Quartz-enhanced photoacoustic spectroscopy exploiting low-frequency tuning forks as a tool to measure the vibrational relaxation rate in gas species

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A B S T R A C T
We demonstrated that quartz-enhanced photoacoustic spectroscopy (QEPAS) is an efficient tool to measure the vibrational relaxation rate of gas species, employing quartz tuning forks (QTFs) as sound detectors. Based on the dependence of the QTF resonance frequency on the resonator geometry, a wide range of acoustic frequencies with narrow detection bandwidth was probed. By measuring the QEPAS signal of the target analyte as well as the resonant properties of different QTFs as a function of the gas pressure, the relaxation time can be retrieved. This approach has been tested in the near infrared range by measuring the CH4 (ν4) vibrational relaxation rate in a mixture of 1% CH4, 0.15 % H2O in N2, and the H2O (ν1) relaxation rate in a mixture of 0.5 % H2O in N2. Relaxation times of 3.2 ms Torr and 0.25 ms Torr were estimated for CH4 and H2O, respectively, in excellent agreement with values reported in literature.

1. Introduction
Quartz-enhanced photoacoustic spectroscopy (QEPAS) has been widely used for trace gas sensing applications due to its high sensitivity and selectivity, and the very small volumes required [1-5]. QEPAS is based on the detection of sound waves generated by absorption of modulated optical radiation from gas target molecules. The sound detector is a piezoelectric quartz tuning fork (QTF) which converts small deflections of the prongs generated by the pressure waves into an electrical signal. The excited QTF in-plane flexural resonance modes are characterized by a high-quality factor as well as high immunity to environmental acoustic noise [6,7]. A crucial aspect in QEPAS detection is the dependence of the QEPAS signal on the radiation-to-sound conversion efficiency, which affects the acoustic waves generation within the gas. It is mainly determined by the transfer rate of the vibrational energy of excited analyte molecules into kinetic energy (translation) of the surrounding molecules (V-T relaxation) [8]. Starting from 2002 [1], standard QTFs operating at a frequency as high as 32.7 kHz were commonly used for QEPAS sensing. In relation to this frequency, the gas species can be categorized in two groups, fast and slow relaxing gases, usually referring to relatively low concentrations (ppm range or lower) of the absorbing analyte in a matrix of inert gas, typically N2. For slow relaxing molecules, the 32.7 kHz laser modulation frequency is significantly higher than the effective analyte relaxation rate in the gas matrix, not allowing a complete release of the absorbed energy during each oscillation period. Thereby, the realization of custom QTFs with resonance frequencies of <32.7 kHz paved the way to the efficient detection of slow-relaxing molecules concentration leading to improved sensitivity levels [7,9-12]. Conversely, for fast relaxing gas species, the relaxation rate is significantly faster than the optical modulation frequency and an efficient energy transfer occurs between absorbing molecules and surrounding gas matrix during each oscillation period.

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However, the effective relaxation rate of a target gas depends on the surrounding matrix composition. Therefore, fast relaxing gases (such as H$_2$O and SF$_6$) can be added in the gas matrix to act as relaxation promoters, thereby enhancing the target analyte relaxation rate and the QEPAS detection sensitivity [14-16]. In this case, the excited target molecules can relax in different channels through collisions with the different types of molecules composing the matrix, including both the buffer and the promoter. The relaxation rate is then given by the sum of the relaxation rates of every possible energy transfer pathway, weighted by the concentration of each species in the mixture [17,18]. However, since the slow-relaxing gas QEPAS signal depends on the promoter concentration within the mixture, the promoter concentration has to be detected and monitored, increasing the complexity of the sensing systems. This issue has been addressed by exploiting the capability of QTFs to simultaneously operate at two different vibrational modes [19]. The QTF flexural 1st overtone mode can be excited along with the fundamental one, allowing simultaneous dual-gas QEPAS detection of target and relaxation promoter gas species via frequency division multiplexing (FDM) technique [20,21].

