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Dipole saturated absorption modeling in gas phase: Dealing with a Gaussian beam

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ABSTRACT

With the advent of new accurate and sensitive spectrometers, cf. combining optical cavities (for absorption enhancement), the requirement for reliable molecular transition modeling is becoming more pressing. Unfortunately, there is no trivial approach which can provide a definitive formalism allowing us to solve the coupled systems of equations associated with nonlinear absorption. Here, we propose a general approach to deal with any spectral shape of the electromagnetic field interacting with a molecular species under saturation conditions. The development is specifically applied to Gaussian-shaped beams. To make the analytical expressions tractable, approximations are proposed. Finally, two or three numerical integrations are required for describing the Lamb-dip profile. The implemented model allows us to describe the saturated absorption under low pressure conditions where the broadening by the transit-time may dominate the collision rates. The model is applied to two specific overtone transitions of the molecular acetylene. The simulated line shapes are discussed versus the collision and the transit-time rates. The specific collisional and collision-free regimes are illustrated, while the Rabi frequency controls the intermediate regime. We illustrate how to recover the input parameters by fitting the simulated profiles.

1. Introduction

The development of new optical devices such as spectrally narrow laser source, high-finesse cavities, frequency combs (OFC) is opening new opportunities for probing the fundamental physics, and the physical chemistry of the collisional processes, as well as for testing ab-initio calculations of molecular level energy which can only approach the experimental accuracy on molecular hydrogen. High-finesse cavities ($\mathcal{F} > 100,000$) have been developed to improve the limit of detection by maximizing the equivalent absorption length. However, the multiple intracavity counter propagating beams bounced by high reflectors, promotes the intracavity electromagnetic field (EMF) with intensity large enough to electromagnetically saturates even weak transitions. The occurrence of narrow (i.e., sub-Doppler) saturation dips was originally described by Lamb [1]. The Lamb-dip shape is known to be controlled by a "parameter of saturation" which depends on the ratio of the Rabi frequency of the transition to the energy level width, or to equivalent broadening. From a metrology point of view, the relevant matter is: what is the ultimate sub-Doppler resonance narrowing which can be experimentally reached with regard to the best transition center determination? The resonance width determines the ultimate accuracy of the transition frequency achievable. In the near-infrared (NIR) domain, the precision of the frequency standards is better than 1 Hz (accuracy of 10^{-14}) [2,3]. Is it possible to reach such an accuracy on the transition frequency determination? It is well established that in absence of collision (the radiative lifetime of the upper state is large enough to be neglected in the NIR), the only limiting factor becomes the coherent interaction time between the molecular (or atomic) species, and the external EMF (semi-classical treatment). From an experimental point of view, it is necessary to maximize this interaction time. It is likewise valuable to have a soundly-based model of the Lamb-dip shape to extract, not only the resonance center (assuming non-degenerate transitions), but also any other physical information related to the resonance shape (e.g., the amplitude or the integral, and the linewidth).

The line shape modeling under Doppler (inhomogeneous) broadening conditions has generated an abundant literature [4]. It basically requires an accurate description of the molecular collisional processes, and ultimately a full knowledge of the interaction potential (like Lennard-Jones potential), as well as, of the velocity-changing collisions (VCC) and phase-changing collision (PCC) processes [5,6]. However, additional complexities come from possible dependence of the frequency of the VCC on the speed of the ab-

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sorber, or even from the inherent correlation between VCC and PCC [7]. Pressure broadening, frequency shift, and narrowing (confining) Dicke effects [8,9] are usual experimental evidences of these multiple processes affecting the line profile which can even exhibit asymmetry [10]. Empirical approaches, like speed-dependent Voigt profile (SDVP) [11], as well as ab-initio approaches based on molecular dynamics simulations [12] can give similar information, and lead to a realistic description in the "high" pressure range [13,14]. However, even in the linear absorption regime, deviations can be observed under low pressure conditions [15], or/and under high signal-to-noise-ratio conditions.

In all the "high-pressure" studies, the interaction time between the molecular species and the EMF is neglected, because it is longer than the reciprocal collision rate. In the low-pressure regime which can be probed by high-sensitive detection technique, the interaction time can dominate the mean collision time. Actually, quasi collision-free regimes can even be reached. Under saturated absorption (SA) conditions involving two counter propagating beams, only molecules with almost null component of speed along the z propagation axis are probed (zero-longitudinal-velocity molecules). In addition, in first approximation only collisions keeping v_z constant (defined by a scattering angle [16]) can be probed by such a Doppler-free technique. We can easily anticipate that pressure dependence of the width of "sharp" dip should provide information about the VCC (cross relaxation [17]) which is hard to obtain from conventional Doppler-broadening techniques.

The NIR spectral range offers the advantage of the quasi absence of spontaneous emission. Thus, collisional processes dominate the molecular population transfer. The collision-free or low collision regimes, become ideal environments to probe the interaction by applying an EMF. The transit-time (or linebreadth) can be questioned through the EMF. As a result, the usual approximation associated with the monochromatic fields (or with the multimonochromatic fields associated with the phase modulation spectroscopy [FMS]) needs to be revisited.

