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High performance resonance Raman spectroscopy using volume Bragg gratings as tunable light filters

Thomson scattering using an atomic notch filter
Note: Rotational Raman scattering on CO$_2$ plasma using a volume Bragg grating as a notch filter

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We present a novel approach for filtering Rayleigh scattering and stray light from Raman scattering in a gas discharge, using a volume Bragg grating as a notch filter. For low frequency rotational Raman contributions, it is essential to filter out Rayleigh scattering and stray light at the laser wavelength to be able to measure an undisturbed Raman spectrum. Using the Bragg grating, having an optical density of 3.1 at the central wavelength of 532 nm and a full width at half maximum of 7 cm$^{-1}$, we were able to measure a nearly full rotational CO$_2$ spectrum (1.56 cm$^{-1}$ peak-to-peak separation). The rotational temperature in a CO$_2$ discharge was determined with an accuracy of 2%. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4918730]

The Raman spectrum of a molecule is specific to the molecule’s symmetry and chemical bonds. Therefore, Raman spectroscopy is typically used to examine molecular structures and to determine the composition of a sample. In addition, in gas and plasma physics the technique is used to measure rotational or vibrational temperatures and particle number densities.1–3 We use the rotational temperature as a measure for the translational and thus gas temperature in a dielectric-barrier discharge (DBD) in undiluted CO$_2$.3

In general, the intensity of the elastically scattered laser light (i.e., Rayleigh scattering) and stray light is several orders of magnitude higher than that of the inelastically scattered Raman light. This particularly causes a challenge when studying pure rotational spectra with frequencies as low as 10 cm$^{-1}$ (e.g., for N$_2$, O$_2$, and CO), or even 2.34 cm$^{-1}$ for CO$_2$.4,5 Hence, in order to prevent saturation of the camera and distortion of the Raman spectrum it is essential to use an ultra-narrow-band, steep notch filter to selectively filter out elastically scattered light.

Filtering is commonly done using triple-stage monochromators in which the laser light is rejected as close as 2–3 cm$^{-1}$ from the laser wavelength ($\lambda_l$, 532 nm in this study).6,7 Although the filtered spectral range of these systems is sufficiently small, they are relatively complex to align. Furthermore, when compared to single-stage monochromators, triple grating systems result in a significantly reduced transmission efficiency due to reflection losses and efficiencies of the additional gratings. A system of two 70% efficient gratings including additional optics has an efficiency of ca. 40%. An alternative, comprising higher efficiency, is a physical spectral mask which is positioned directly after a single grating. However, depending on the width of the mask and the grating’s spectral convolution, the filter width is limited to approximately 35 cm$^{-1}$ (≈1.0 nm) from $\lambda_l$.3,8,9 Such a blocked spectral range would cover the first 11 rotational CO$_2$ peaks.

To maintain both, a reasonable optical throughput and the ability to measure low frequency rotational modes, we use a single monochromator system, containing a Bragg-Grate™ notch filter. Similar filters are used by Tan et al. to be able to study low frequency modes of multilayer graphene in a confocal Raman system.9 The filter is a reflecting volume Bragg grating (VBG) and is specified to block light with an optical density (OD) of 3–4 with a full width at half maximum (FWHM) of 5–8 cm$^{-1}$ (≈0.14–0.23 nm).8 The transmission of the filter outside the blocking region is 80%.9 The reflected wavelength can be tuned by rotating the filter. Setting an angle of 6° between the filter normal and the direction of the incoming light results in the reflection of 532 nm light, which is the operating wavelength ($\lambda_l$) of the laser (frequency-doubled Nd:YAG, Spectra Physics, Quanta-Ray, GCR-4). The main drawback of the VBG filter is the small angular acceptance of less than 0.1°. Therefore, adequate collimation of the scattered light is a key concern for the Raman spectrometer.6,7

Fig. 1 shows the experimental setup that is used here to study Raman spectra of CO$_2$. The DBD reactor is designed as a parallel-plate configuration to facilitate optical access, particularly for laser scattering experiments. The quartz tube that guides the gas flow also serves as the dielectric barrier (1 mm width). The reactor has an electrode area of 70 mm × 16 mm. The gap width of 3 mm promotes considerable amounts of stray light from the laser beam.