The influence of V-T relaxation rate on photoacoustic signal was first investigated in 1996 by Repond and Sigrist [22], studying its dependence on fundamental thermodynamic parameters, namely the pressure and temperature. In 2006, Wysocki et al. [23] studied the vibrational relaxation rate on a QEPAS sensor employing a 32.7 kHz-QTF. In this work, the amplitude and phase of the QEPAS signal of CO$_2$ at a fixed concentration are analyzed as a function of the concentration of H$_2$O vapor, acting as V-T promoter. The obtained results highlight the possibility of estimating absolute relaxation rate, which is the relaxation time of a molecule on itself, starting from known concentrations of the molecules in the mixture, but the evaluation of the effective relaxation rate of an unknown gas sample is not feasible. However, a QTF frequency as high as 32.7 kHz is not appropriate for a slow relaxing gas like CO$_2$. In general, an accurate estimation of the gases vibrational relaxation rate can only be performed by exploiting different quartz tuning forks having resonance frequencies in a wide frequency range, in order to comprehensively investigate both slow and fast relaxing gases.

Therefore, the experimental apparatus conceived in the present work implements a QEPAS sensor with interchangeable QTFs, whose resonance frequencies range from 3 kHz to 45 kHz, to measure the effective relaxation time of a slow relaxing analyte (methane) and a fast one (H$_2$O vapor). Two diode lasers, one resonant with a CH$_4$ absorption line located at 6046.96 cm$^{-1}$ and one targeting an H$_2$O absorption line at 7226.02 cm$^{-1}$ have been used as the light sources to generate QEPAS signals. For each QTF and respective resonance mode, the CH$_4$ and H$_2$O QEPAS signals, as well as the quality factor of the QTFs have been measured as a function of pressure. Thus, the radiation-to-sound conversion efficiency trends have been reconstructed as a function of pressure, for different acoustic frequencies. The analysis of these trends allowed the estimation of the effective relaxation rates for both gas species.

2. Classical theory on vibrational relaxation rate

A fundamental vibration is activated when a molecule in its ground state absorbs a quantum of energy. The molecule can be deactivated by emitting a photon or colliding with surrounding molecules. Since the radiative lifetime for infrared radiation is long (usually between $10^{-1}$ and $10^{-3}$ s), this mechanism can be neglected. Thus, the molecule mainly looses vibrational energy through collisions with its nearest neighbors. Landau [24] proposed a theoretical model to consider a collinear collision between a vibrating molecule and a non-vibrating one. The model is based on the elementary kinetic theory, in which molecules are treated as hard spheres with a finite collision diameter. It supposes a $S(1\rightarrow0)$ transfer when a molecule in the $\nu = 1$ state collides with another molecule in the $\nu = 0$ state. All other non-excited molecules are supposed to be in the state $\nu = 0$ and a Boltzmann distribution is assumed to rule the population between two levels. With these assumptions, the relaxation time $\tau$ is introduced, which is proportional to the inverse of the number of collisions suffered by one molecule per second. Since the rate collision is proportional to the number of molecules in a given volume, and hence to the gas pressure $P$, $\tau$ is inversely dependent on $P$. Thus, the relaxation time is expressed as the inverse of the product between a rate constant $k$ and $P$. In other words, $\tau$ represents the V-T relaxation time, i.e. the time required to transfer the vibrational energy of the excited molecule into kinetic energy (translation) of the surrounding ones. These V-T energy transfer processes result in a heat production rate. Analyses based on level population are widely adopted. The molecule density $N_{mol}$ of the absorbing gas is modelled by a two-level system, consisting of a vibrational ground state having molecule density $N$ and an excited state with molecule density $N'$. In the approximation that $N' < N$, the rate equation for $N'$ is given by:

$$\frac{dN'}{dt} = N\tau \Psi - N'$$

where $\Psi$ and $\tau$ denote the photon flux and the absorption cross-section, respectively. Radiative relaxation time and stimulated emission from the excited state have both been neglected. For a harmonic modulation at frequency $f$ of the photon flux $\Psi = \Psi(1+i\varepsilon f)$, periodic heating occurs in the sample, generating pressure waves. The frequency-dependent QEPAS signal generated at the modulation frequency $f$ will be given by:

