

V-T Relaxation Related Aspects of Quartz-Enhanced Photoacoustic Spectroscopy

Anatoliy A. Kosterev and Frank K. Tittel

Rice Quantum Institute, Rice University, Houston TX 77251-1892
akoster@rice.edu

Influence of vibrational energy transfer processes on QEPAS-based trace gas detection will be considered. Relevant published results will be analyzed. The potential of QEPAS as research tool of relaxation processes will be discussed.

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Photoacoustic spectroscopy (PAS) is a sensitive indirect method of detecting a weak optical absorption [1]. It is based on monitoring sound waves that are generated in the media upon absorption of the modulated optical radiation. Spectroscopic detection of trace molecular species in the gas phase is usually performed by accessing their strong absorption lines in the mid-IR region that correspond to vibrational transitions. For some applications weaker lines in the near-IR region are used which correspond to vibrational overtones and combination bands. In both cases, electromagnetic radiation initially provides vibrational excitation of the molecules. This excitation is subsequently converted to the translational molecular motion (V-T relaxation), which means heating of the gas, thermal expansion and a resulting sound wave generation. In contrast to dense media (solids and liquids) where energy transfer processes occur on a sub-nanosecond time scale, V-T relaxation in gases can be relatively slow, thus limiting the bandwidth of the photoacoustic sound generation. It was shown [2] that in a simple case of direct one-channel V-T relaxation with a time constant τ the amplitude S of the photoacoustic sound is

$$S = S_0 \frac{1}{\sqrt{1 + (2\pi f\tau)^2}} \quad (1)$$

where S_0 is the photoacoustic signal for instant V-T transfer and f is the thermal input modulation frequency.

PAS detection is conventionally performed by means of a broadband microphone that detects the sound generated in a nonresonant or resonant gas cell enclosing an analyte gas sample [3]. Quartz-Enhanced PAS (QEPAS) is a new, alternative way to detect weak photoacoustic excitation [4]. Its key feature is utilization of a sharply resonant, high-Q acoustic transducer. In this case, both resonant signal enhancement and its conversion to electrical response occur in this transducer. From a variety of commercially available piezoelectric materials the quartz tuning fork (TF) was found to be the most suitable transducer for this kind of measurements. Thus, the acronym QEPAS was chosen to denote this technique. The majority of commercially available quartz TFs are designed to be used as frequency standards in electronic clocks, resonating in vacuum at $f_0=32\,768$ (2^{15}) Hz and at a few Hz lower frequency f when exposed to air. This frequency is significantly higher than the usual PAS 10 Hz – 5 kHz range. Therefore, QEPAS based gas detection capabilities strongly depend on the vibrational energy transfer rates [5]. Table 1 provides a summary of the published results to date on QEPAS based gas sensing. Normalized noise equivalent absorption coefficient (NNEA) is determined by

$$NNEA = \frac{\alpha_{\min} P}{\sqrt{\Delta f}} \quad (2)$$

where α_{\min} is the absorption coefficient resulting in the noise-equivalent QEPAS signal, P is the optical excitation power, and Δf is the detection bandwidth. It can be seen that NNEA shows noticeable species-to-species variation, indicating the differences in the V-T transfer mechanisms and rates. The highest sensitivity was obtained for NH_3 , and ammonia is known to exhibit V-T energy transfer on a nanosecond time scale.

Difference in the V-T relaxation rate can be used as an additional spectroscopic parameter, allowing to distinguish between the molecules with the overlapping absorption spectra. Relaxation delay results in a molecule-dependent phase shift of photoacoustic response with respect to the optical excitation. In [9], the phase shift difference was utilized to detect CO impurity in propylene.

CTuGG5

Table 1. Summary of published results on QEPAS based gas sensing.

| Molecule (Host) [Reference] | Frequency, cm ⁻¹ | Pressure, Torr | NNEA, cm ⁻¹ W/Hz ^{1/2} |
|---|--------------------------------|-------------------|---|
| NH ₃ (N ₂) [6] | 6528.76 | 60 | 7.2×10 ⁻⁹ |
| H ₂ O (exhaled air) [7] | 6541.29 | 90 | 8×10 ⁻⁹ |
| CO ₂ (exhaled air) [7] | 6514.25 | 90 | 1.0×10 ⁻⁸ |
| N ₂ O (air+5%SF ₆) [5] | 2195.63 | 50 | 1.5×10 ⁻⁸ |
| CO (N ₂) [5] | 2196.66 | 50 | 5.3×10 ⁻⁷ |
| CO (propylene) [8] | 2196.66 | 50 | 7.4×10 ⁻⁸ |
| CH ₂ O (air) [9] | 2832.48 | 200 | 2.2×10 ⁻⁸ |

NNEA – normalized noise equivalent absorption coefficient (see Eq. 2)

QEPAS has a potential to be a powerful tool in relaxation studies, especially in its simplest implementation when the TF is excited directly by the laser beam acoustic field (no additional acoustic resonator). In this case the resonant frequency and coupling to acoustic signal remain virtually constant in a wide range of temperature, pressure and gas composition. Thus, amplitude and phase response of the TF to the laser excitation of the molecules in the gas phase as a function of these three parameters can provide valuable information about the vibrational relaxation processes.

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