

EFFECTS OF INTRA-MOLECULAR INTERACTION ON CARS DIAGNOSTICS OF COMBUSTION

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Abstract

Intra-molecular interaction, although pertaining to the realm of molecular physics, has consequences for spectroscopic diagnostics based on Raman processes in light molecules. Here, we focus on Coherent anti-Stokes Raman scattering (CARS) that is acknowledged mainly for its thermometric potential. In particular, we examine CARS responses of fundamental diatomics and show that, depending on the molecular weight, corrections are expected for thermometry as well as concentration measurements. Clearly, strong corrections are found for the lightest molecule in nature, that is hydrogen. Other diatomics are less sensitive by virtue of their greater moments of inertia and, nonetheless, corrections are on the same order of the accuracy associated with this optical technique.

Introduction

Methods of laser diagnostics have proven extremely useful to promote and support research in combustion science [1]. Among them, coherent anti-Stokes Raman scattering (CARS) is known for its thermometric applications in a variety of harsh environments [1]. The reason of this popularity within the combustion community resides in the optical coherence of the anti-Stokes beam that emerges after a non-linear dielectric interaction between three laser beams and the molecules in the gas phase. Most of this interaction is understood in terms of the so-called rigid rotor approximation (RRA), which provides the basic framework useful to approach the coarse structure of Raman spectra. Under this hypothesis, the change of the molecular polarizability during the internal molecular motion is decoupled in such a way that molecular vibrations are treated independently from the rotations. But, if this assumption simplifies the spectral analysis to a great extent, one soon realizes that there is significant mismatch between the measured and theoretical frequencies (or wavenumbers) characterizing the Raman transitions of a given molecule. For this reason, it is necessary to introduce corrections to the RRA model [1]. For instance, one of the most popular deviations from the rigid rotor is due to centrifugal stretching that makes the rotating nuclei vary their relative distance and thus the expression of the rotational energies is purposely recast in a suitable form with the inclusion of centrifugal corrections.

The failure of the RRA model is not only limited to the spectral positioning of the

spectroscopic lines. Indeed, corrections are expected for the linestrengths (or line intensities) as well. It follows that the evaluation of such a problem becomes irrevocable if the aim of accurate spectral analysis is in prospect.

The failure of the RRA model in reference to the line intensity was first theorized by Herman and Wallis (HW) [2] and, based on this pioneering work, a revision of CARS spectroscopy has been launched recently [3-11]. We will avoid the details of the general problem that are, however, available in the specific literature, but it is important to emphasize that HW corrections to the CARS line intensities become relevant for molecular transitions between high rotational levels that are usually populated at those temperatures characterizing combustion science. The most important effect is, for instance, in hydrogen. Its thermometry at flame temperatures can be considerably inaccurate, whereas moderate effects are expected for other light molecules of medium weight.

CARS intensity and role of the HW factor

The effect of the vibration-rotation (VR) interaction on CARS linestrengths is mediated by the Raman cross-section, which contains the matrix elements of the rovibrational transitions $(v, J) \rightarrow (v', J')$ with v, J and v', J' the initial and final vibrational and rotational quantum numbers. Since we are mostly interested in vibrational CARS spectra, the strongest bands in the Q-branch (i.e., $\Delta v = v' - v = 1$ and $\Delta J = J' - J = 0$) are characterized by the differential cross-section that generates the anti-Stokes field

$$\left. \frac{\partial \sigma}{\partial \Omega} \right|_{\substack{v \rightarrow v+1 \\ J \rightarrow J}} = \frac{\hbar \omega_s^4}{2 \omega_e c^4 M} \left(a'^2 F_a(J) + \frac{4}{45} b_{J,J} \gamma'^2 F_\gamma(J) \right) (v+1) \quad (1)$$

where ω_s and ω_e are respectively the Stokes and vibrational wavenumbers, M is the reduced mass, a' and γ' are connected to the polarizability invariants (here, called a and γ) and, finally, $b_{J,J}$ is the Placzek-Teller coefficient known from various references. In Eqn. (1), the key elements of our problem are contained in $F_a(J)$ and $F_\gamma(J)$. These are termed HW factors for the isotropic and anisotropic components a and γ , but the typical assumption in CARS analysis discard any role of these factors as if they were taken with unitary value (i.e., $F_a(J) = F_\gamma(J) = 1$) corresponding to the RRA model usually adopted in CARS diagnostics. By contrast, the HW factors can be significantly greater than one for high rotational levels J . On this account, the CARS intensity I_{CARS} can undergo a correction and we could ask ourselves if its quantification can assume a relevant meaning for the analysis of spectral data. In order to answer the question it is fitting to recall that I_{CARS} rescales ideally with a power law, or $I_{\text{CARS}} \propto (\partial \sigma / \partial \Omega)^2$.