$$S = KQ(P)P_2I_2(P)^2\epsilon(f, \tau(P))$$

where $K$ is a sensor constant, $Q(P)$ is the QTF quality factor and $P_2$ is the laser power, $I_2(P)$ is the peak intensity of the second-derivative of the absorption line simulated by HITRAN database (as usually obtained when operates in wavelength-modulation and 2f-detection [25]), and $\epsilon(f, \tau(P))$ is the radiation-to-sound conversion efficiency, given by:

$$\epsilon(f, \tau(P)) = \frac{1}{\sqrt{1 + [2\tau f\varepsilon(P)]^2}}$$

where $\tau$ can be expressed as:

$$\tau = \frac{1}{KP}$$

For instantaneous relaxation, i.e. $2\tau f < < 1$, $f = 1$ and the QEPAS signal is independent on the modulation frequency.

3. Methane relaxation rate in standard air

Methane QEPAS sensors reported in literature often investigated gas mixtures of methane in an N$_2$-H$_2$O matrix [6]. Water vapor is added to N$_2$ buffer to increase the CH$_4$ QEPAS signal because its V-T relaxation rates are several orders of magnitude faster than those of other molecules with comparable energy levels, but not hydrogen bonded. This is because water presents a wide absorption spectrum and is a polar molecule [26,27]. Several works demonstrated the linear increment of the CH$_4$ photoacoustic signal with the water content, when the CH$_4$ concentration is below 1% [6,20,28,29]. N$_2$ molecules are high-density collisional partners for excited CH$_4$ molecules. The presence of H$_2$O in the gas mixture opens an additional relaxation path. Thus, all energy transfer paths in the CH$_4$-N$_2$-H$_2$O gas mixture contribute to the relaxation process from the excited analyte state. The vibrational modes of methane include two bending modes, $\nu_2$ (1533 cm$^{-1}$) and $\nu_4$ (1311 cm$^{-1}$), and two stretching modes $\nu_1$ (2917 cm$^{-1}$) and $\nu_3$ (3019 cm$^{-1}$). The two stretching mode wavenumbers are approximately twice the bending mode ones, leading to a distribution of the vibrational levels in polyads. When the methane is optically excited in the near-infrared range at 6038 cm$^{-1}$, the $2\nu_3$ level is excited in the P4-Tetradecad. The
Due to the strong interactions existing between the states in P4-Tetradecad, very fast energy transfers (in the nanosecond range) occur between $2\nu_3$ and $4\nu_4$, which is the lowest level of P4-Tetradecad, via vibrational-to-vibrational processes. Then, the energy transfer between consecutive polyads essentially occurs via the exchange of one $\nu_4$ vibrational quantum via V-T relaxation processes with all collisional partners [17]. Therefore, a rate constant can be introduced for each collisional partner, namely $k_{\text{H}_2\text{O}}$, $k_{\text{N}_2}$ and $k_{\text{CH}_4}$. In this way, the relaxation time of $2\nu_3$ excited state of CH$_4$ is given by a weighted sum of the relaxation rates corresponding to collisions with the different types of neighbor molecules (H$_2$O, N$_2$ and CH$_4$ itself), and taking into account the concentration of each species:

$$k = k_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}} + k_{\text{N}_2}C_{\text{N}_2} + k_{\text{CH}_4}C_{\text{CH}_4}$$

being $C_{\text{H}_2\text{O}}$, $C_{\text{N}_2}$ and $C_{\text{CH}_4}$ the concentration of H$_2$O, N$_2$ and CH$_4$, respectively. The rate constants are provided in literature and summarized in the following table.

Methane collisions with water have a rate constant two orders of magnitude higher than with CH$_4$ and three orders of magnitude higher than with N$_2$. If the concentration of the three gas components are known, the effective relaxation time of methane in the gas matrix can be calculated.

