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Depletion of the vibrational ground state of CH_4 in absorption spectroscopy at 3.4 µm in N_2 and air in the 1–100 Torr range

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ABSTRACT

A model presented in an accompanying work predicts that mid-IR absorption signals from methane in trace concentrations in various buffer gases detected at pressures in the 1–100 Torr range can be reduced and distorted due to depletion of the vibrational ground state if the molecules are exposed to laser powers in the tens of mW range or above. This work provides experimental evidence of such depletion in a resonant cavity under a variety of conditions, e.g. for intracavity laser powers up to 2 W and for buffer gases of N_2 or dry air, and verifies the applicability of the model. It was found that the degree of depletion is significantly larger in N_2 than dry air, and that it increases with pressure for pressures up to around 10 Torr (attributed to a decreased diffusion rate) but decreases with pressure for pressures above 20 Torr (caused by an increased collisional vibrational decay rate). The maximum degree of depletion (~80%) was obtained for methane in N_2 at around 15 Torr. This implies that absorption spectrometry of methane can experience significant non-linear dependencies on laser power, pressure, as well as buffer gas composition. It is shown that depletion takes place also in $^{13}CH_4$, which verifies the applicability of the model also for this isotopologue, and that NICE-OHMS signals detected in absorption phase are less affected by depletion than in dispersion. It was concluded that the absorption mode of detection can provide concentration assessments that are virtually free of influence of depletion for intracavity powers below 0.8 W.

1. Introduction

Laser-based spectroscopic techniques are nowadays frequently used for detection of gaseous species. Over the years, a number of techniques, with a variety of properties, have been developed for a wide range of applications, not least trace gas detection. To obtain the highest accuracy, several of these are based upon absorption spectroscopy (AS). Moreover, to achieve the highest detection sensitivity (to increase the interaction length between the gas to be analyzed and the light), they often incorporate an external cavity, often of resonant type [1].

To ensure accurate concentration assessments, it is of importance that all phenomena and processes that can influence the measured signal are well understood and that all entities of importance that can influence any such assessment are well known and under control. If this is not the case, the technique may suffer from systematic errors, e.g. non-linear responses, drifts of signals strengths, or inaccurate calibrations.

When molecular absorption spectroscopic techniques are utilized, one so far not fully understood and partly uncharacterized phenomenon is depletion of the population in the lower state(s) addressed by the laser light. This can take place when the excitation rate constitutes a non-negligible fraction of the deexcitation rates in the system. In fact, for systems in which the decay rates of the molecules under study are slow, a narrow linewidth laser can, in many cases, significantly alter the thermal equilibrium of molecules among various (quantum) states already at low laser powers, in particular when external cavities are used. As the population of the level addressed by the laser light is being affected by the excitation, so it is no longer equal to the level's thermal population, the absorption signal will no longer be related to the concentration of molecules according to conventional descriptions, e.g. Beer's law. Various non-linear responses will then result.

One particular case when this can take place is for methane in nitrogen since the vibrational energy levels of these two types of molecules are widely dissimilar. In this system the deexcitation of vibrationally excited methane molecules does not primarily take place by collision-induced vibration-to-vibration transfer of energy to the buffer gas molecules, as is common in many other

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systems, but it is instead dominated by exceptional slow vibration-to-translation processes [2,3]. This is therefore a system that is prone to be affected by depletion of not only the rotational-vibrational state addressed by the laser, but also, as is shown below, the entire lower vibrational state.

When non-linear responses are obtained from atomic or molecular systems under low pressure conditions (well below the Torr region) the phenomenon is often attributed to optical saturation (OS) of the transition addressed, affecting the populations in the two laser-addressed rotational states [4–6]. For higher pressures, for which rotational states and velocity groups within a given vibrational state starts to be coupled by collisions, multi-level descriptions are generally needed so as to describe the transfer of population between various (quantum) states [7,8]. However, to be able to utilize AS for quantitative assessments of methane, including its various isotopologues, under optimal conditions (which encompass such pressures), and, in particular, to estimate the conditions when the measurements and *not* affected by depletion, a simple model for the redistribution of population and AS of methane in the presence of either N_2 or dry air that takes depletion into account has been given in an accompanying work [9]. We argue in that work that for sufficiently high pressures, in the 1–100 Torr range for the particular system considered, it is possible to consider the collisions between rotational states and velocity groups to be so frequent that no multi-level description is needed; it suffices to describe the molecular system as a simple three-level system in which the lowermost and uppermost levels represent the vibrational states (or cluster of vibrational states) between which the laser excitation takes place.