The effects of the transit-time broadening (or time-of-flight broadening) has been pioneering studied on molecular system by J. Hall [18] early in the seventies with the first laser systems (HeNe) at 3.39 µm. Modest agreement between experimental data and expectation, if not diverging results [19], has been reported for the pressure broadening coefficients. From the pressure Lamb-dip dependence, S. Bagaev et al. [19], studying the same transition than J. Hall, questioned the phase-shift theory and the hard-core model to match the pressure shift (due to anomalous broadening). They concluded that the collision may fail to be adiabatic. The same group also studied the Lamb-dip pressure-shift [20], and the temperature-shift [21] of the same transition. Recently, differential pressure effects on ortho- versus para-transitions of acetylene have been proposed which questions the collisional processes [22,23]. Carbon monoxide studied at 5 µm by SA displays a nonlinear variation of the pressure broadening coefficient at low pressure ($\sim$0.1 Pa), while the linear low pressure dependence is four times larger than that measured in the high pressure under Doppler-broadened conditions [17,24].

Here, we propose a formalism applicable to a non radiative two-level system interacting with any derivable spectral shape of a classical EMF. However, it will be particularized to Gaussian-shaped beam that is the shape which is associated with the usual continuous wave EMF, or with the EMF trapped inside an optical cavity if it is mode matched against the TEM_{00} eigen cavity mode. Spatial variations of the EMF along the z axis will be ignored (cylindrical beam). However, beam divergence can be easily added to the model by running an additional integral along the z axis. Nevertheless, if the Rayleigh length of the EMF is large enough, the curvature effects becomes marginal, minimizing the front-wave broadening [7], and the adiabatic rapid passages can be ignored [25]. Indeed, this effect can be minimized by using symmetrical cavities, and cavities with large radius of curvature (ROC) reflectors. Furthermore, the requirement for long interaction time demands large ROC of the EMF, and the change of the wavefront phase along the cavity axis is fully balanced by the increase of the beam size.

To facilitate the integral processes, the frequency domain space is adopted in the present approach. To solve the coupled system of equations (based on the density matrix formalism) under saturation conditions, a perturbative development is proposed, a trivial way to deal with the complex third order molecular susceptibility when the medium is optically thin. That way, we establish the spectral response of the molecule to an external EMF in the dipole approximation. However, only the low frequency (or quasi stationary) behavior is fully analyzed.

The present approach deals with the EMF impact parameter, with the Doppler frequency shift, with the 2-dimension molecule velocity distribution in a plane perpendicular to the propagation axis, and with a 1-dimension velocity distribution along the EMF propagation axis. The individual contribution of each Zeeman (or magnetic) sub-transition, constituting of a usual electric dipole polarization are calculated. Different approximations associated with a Gaussian EMF will be discussed.

The typical applications of the present model are the saturated absorption (SA) [26,27], the cavity ringdown spectroscopy (CRDS) [28–30], and the wavelength modulation spectroscopy (WMS) with cavity [31], or without cavity [24]. The extension of the model to multichromatic EMF [32], as well as to N-level systems is quite trivial despite that additional crossover resonances are anticipated [33]; the fields of application are typically the FMS without cavity (but with 2 equivalent counter propagating beams) [34], and the NICE-OHMS [35,36]. Power mode pulling, mode splitting, mode beating [37], relativistic Doppler shift and recoil effects [38–40] are disregarded from the present formalism. The dispersion effects [41] can be neglected, because an optically thin medium is assumed. However, they can furthermore be treated if required.

Species trace detection by saturated absorption is possible as demonstrated by Ma et al. [42]. However, because the intensity of the saturated absorption signal is a nonlinear function of the pressure conditions (it shows a maximum versus the pressure [43]), it is of crucial importance to properly model the shape, (e.g. the amplitude and width) of the Lamb-dip. Indeed, this should rise the question of the sensitivity of a nonlinear detection (SA) compared with a linear absorption detection.

After working out the SA model in Section 2, we will discuss the features of the model by performing various simulations relevant for experimental conditions in Section 3. We mainly review the Lamb-dip shape under different saturation conditions, by varying the impinging beam power, the collision rate, and the transit-time rate. This includes a discussion about different analytical profiles which can be used for fitting the saturated profile. For the sake of experimental relevance, two transitions R_0, belonging to the polyads 10 and 11 of the acetylene molecule have been drawn to our attention. It is worthy of attention that one of the chosen transitions belongs to a vibrational band which has already been intensively studied under saturation conditions, by coupling against an OFC [44]. Indeed, the combination band $1^1_0\,3^1_0$ has been proposed as a frequency standard [45–47]. The purpose of Section 3 is also to demonstrate that the inputs used for the simulations can be recovered by using elementary fitting functions to describe the saturated line profiles. Validation domains, and limit cases are discussed.