4. Experimental investigation

The estimation of vibrational relaxation rates will be obtained by measuring the radiation-to-sound conversion efficiency. However, both the QTF quality factor $Q$ and $\varepsilon$ are pressure-dependent. When the gas pressure varies, Eq. (2) shows that the ratio $S(P)/\{Q(P)\cdot I_2^2(P)\}$ follows the same trend as $\varepsilon$. In addition, $\varepsilon$ depends on the sound frequency, i.e. on the QTF resonance frequency, at the selected flexural mode. Thus, for different QTFs and excited modes, a family of $\varepsilon_i$ functions is expected. In order to perform this investigation, a set of five QTFs was selected: six flexural resonance modes were excited in order to have a suitable frequency span from 3 kHz up to 44 kHz. In Table 2, selected QTFs are

![Fig. 1. Energy-level diagram of CH$_4$ molecule, showing the laser excitation ($\gamma$) to the 2$\nu_3$ state and the subsequent preferential relaxation scheme.](image1)

![Fig. 2. Experimental setup for relaxation rate measurements with custom QTFs optimized for QEPAS sensing. LD: Laser diode, TEC: Thermoelectric cooler, CD: Current driver, WFG: Waveform generator, TA: Trans-impedance amplifier, L: Focusing lens, bMQ: Data acquisition card, PM: Power meter, REF: TTL reference signal, $\Sigma$: Adder.](image2)
labelled and the frequencies of the selected resonance modes are reported. QTFs’ geometry and prong sizes are described in detail in the references listed in the leftmost column.

The quality factor of each resonance mode has been evaluated by acquiring the QTF resonance curve as a response to an electrical excitation. A function generator (Tektronix model AFG3102) was used to provide a sinusoidal voltage as excitation signal to the QTFs. The output voltage is demodulated by a lock-in amplifier (Stanford Research Model SR830) at the excitation frequency. By gradually varying the excitation frequency, the resonance curve is reconstructed. The ratio between the peak frequency and the full-width-half-maximum value of the resonance curve provides an estimation of the quality factor. All QTFs have been mounted in a stainless-steel enclosure in order to fix and control the gas pressure. The investigated pressure range was 30–760 Torr.

The setup for generating the QEPAS signal is depicted in Fig. 2.

A single-mode continuous-wave pigtailed diode laser was used as CH₄ excitation source to generate QEPAS signals. With an optical power of 14 mW, the diode laser targets a methane absorption line located at 6046.96 cm⁻¹, having line strength of 1.46⋅10⁻²¹ cm/molecule [32]. The laser was coupled with a fiber collimator whose output beam was focused between the QTF prongs using a lens with a focal length of 50 mm. A stainless-steel enclosure equipped with two near-IR windows was realized in order to accommodate and easily interchange QTFs. A certified gas mixture composed of 1% of CH₄, 0.15% of H₂O and nitrogen as rest was used as test mixture. A flow-rate controller fixed the gas flow rate to 20 scmm, while a pressure controller, a valves system and a pump (not shown in Fig. 2) stabilized the gas pressure within the enclosure to a selected value. The QEPAS sensor operated with a wavelength modulation and dual-frequency detection approach, i.e. the laser beam was wavelength-modulated at half of the selected resonance mode frequency providing an external sinusoidal oscillation to the current driver, while the lock-in amplifier demodulated the signal at the resonance mode frequency. A QEPAS scan across the absorption line was acquired by applying a slow ramp to the current driver. The laser beam waist in the lens focal plane, i.e. between QTF prongs, was measured by using an infrared pyrocamera (Ophir, Spiricon) and it was ~200 μm, well below the smallest employed prongs spacing (300 μm for QTF#4).

As a result, more than 99% of the laser optical power passed through QTF prongs without touching them.

5. Measurement of methane relaxation rate in nitrogen/water mixture

A QEPAS scan of the selected methane absorption line was acquired for eleven pressure values in the range 30–760 Torr. For each gas pressure, the peak-to-peak amplitude as well as frequency of the current modulation were adjusted in order to maximize the peak value of the QEPAS scan. Indeed, the amplitude modulation is related to the full width at half maximum (FWHM) value of the absorption line, which depends on the pressure broadening. I_{Q} (see Eq. (2)) is pressure-dependent and proportional to the product between the second derivative of the absorption coefficient peak and the squared modulation amplitude of the emission frequency [25]. However, considering the experimental modulation depths optimizing the QEPAS signals and the absorption coefficient values provided by the HITRAN database [32], it has been verified that the I_{Q} dependence on pressure can be neglected, as it provides a nearly constant value. The QTF resonance frequency is also pressure-dependent and it linearly decreases when the pressure increases. Then, peak values of each QEPAS scan have been extracted, for all the resonance modes reported in Table 2. Fig. 3 depicts the quality factor and the QEPAS peak signal trends as a function of pressure when the certified gas mixture is flowing through the acoustic detection module. In order to make the comparison more effective, all the data have been normalized to their respective peak values.

