A Graphical User Interface (GUI) for Flexible CARS Library Generation

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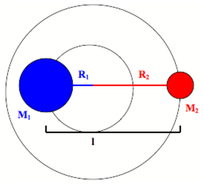
Abstract: Spectral library generation is a technique to produce libraries of theoretical spectra which are used to analyze experimental spectra gathered by femtosecond/picosecond Coherent anti-Stokes Raman scattering (fs/ps CARS). Chen et al. [1] built a model to generate the theoretical spectra based on theory outlined in [2]. However, the model wasn't user-friendly because it was dispersed among many files and changing modeling parameters was not intuitive. We consolidated the existing code into a single program with a graphical user interface (GUI). Here we present the experimental technique, the underlying theory, and the GUI.

Modeling Energy Levels of Diatomic Molecules

To get the vibrational energies of a diatomic molecule, we solve the Schrödinger equation with a harmonic oscillator potential. The allowed energies depend on the reduced mass μ, a force constant k, and the vibrational quantum number, υ.

$$E_\upsilon = \hbar\left(\frac{k}{\mu}\right)^{1/2}\left(\upsilon+\frac{1}{2}\right) \qquad \upsilon = 0,\ 1,\ 2,\ \ldots$$

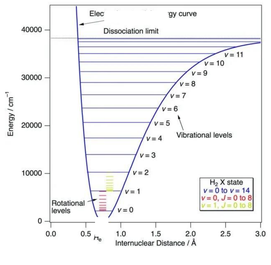


We used the rigid rotator model to calculate the rotational energy levels of the molecules. The rotational energies are quantized and inversely proportional to the molecule's moment of inertia.

$$E_J = \frac{\hbar^2}{2I}J(J+1) \quad J = 0,\ 1,\ 2,\ \ldots$$

As a molecule vibrates/rotates at a higher energy, the bond length stretches. The total rotational energy includes corrections for these effects that are known as vibrational-rotational interaction and centrifugal distortions.

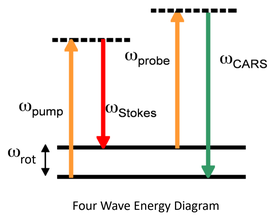
$$F(J) = \tilde{B}_\upsilon J(J+1) - \tilde{D}_\upsilon J^2(J+1)^2$$



Rotational energy levels exhibit closer spacing relative to vibrational energy levels. This highlights the fine structure that is encoded by a molecule's rotational levels which acts as its unique fingerprint.

Coherent anti-Stokes Raman Scattering (CARS)

CARS is a powerful diagnostic technique sensitive to a molecule's rotational and vibrational energy levels.



Four Wave Energy Diagram

Pump and Stokes photons excite a gas phase molecule to a higher energy state. The probe photon is then scattered inelastically. The scattered photon, called the CARS signal, has a frequency

$$\omega_{CARS} = \omega_{pump} - \omega_{Stokes} + \omega_{probe}.$$

The frequency of the CARS signal depends on the energy levels of the molecules in the sample. Therefore, from the spectrum created, we can extract information about the sample's temperature and the concentrations of molecular species in the sample.

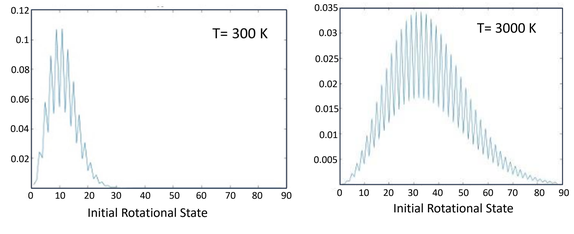
Applications of CARS include high-temperature thermometry of flames and combustion engines, where direct measurements aren't possible. CARS can also measure the molecular concentrations of combustion processes to help improve emissions.

Molecular Response Function

The Molecular Response Function is the key component in modeling of the CARS signal.

$$R_{\mathrm{CARS}}(t) = \sum_\upsilon\sum_J I_{\nu,J;\upsilon,J+2} \times \exp\left[\frac{t}{\hbar}\left(i\Delta E_{\upsilon,J;\upsilon,J+2} - \frac{1}{2}\Gamma^S_{\upsilon,J;\upsilon,J+2}\right)\right]$$

$I_{\nu,J;\nu,J+2}$ is the intensity of the response for a specific quantum transition. It's proportional to the difference in Boltzmann populations between the initial and final energy levels of the transition.



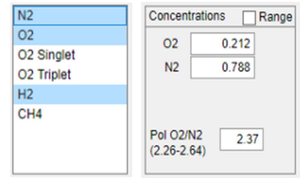
Boltzmann distributions for different temperatures of a sample. Higher energy rotational states are populated at higher temperatures.

$\Delta E_{\upsilon,J;\upsilon,J+2}$ is the difference in energies between the initial and final state which determines the frequency of the CARS signal.

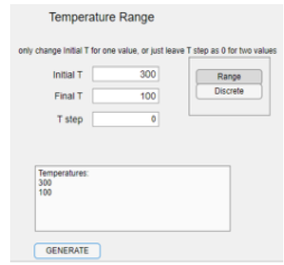
$\Gamma^S_{\upsilon,J;\upsilon,J+2}$ is the decay of the response function resulting from the energy transfer of molecules due to collisions. These collisions are prominent at pressures >1 atm.

Graphical User Interface (GUI)

We adapted the existing modeling code to consolidate it into a single program with a GUI as shown in the figures.



The user can easily define the sample as a mixture of multiple molecular species with their respective concentrations.



The spectra can be generated for different temperatures. The temperature can be defined as a range or as a discrete value.

	Value	Units
Pump Delay	0	s
Probe Delay	6.5000e-10	s
Pump Freq	3.7474e+14	s-1
chirp_pump	0	s-2
chirp Stokes	0	s-2
chirp Probe	0	s-2
INR	1	unit
GammaINR	100	unit
Guass Param	1	unit
Slit Function Width	1	cm-1
Wave Number Max	250	cm-1
Wave Number Min	0	cm-1

The parameters table allows users to easily change parameters for the spectral libraries they generate.

Discussion

Consolidating the existing code into one program increases organization and makes distribution easier. Additionally, the GUI presents users with an intuitive way to adjust experimental parameters. Future work can be done to include support for more molecular species and to test for accuracy.

References and Acknowledgments

1. Timothy Y. Chen, Christopher J. Kliewer; Numerical study of pure rotational fs/ps CARS coherence beating at high pressure and for multi-species rotation-vibration non-equilibrium thermometry. *J. Chem. Phys.* 28 October 2022; 157 (16): 164201

2. Hans U. Stauffer, Joseph D. Miller, Mikhail N. Slipchenko, Terrence R. Meyer, Benjamin D. Prince, Sukesh Roy, James R. Gord; Time- and frequency-dependent model of time-resolved coherent anti-Stokes Raman scattering (CARS) with a picosecond-duration probe pulse. *J. Chem. Phys.* 14 January 2014; 140 (2): 024316.

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