Furthermore, Fig. 1 shows the implementation of the VBG in the detection arm of the spectrometer. First, the collected light is focused (focal distance $f = 50$ mm) on a pinhole to spatially filter out light not originating from the focal point of the laser. The pinhole can be considered as a point source, from which the light is collimated using a second lens ($f = 30$ mm). Hereafter, the VBG is positioned to rejected light at $\lambda_l$. The remaining light is

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The experimental setup, including the reactor (for clarity, rotated by 90° around the central axis) and the detection branch of the Raman spectrometer (not to scale).

focused \((f = 30 \text{ mm})\) into an optical fiber which is connected to the monochromator (Andor, Shamrock, SR-303i-A, incl. 2400 lines/mm holographic grating, Andor, SR3-GRT-2400-GH) after which the signal is detected by an intensified CCD camera (Andor, iStar, DH734-18U-03). The achromatic lenses are selected in order to use the maximum solid angle of detection allowed by the setup (26 msr, 0.18 mrad apex light cone), while matching the numerical aperture of the monochromator (\(NA = 1/8\)). Irises are used to decrease the amount of stray light from the reactor.

Since the divergence of the collimated beam is proportional to the width of the pinhole, a smaller pinhole results in a better collimation and therefore in a higher attenuation by the notch filter. However, a smaller pinhole will block more light and therefore the intensity of the measured Raman signal decreases. Hence, considering signal intensity, a larger pinhole is preferable. The angular behavior of the VBG was characterized using two pinholes of 20 \(\mu\text{m}\) and 100 \(\mu\text{m}\), respectively. For these measurements, the reactor in Fig. 1 is replaced by a diffuse reflector, creating a bright 532 nm light cone in the detection arm. Fig. 2(a) shows the resulting angular dependency on the transmittance of 532 nm light. The maximum attenuation is measured to be 0.99983 (OD 3.8) and 0.99926 (OD 3.1) for the 20 \(\mu\text{m}\) (triangles) and 100 \(\mu\text{m}\) (circles) pinhole, respectively. Both values agree with the specifications of OD 3–4 as given by the supplier. As expected, the smaller pinhole results in a stronger attenuation. Since Raman measurements showed that the attenuation of the 100 \(\mu\text{m}\) pinhole suffices for measuring rotational spectra of \(\text{CO}_2\) in the gas phase, this pinhole is used for the experiments described below. Furthermore, it can be seen that for both pinholes the attenuation rapidly decreases if the VBG is rotated more than 0.1° from its optimal angle of 6°. This agrees with the previously mentioned small angle of acceptance and again stresses the importance of adequate collimation.

The filter profile is characterized using the black-body radiation of a W-ribbon lamp. The lamp is positioned at the place of the reactor in Fig. 1, while using the 100 \(\mu\text{m}\) pinhole. The resulting transmittance profile is shown in Fig. 2(b) and is fitted using a Voigt profile, convolved with the spectral broadening by the monochromator (Gaussian, FWHM = 2.8 \(\text{cm}^{-1}\) ≈ 0.078 nm). The fit is displayed as a solid line and shows an apparent attenuation of 0.884 (OD 0.9). However, after deconvolution, the actual filter profile (dashed line) is obtained of which the attenuation is in agreement with Fig. 2(a). A FWHM of 7 \(\text{cm}^{-1}\) ≈ 0.20 nm is determined from the deconvolved profile, which agrees well with the specifications. Hence, at least the first two rotational peaks of \(\text{CO}_2\) (2.34 \(\text{cm}^{-1}\), 5.45 \(\text{cm}^{-1}\)) cannot be used in the analysis of the Raman spectra.

To benchmark the Raman setup, a measurement is carried out on pure \(\text{CO}_2\) at a pressure of 1000 millibars and an ambient temperature of 293 K. A Raman spectrum is obtained by averaging 4 images composed of 9000 laser shots each (18 mJ/pulse, 7 ns/pulse, 10 Hz). The spectrum is presented in Fig. 3. At \(\lambda_1\), only a small residue remains of the elastically scattered light, preserving nearly the full rotational spectrum of \(\text{CO}_2\). As expected, only the first two peaks are significantly influenced by the VBG filter and are therefore omitted from further treatment.

The spectrum is analyzed using Raman theory as described in Ref. 1. In short, when a photon of energy \(\tilde{\nu}_i = 1/\lambda_1\) induces a Raman transition of a state with quantum number \(J\)
Gas temperature versus the power dissipated in the plasma.

\[ \nu_{J \rightarrow J'} = \nu_0 - \begin{cases} +4B(J + \frac{3}{2}) & \text{Stokes (} J' = J + 2 \text{)} \\ -4B(J - \frac{1}{2}) & \text{anti-Stokes (} J' = J - 2 \text{)} \end{cases} \]  