For each resonance mode, the quality factor monotonically decreases as the pressure increases. This is due to the gas surrounding the QTF, which acts as a damper for the prong vibrations. Gas damping is the main loss mechanism for the fundamental and first overtone mode and it is proportional to the viscosity and density of fluid. A good approximation for the dependence of the quality factor on the gas pressure is provided by the following equation [33,34]:

Q(P) = \frac{Q_0}{1 + b P^{1/2}} \quad (6)

where Q_0 is the quality factor at P = 0, which includes all pressure independent loss mechanisms (support losses and thermoelastic damping), and b is a fitting parameter. Both Q_0 and b are mainly related to QTF geometry and gas viscosity, thus vary for each QTF. Starting from P = 30
Torr, the QEPAS signal rapidly increases until it reaches a maximum value; then it slightly decreases. When the pressure decreases, the QTF quality factor increases while the number of molecules decreases, negatively affecting the radiation-to-sound conversion efficiency (see Eqs. (2) and (3)). Conversely, at high pressures a larger number of molecules guarantees an efficient sound generation but the QTF quality factor increases while the number of molecules decreases, negatively affecting the radiation-to-sound conversion efficiency (see Eq. (3)). The maximum point in the QEPAS signal corresponds to the pressure value at which the tradeoff between the opposite behaviors of $\varepsilon$ and $Q$ occurs. This tradeoff pressure varies with the modulation frequency. This is expected because the radiation-to-sound conversion efficiency depends on the sound frequency (see Eq. (3)). The maximum point in the QEPAS signal versus pressure dependence is more distinct at frequencies below 21 kHz, where it occurs at comparably low pressures. For $f = 32.76$ kHz and 44.13 kHz the QEPAS signal reaches its maximum value around ~500 Torr; above that, the QEPAS signal remains almost unchanged. This aspect is crucial for studying the vibrational relaxation time of CH$_4$ in the gas mixture and can be better understood by analyzing the radiation-to-sound conversion efficiency as a function of the resonance frequency. As discussed, this study can be carried out in terms of the ratio between the QEPAS signal and the quality factor. Thereby, for each resonance modes, the ratio $S/Q$ is reported in Fig. 4 as a function of the investigated pressure values (data points).

For each frequency, the ratios $S/Q$ have been normalized to the corresponding maximum values. The results reveal the strong dependence of $S/Q$ on the sound frequency. At the lowest investigated frequency (3.44 kHz), $S/Q$ reaches the plateau level at P~400 Torr and then remains almost constant up to atmospheric pressure. As the frequency increases, the plateau level is reached at higher pressures. However, for 32.76 kHz and 44.13 kHz, the plateau level is not reached, suggesting that the maximum $S/Q$ value should occur at pressures higher than the atmospheric one. Normalized $S/Q$ values can be fitted by using the theoretical expression introduced for the radiation-to-sound conversion efficiency (see Eq. (3)), thus the fitting function has the form:

$$F(p) = \frac{z}{\sqrt{1 + \left(\frac{A}{p}\right)^2}} + w$$

where $A = 2\pi f/k$, $z$ and $w$ are just fitting parameters.

The fits of experimental data are shown in Fig. 4 as solid lines. The resulting fitting parameters are listed in Table 3:

The $A$ parameter, defined as the product between the sound frequency and the time constant $\varepsilon$, rules the growth rate of the radiation-to-sound conversion efficiency as a function of pressure. $z$ is the maximum value reachable when $P$ tends to infinity. It can be noticed that for the QTFs with higher resonance frequency ($32.76$ kHz and $44.13$ kHz) $z$ tends to increase, validating the hypothesis that the investigation pressure range should be extended to pressures higher than the atmospheric one for reaching a plateau level. By fitting the $A$ parameter as a function of the sound frequency, the rate constant can be retrieved by a linear fit. The results are shown in Fig. 5.