Furthermore, in vibrational CARS we have the main contribution from $F_a(J)$ and we can finally assume that $I_{CARS} \propto F_a^2(J)$.

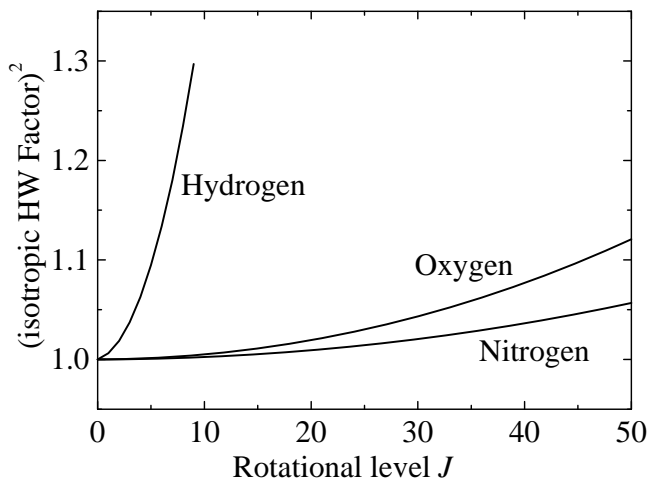


Figure 1. Plots of the square of the isotropic HW factor, or $F_a^2(J)$, for three homonuclear diatomics

The squared law $I_{CARS} \propto F_a^2(J)$ is used in Fig. 1 to compare the relative variation of the vibrational CARS intensity for hydrogen, nitrogen and oxygen. The unitary value on the vertical axis corresponds to the rigid rotor (i.e., $F_a(J) = 1$), whereas the HW factor used for the plots of the figure is taken from Tipping and Bouanich [12], who came up with an expression that proved to be reliable. The most evident comment on Fig. 1 is that hydrogen shows the largest variation. Being the lightest molecule, hydrogen is prone to the highest sensitivity to the inadequacy of the RRA model. Surely, the effect is attenuated in the case of nitrogen and oxygen, which are heavier than hydrogen and, for this reason, their nuclei possess larger inertia that moderates the influence of the fast rotations on the oscillations. Nevertheless, variations on the order of a few percent are predicted at high rotational levels with the peculiarity of oxygen doubling the deviation found for nitrogen. The reason of this higher sensitivity of oxygen despite its slightly greater molecular weight is composite and explained in terms of a larger VR coupling constant, stronger anharmonicity of the internuclear potential and a more prominent variation of the polarizability with the internuclear distance.

Effects of HW corrections on CARS diagnostics: vibrational CARS

Vibrational CARS is the traditional method to measure mostly high temperatures

of gas mixtures, even though applications to study mole fractions are known [1]. It is based on the excitation of vibrational transitions in simple molecules that are used as temperature markers. In particular, the typical CARS molecule is nitrogen, which is ubiquitous in combustion of fuels mixed with air. Unfortunately, its spectral response is rather complex and deserves special attention. The ideal CARS molecule is instead hydrogen, which has very well isolated spectroscopic lines and, as a consequence, their interpretation is surely simpler than in any other molecule. For the reasons mentioned above, both molecules have attracted the attention for their HW correction [3-7]. As an example, we show in Fig. 2, the expected variation of N_2 vibrational CARS intensities between the corrected and uncorrected spectra (i.e., RRA). In this case, deviations of about 1 % are observed and they result in thermometric corrections that equal the absolute accuracy associated with the technique [5, 6].