Moreover, since molecules in this pressure range are exposed to a high collision rate they have a mean-free path that is significantly shorter than other length dimensions in the system. This implies that it is not appropriate to model the decay of excited molecules due to their finite time in the interaction region as the inverse of a constant transit time, which often is used in OS models. Instead, we argue in our accompanying work that the transfer of molecules in the system needs to be seen as a diffusion process in the radial direction. In the model presented, diffusion was modeled according to Fick's law, applied to each level individually. Since diffusion is strongly pressure dependent, this implies that the transport of molecules in the system will be significantly dissimilar to what it is under low pressure conditions.

All this implies that the three-level model presented in our accompanying paper [9], which thus incorporates level-specific diffusion, is a possible candidate to simulate and predict depletion and the non-linear responses of AS this gives rise to from molecular system under conditions for which traditional OS models are not applicable (which would predict only insignificant amounts of distortion of AS signals), for the case with methane for pressures above 1 Torr.

The model predicted that depletion of the lowest vibrational level can significantly alter the amount of light being absorbed by methane in trace concentrations probed at its strongest band at 3.2–3.5 µm [9], which is a frequently addresses wavelength band [10–15], under a wide range of conditions. The present work provides experimental evidence of non-linear responses in such a system in the 1–100 Torr pressure range, using both direct cavity enhanced absorption spectrometry (DCEAS) and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS). As oxygen is a much stronger quencher of excited methane molecules than nitrogen, studies were performed on methane in both neat nitrogen and dry air. It is demonstrated, among other things, that depletion can reduce the signal significantly (up to 80%).

Since it is of importance to detect also low abundant isotopologues of many types of species, in particular of methane [16–21], and a variety of laser based spectroscopic detection systems have been developed to address this concept [12,22–31], measurements were also performed on the $^{13}CH_4$ isotopologue.

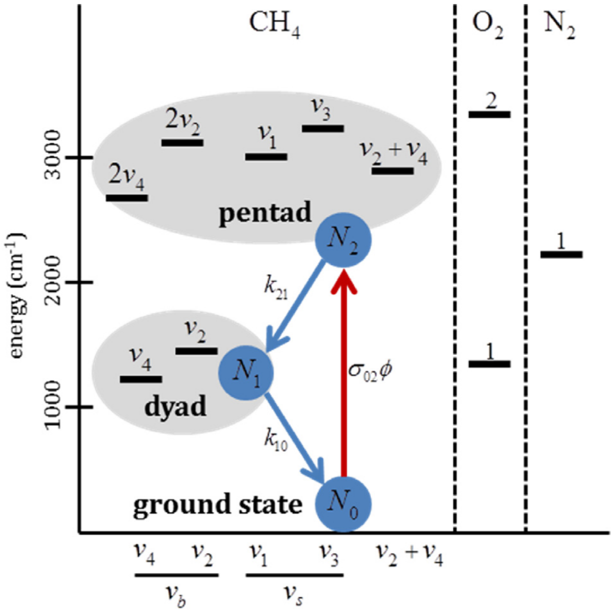

Fig. 1. Vibrational energy level diagrams of CH_4, O_2, and N_2 for energies up to 3500 cm^{-1}. The energy levels of methane consist of two types of bending modes, ν_2 and ν_4, jointly denoted ν_b, and two types of stretching modes, ν_1 and ν_3, jointly referred to as ν_s, that form two clusters of levels referred to as the dyad (with energies of around 1500 cm^{-1}) and the pentad (at around 3000 cm^{-1}). Not shown in the figure are the symmetry subcomponents and rotational states of the levels.

The paper verifies the validity of the three-level model and demonstrates that it can be used to adequately predict and describe depletion of the vibrational ground state of methane ($^{12}CH_4$ as well as the $^{13}CH_4$ isotopologue) in N_2 and air and the non-linear experimental responses this gives rise to in the 1–100 Torr range.

Possible remedies to circumvent the effect of depletion, e.g. reduction of laser power or addition of a fast quencher of CH_4 molecules (i.e. O_2 or CO_2), are suggested.

2. THEORY

To be able to assess the concentration of molecules in a given compartment from the absorption of light when the light is affecting the population of molecules on the levels addressed requires knowledge about the population transfer processes that govern the distribution of molecules on various levels. To assess this, knowledge is, in turn, needed about the energy structure of the addressed molecule as well as its most abundant collision partners [9].

2.1. Energy structure of methane

The methane molecule has four vibrational modes: two bending modes, jointly termed ν_b, and two stretching modes, referred to as ν_s. As is shown in Fig. 1, the first excited bending levels have approximately half the energy of the first excited stretching levels, where the latter are around 3000 cm^{-1}. This implies that the vibrational energies of methane form clusters of levels whose energies are separated about 1500 cm^{-1}. The various clusters are referred to as polyads, of which the first one is termed the dyad while the second one is denoted the pentad [9,32–35].

Each individual vibration mode comprises a number of rotational states, often denoted by the rotational quantum number J (taking integer numbers), and a rotational symmetry, denoted E,