The trend shows a linear behavior of the $A$ parameter as a function of frequency up to a cut-off value. The fitting procedure clearly underestimates the $A$ parameter for $32.7$ kHz and $44.1$ kHz. This result, together with related comments above, demonstrates that sound frequencies greater than $30$ kHz are not suitable to investigate the

![Fig. 4. Normalized S/Q of methane on a mixture of 1% CH$_4$, 0.15 % H$_2$O and 98.85 % N$_2$ for all the resonance modes investigated. The lines represent the best fit using Eq. (7).](image)

![Fig. 5. Black squares: values of parameter $A$ obtained by fitting on the experimental curves of the S/Q methane normalized ratio. Red line: linear fit performed on the first four values of the parameter $A$. The effective relaxation time constant results $k^2 = m/2z$, where $m$ is the linear fit slope.](image)

### Table 1

| Reaction | Rate constant ($s^{-1}Torr^{-1}$) | Ref |
|----------|----------------------------------|-----|
| CH$_4$(v$_2$) + CH$_4$ → CH$_4$(v$_4$) + CH$_4$ | 1.05 $\times$ 10$^3$ | [30] |
| CH$_4$(v$_2$) + CH$_4$ → CH$_4$(v$_1$) + N$_2$ | 1.05 $\times$ 10$^2$ | [30] |
| CH$_4$(v$_2$) + H$_2$O → CH$_4$(v$_1$) + H$_2$O | 1.32 $\times$ 10$^2$ | [5] |

### Table 2

| # | Resonance mode | Frequency (kHz) | Ref. |
|---|----------------|-----------------|------|
| QTF#1 | Fundamental | 3.44 | [6] |
| QTF#2 | Fundamental | 9.78 | [31] |
| QTF#3 | Fundamental | 15.23 | [7] |
| QTF#4 | First overtone | 21.43 | [6] |
| QTF#5 | First overtone | 44.13 | [6] |

### Table 3

| Frequency (kHz) | $z$ | $w$ | $A$ |
|----------------|-----|-----|-----|
| 3.44           | 1.26 | -0.25 | 101 |
| 9.78           | 1.24 | -0.17 | 220 |
| 15.23          | 1.3  | -0.16 | 339 |
| 21.42          | 1.24 | -0.06 | 459 |
| 32.76          | 1.37 | -0.08 | 578 |
| 44.13          | 1.52 | -0.07 | 576 |
of the CH of the gas sample (1% CH) in Fig. 7. Experimental curves of the following the same procedure described in Section 5, the QEPAS water sample. By using the QTF resonance modes listed in Table 2 and [32]. A certified gas mixture with 0.5 % of water in N 2 was used to measure the relaxation time constant of 3.2 ms Torr, which corresponds to the experimental result within the uncertainty interval estimated with our approach.

7. Conclusions

In conclusion, the possibility to use the QEPAS technique to measure the vibrational relaxation rate of both slow and fast relaxing molecules in a defined gas matrix has been demonstrated. A QEPAS sensor implementing a set of QTFs whose resonance frequencies span from 3 kHz to 45 kHz has been employed to evaluate the CH 4 non-radiative relaxation time in a gas sample composed of 1% CH 4, 0.15 % H 2 O and 98.85 % N 2. The values of the CH 4 radiation-to-sound conversion efficiency as a function of pressure were estimated by measuring the QEPAS signal and the QTF resonance mode quality factor. A relaxation time constant for CH 4 of 3.2 ms Torr was extracted, in excellent agreement with the data present in literature. The same QEPAS sensor architecture was used to measure the relaxation time of water vapor in a mixture of 0.5 % of H 2 O in nitrogen. A water relaxation time constant of 0.25 ms Torr was estimated, about an order of magnitude smaller than the value obtained with methane. This value is in good agreement with the results reported in literature. The obtained results demonstrate that QEPAS is an accurate and robust technique for energy relaxation rate measurements of gas species.

