity. In the Carson et al. experiment discussed below, contrary to the model assumptions, a large amplitude sawtooth modulation to the laser cavity length made the intrinsically narrow-band $CO_2$ laser effectively broadband, with an additional complication of varying power as a function of wavelength.

## THE EXPERIMENT

There are several seeming design flaws in the Carson et al. experiment. Beginning with Figure 2 of the paper, the most obvious concerns are a lack of an external reference cell and the lack of a $^{12}CO_2$ monitor. The former is necessary for laser stabilization and normalization, the latter is required to determine $CO_2$ concentration. Carson et al. note that they have a port in their sample cell that should be used for $^{12}CO_2$ measurement but make no mention of why they omit this crucial monitor. More significant and the apparent "fatal flaw" of the experimental design is their use of *sawtooth modulation* of 15 V at 19 Hz as the laser cavity is slowly varied in length to monitor the optogalvanic effect. They do not provide the important calibration of volts to frequency, but based on the data of their Figure 4 and knowledge of $CO_2$ lasers, the amplitude of the modulation can be estimated to be greater than 100 MHz. By modulating the wavelength with such a large sawtooth variation, Carson et al. ensure that their laser is almost never on the peak of the $^{14}CO_2$ resonance. What they are measuring is simply related to intercavity enhanced background effects within the gain profile of their laser. This would have been clear if Carson et al. had included an external reference cell as was done as early as 2005 in a reference that they cite (Murnick and Okil 2005).

I believe that Carson et al. misinterpret the data presented in their Figure 4 where the amplitude of the modulation in the power of the laser (their Figure 4A) and the amplitude of the optogalvanic response (their Figure 4B) to the piezoelectric transducer sawtooth modulation of 15 V at 19 Hz as the laser cavity is slowly varied in length with the piezo voltage changed from 0 to about 100 V are shown. Figure 4A is a course absolute value derivative of the laser gain profile and Figure 4B is the same for the intracavity enhanced optogalvanic effect. They further fit a Gaussian function to a portion of the derivative spectrum without a theoretical justification. On a low-resolution spectrum analyzer, the laser is observed to "line-hop"

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from P(20) to P(24) to P(22) as the cavity length changes. [The text only refers to P(20) and P(24).] It would have been more useful to show the *power* itself, rather than its modulation, as the power versus wavelength (or voltage) yields the gain profile of the laser and Figure 4B claims to show the optogalvanic signal amplitude normalized to power. If, as stated, the voltage is normalized to power, at mode hops the power goes to zero, which should lead to large spikes at some voltages. The only stabilization mentioned is that the "offset voltage applied to the piezo controller could be adjusted to keep the phase of the fast response pyrometer at a constant value." It is not clear what this phase stabilization accomplishes. In any case, the experiment is clearly designed for continuous wavelength change over a relatively broad frequency band, whereas for sensitivity to $^{14}C$, the interest is in a very narrow wavelength range at the peak of the $^{14}C$ resonance. In addition, the data was averaged with a "6-point low-pass filter," further washing out any possible sharp resonance structure. There are good reasons why a stabilized narrow-band laser is required for analyzing dilute species in the presence of overlapping background moieties as explained very well in the Galli et al. references that are cited by Carson et al.

In order to measure $^{14}CO_2$ content with wavelength modulation, it is best to use *square wave modulation* with a voltage equal to about one half-width of the expected $^{14}CO_2$ resonance width while keeping the laser stabilized on the peak of the derivative. In this way, the signal is the difference between on resonance to off resonance, analogous to the more common laser chopped method of difference between laser-on and laser-off at resonance.

A second independent experimental result is presented in Figure 3 of Carson et al. The figure shows an intercavity optogalvanic waveform with the laser chopped at 71 Hz using a newly designed differential amplifier. The waveform was obtained at an unknown unstabilized wavelength and is not related to the data of their Figure 4 where the signal was obtained by sawtooth cavity length modulation. Carson et al. claim that the transient part of the waveform is an "artifact." It is, however, obviously real and its existence is obscured, but not erased with narrower band pass filtering. With the FFT analysis method, the strength of the transient affects both the amplitude and phase of the fundamental. Murnick (2015) has shown the importance of including phase information in ICOGS signal analysis. With this analysis in mind, the statement by Carson et al.: "These artifacts are so pronounced that they call into question whether $^{14}CO_2$ could have ever been detected at all" is specious. A similar waveform should have been shown for the experiment with wavelength tuning.

## SUMMARY

As the experimental design and model employed in this work are not at all suitable for intracavity optogalvanic detection of $^{14}C$, in my view, the results presented cannot yield useful information on the subject of this manuscript's title. The conclusion implied by the title of Carson et al. is not supported by the model or data they present. Their Figure 6 and the discussion thereof are particularly unclear. As Carson et al. recognize, an intracavity optogalvanic effect is dependent on gas species, pressure, power, discharge conditions, laser wavelength, and temperature. The $^{14}C$ contribution and the background contribution to a measured signal have differing responses to the many dependent variables. The extraction of a single number from different experimental systems with differing conditions and differing data reduction algorithms and normalizing same to unity serves to obscure important details of individual measurements with differing backgrounds and nonlinearities. What is important for $^{14}C$ detection is extraction of the $^{14}C$ component of the signal. However, in the experiment reported by Carson et al., the experimental design was such that the measured effect was almost

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entirely background by virtue of the sawtooth wavelength modulation. The other data cited in the figure used $^{14}CO_2$ lasers on resonance, but handled background and other experimental variables differently, hence showing differing relative responses.

The work of Murnick et al. (2008) first demonstrated intracavity optogalvanic quantitation of $^{14}C$ with a well-designed system and careful data reduction. While at that time the experimental system in use did not yield easily reproducible and routine measurements, its deficiencies were documented and data were collected carefully and repeatedly (Ilkmen 2009). Similarly, at that time, there was a gap in the theoretical understanding requiring that all dependent variables including pressure, laser parameters, and discharge parameters needed to be held rigorously constant. With time, as modifications were added to the system, the data has become more consistent and easier to gather. At present, a more complete theoretical understanding of the measured effects exists as does a better engineered system and quality results are being reproduced on a routine basis (Murnick 2015).

Carson et al. have assembled components for a potentially sensitive system for optogalvanic detection of radiocarbon in $CO_2$. They have built a new differential amplifier to better determine the optogalvanic effect waveform and have recognized the potential advantage of wavelength tuning as opposed to laser chopping in order to reduce background.

My advice would be that their system should include an external reference cell for wavelength stabilization and normalization, and a $^{12}CO_2$ detector. Most importantly, the intrinsic narrow linewidth of their laser must be utilized by stabilization and measurement comparison on and off resonance, rather than by rapidly scanning through a broad laser gain profile. Then, they would be in a position to test their hypotheses and move forward to advance the development of intracavity optogalvanic instrumentation for $^{14}C$ detection.

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