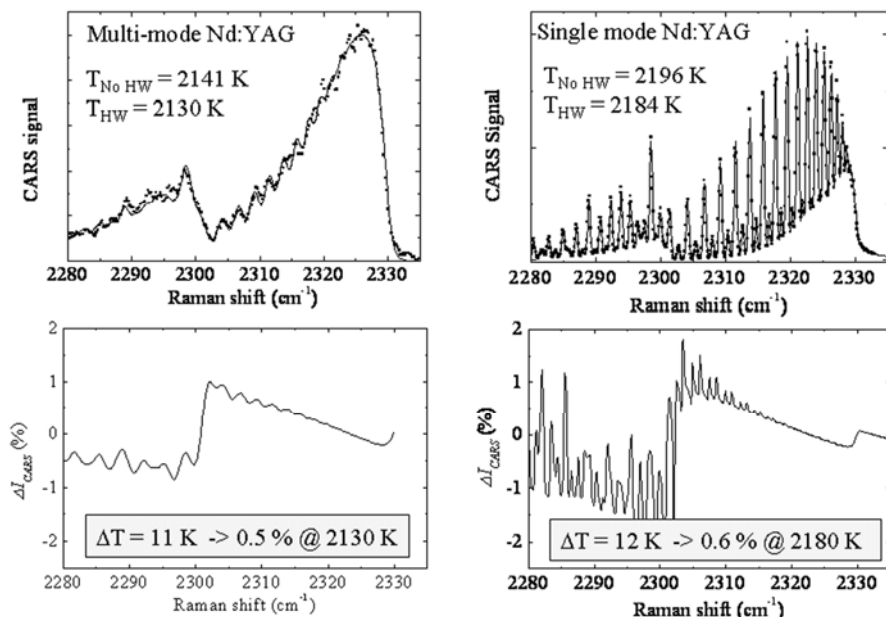


Figure 2. CARS Spectra of nitrogen at high temperatures (plots at the top). Below the spectra, the deviation between the corrected CARS intensities and the RRA result is shown (plots at the bottom).

Besides nitrogen, other molecules are interestingly sensitive to the HW factor. Indeed, the cases of hydrogen and oxygen have been studied and it turns out that these diatomics are subject to larger HW corrections [3-5, 8, 9]. In particular, the calculated thermometric changes are of basic relevance for accurate measurements and the results indicate that hydrogen CARS thermometry can reveal about 100 K mismatch from real flame temperatures [3, 4]. An analogous conclusion can be drawn for oxygen CARS, but this time the thermometric mismatch is smaller and

corresponding to about 20 K at flame temperatures [8, 9].

Another point of interest is suggested by the secondary CARS application to the measurements of mole fractions. Indeed, if the signal interpretation is prone to HW corrections, it means that the evaluation of the number density has to be modified accordingly. An example is given in Fig. 3 based on an experiment run at the George Washington University with a quasi-adiabatic flame (Hencken burner) [9].

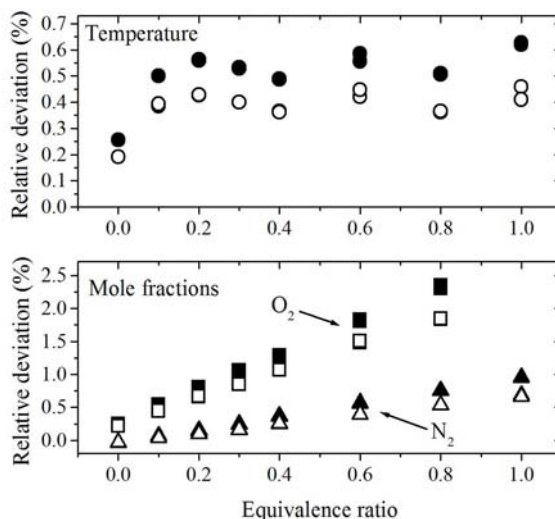


Figure 3. Deviation of temperature and mole fractions in dependence on the experimental conditions summarized by the equivalence ratio.

Effects of HW corrections on CARS diagnostics: rotational CARS

In addition to vibrational CARS, Raman transitions can be excited by selecting purely rotational states. These undergo HW corrections that are analogous to what seen for vibrational CARS and specific research has been realized lately for nitrogen and oxygen to clarify this point [7, 10]. As expected, the results indicate that HW effects show general features that were already established for vibrational CARS.

Effects of HW corrections on CARS diagnostics: femtosecond CARS

The most advanced research on CARS applications to combustion science is heading for the use of ultra-short laser pulses and, in particular, pulses with time duration on the order of 100 femtosecond (fs) are nowadays commercially available. The application is termed fs-CARS or time-resolved CARS and, recently, calculations to understand the role of HW corrections have been made [11]. Since the physical meaning of the non-linear optical phenomenon at the base of CARS does not change, it is demonstrated that the effects of the HW factor are replicated in the new context of time-resolved approaches.

Conclusions

The vibration-rotation interaction in the interpretation of CARS intensities of light molecules is investigated. Considering different CARS strategies (i.e., vibrational, rotational and time-resolved), the extraction of diagnostic information is revised in view of a more correct adherence to the physical reality of rotating and oscillating molecular nuclei and the results suggest corrections of about 5 % for hydrogen, 1 % for oxygen and less than 1 % for nitrogen.

References

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