Here, \( B \) is the rotational constant for the vibrational ground state (0.3899 cm\(^{-1}\) for \( \text{CO}_2 \)).\(^4\)\(^5\) When using a vertically polarized laser beam and measuring at an angle of 90°, the scattering power \( P_{J \rightarrow J'} \) for a transition \( J \rightarrow J' \) is given by\(^1\)\(^4\)

\[ P_{J \rightarrow J'} = C \frac{2Bhc n}{(2I + 1)k_B T_{rot}} b_J(2J + 1) \times \exp \left( -\frac{BhcJ(J + 1)}{k_B T_{rot}} \right) b_{J' \rightarrow J} \gamma^2 b_{J' \rightarrow J}, \]  

where \( h \) is Planck’s constant, \( c \) the speed of light, \( k_B \) the Boltzmann constant, \( b_{J \rightarrow J'} \) the Placzek-Teller coefficient,\(^1\)\(^4\) \( n \) the number density of \( \text{CO}_2 \), \( T_{rot} \) the rotational temperature, and \( C \) a scaling constant, containing, e.g., laser power and detection path length. Molecular specific parameters are the nuclear spin quantum number \( I \) (0 for \( \text{CO}_2 \)),\(^4\)\(^4\) the nuclear spin degeneracy \( g_J \) (\( \text{CO}_2 \): 1 and 0 for even and odd values of \( J \), respectively),\(^4\)\(^5\) and the polarizability anisotropy squared \( \gamma^2 \) (4.08 \( \times \) \( 10^{-22} \) \( \text{F}^2 \text{m}^4 \)) for \( \text{CO}_2 \) at 532 nm incident wavelength, interpolated from Ref. 4.

A least square algorithm is used for fitting the \( \text{CO}_2 \) Raman spectrum to the measured data, while adjusting the scaling constant and the rotational gas temperature as fitting parameters. Spectral broadening is added by convolution with a Gaussian profile of 2.8 cm\(^{-1}\) FWHM (similar to the profile used for deconvoluting the W-ribbon data). The calculated spectrum in Fig. 3 yields a rotational temperature of 297 K, close to the ambient temperature of 293 K. Similar measurements resulted in fits varying from 288 K to 299 K. From these measurements, the accuracy of the temperature is determined to be 2%.

As another example, the heating of \( \text{CO}_2 \) gas in the active plasma zone of the DBD is measured and compared to a heating theory proposed by Eliasson et al.\(^10\) A stationary temperature profile is assumed, while making a balance between the dissipated power \( P \) and the heat extraction by the reactor. Applying Fourier’s law of heat conduction results in an expression for the gas temperature,\(^3\)\(^10\)

\[ T_g = T_{wall} + \Delta T_g = T_{wall} + \frac{a_c d_{gap} P(1 - \eta_{diss})}{\kappa A}. \]  

Here, \( T_{wall} \) is the average temperature of the reactor wall, measured with an IR-camera (FLIR, A320). \( d_{gap} \) is the gap distance of 3 mm, \( A \) the area of the electrode of 1060 mm\(^2\), and \( \kappa \) the thermal conductivity in the range of 0.0167–0.0413 W m\(^{-1}\) K\(^{-1}\) for the relevant temperature range of 300–600 K.\(^11\) The cooling coefficient \( a_c \) is dependent on the geometry of the discharge. The fraction of energy \( \eta_{diss} \) that is used for chemical conversion of \( \text{CO}_2 \) is approximately 5% for the conditions under study.\(^12\)

For these measurements, the \( \text{CO}_2 \) flow is regulated between 0.180 and 1.56 slpm (standard liter per minute) using a mass flow controller (Bronkhorst, El-Flow F-201C), while the pressure is set between 200 and 1000 millibars with a controlled valve (Pfeiffer, EVR 116). Flow and pressure were kept constant during the measurements. A power supply (AFS, G108-500K) in combination with a transformer supplies a voltage of 22 kVpp at 62.1 kHz to the reactor electrodes, resulting in a power density in the discharge of 4.8–8.8 W cm\(^{-3}\). Details on the electrical characterization of the plasma excitation can be found in Ref. 12.

The gas temperature with respect to the dissipated power is shown in Fig. 4 (circles). The data are fitted using Eq. (3) (triangles), resulting in a cooling coefficient of \( a_c = 0.040 \) ± 0.005. The variations in pressure and gas flow (not included in the calculation) are apparently of reduced importance for the gas heating in the discharge.

Summarizing, we designed and benchmarked a Raman spectrometer for measuring low frequency transitions in molecular gases. A single volume Bragg grating is used for filtering out Rayleigh scattering and stray light, even under conditions where scattering objects such as reactor walls are in very close proximity. The spectrometer allows the detection of frequencies as low as 7 cm\(^{-1}\) (≈0.20 nm). We show that with this spectrometer, the rotational gas temperature of \( \text{CO}_2 \) can be measured in the active plasma zone of a DBD with an accuracy of 2%.