Table 4

| Reaction | Rate constant (s⁻¹ Torr⁻¹) | Ref |
|----------|---------------------------|-----|
| H 2 O*(ν 1) + N 2 = H 2 O*(ν 1,3 + ν 2 ) + N 2 | 1.32 × 10⁴ | [29] |
| H 2 O*(ν 3 ) + H 2 O = H 2 O*(ν 3,1 + ν 2 ) + H 2 O | 7.00 × 10³ | [27] |

Starting from lower pressures, S/Q rapidly increases up to 200–300 Torr and then remains almost flat for higher pressure values, for all the investigated sound frequencies. This suggests that above 300 Torr the radiation-to-sound conversion efficiency of the water molecules in a nitrogen buffer is quite constant and it is almost independent on the excitation frequency. This is expected because of the fast vibrational-to-translation energy transfer of water molecules. Each curve has been fitted by using Eq. (7) and the A parameter has been extracted and plotted as a function of the frequency in Fig. 7.

The linear fit gives an estimation of the H 2 O effective relaxation time constant k⁻¹ of 0.25 ± 0.05 ms Torr. A relative uncertainty as high as 20 % was obtained, about one order of magnitude higher than that obtained with the methane relaxation time (~ 3%). This can be explained by the fact that the growth rate of S/Q functions with increasing pressure is almost the same for all investigated frequencies. Indeed, the relative relaxation time of water is known to be significantly lower than that of methane and the investigated frequency range should be increased towards higher frequencies. In this way, the measurement uncertainty could be improved. Despite the high measurement uncertainty, a comparison with the measurements reported in literature is instructive. Literature rate constants for H 2 O→H 2 O and H 2 O→N 2 relaxation pathways are summarized in the following table.

From the values listed in Table 4, the estimated effective relaxation time of the gas sample (0.5 % H 2 O and 99.5 % N 2) is k⁻¹ex = 0.21 ms Torr, which corresponds to the experimental result within the uncertainty interval estimated with our approach.

6. Measurement of water relaxation rate in nitrogen buffer

The robustness of the technique has been tested by targeting water vapor, a very fast relaxing molecule. In the experimental setup sketched in Fig. 2, the laser source has been replaced by a pigtailed laser diode with an optical power of 28 mW at 7226.02 cm⁻¹, where the peak of a ν 1 water absorption line with linestrength of 8.71 × 10⁻²² cm/mol is located [32]. A certified gas mixture with 0.5 % of water in N 2 was used as test sample. By using the QTF resonance modes listed in Table 2 and following the same procedure described in Section 5, the QEPAS water peak signals and the QTF quality factors have been acquired at different pressure values of the gas flowing in the enclosure. The normalized ratios S/Q as a function of the pressure are reported in Fig. 6.

Fig. 6. Normalized S/Q of water vapor in a mixture of 0.5 % H 2 O and 99.5 % N 2 for all the resonance modes investigated. Solid lines are guides for eye.

Fig. 7. Black squares: values of parameter A obtained by fitting on the experimental curves of the S/Q water vapor normalized ratio. Red line: linear fit performed on the values of the parameter A. The effective relaxation time constant results k⁻¹ = m/2π.

vibrational relaxation time of the examined gas sample, at pressures lower than the atmospheric one. Therefore, a linear fit was imposed on data points related to the four lower frequencies, allowing an estimation of the CH 4 effective relaxation time constant in the analyzed mixture k⁻¹ of 3.2 ms Torr, with an uncertainty of 0.1 ms Torr. Considering the relaxation rate constants reviewed in Table 1, the effective time constant of the gas sample (1% CH 4, 0.15 % H 2 O and 98.85 % N 2) estimated via Eq. (5) is k⁻¹ex = 3.2 ms Torr, in excellent agreement with the value extracted from the measurement data.

| Reaction | Rate constant (s⁻¹ Torr⁻¹) | Ref |
|----------|---------------------------|-----|
| H 2 O*(ν 1) + N 2 = H 2 O*(ν 1,3 + ν 2 ) + N 2 | 1.32 × 10⁴ | [29] |
| H 2 O*(ν 3 ) + H 2 O = H 2 O*(ν 3,1 + ν 2 ) + H 2 O | 7.00 × 10³ | [27] |

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