

Determination of the Local Temperature at a Sample during Raman Experiments Using Stokes and Anti-Stokes Raman Bands

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Sample heating due to high incident laser power in Raman experiments on (industrial) polymers and catalysts can easily lead to unwanted changes in morphology or desorption of surface species. Therefore temperature of the sample at the laser spot was studied by determining Stokes and anti-Stokes Raman intensities. Temperature can normally be determined within an accuracy of about 5 K, although for samples having nothing but Raman bands above 1000 cm^{-1} , the anti-Stokes lines are very weak and accuracy of temperature determination decreased drastically. For most of the samples studied in the macro-Raman setup, powers up to 250 mW could be used without measurable heating. In the micro-Raman setup heating started earlier due to higher focusing.

Index Headings: Stokes/anti-Stokes intensity ratio; Raman; Temperature determination.

INTRODUCTION

Raman signals are intrinsically weak, their intensities being in the order of 10^{-8} – 10^{-12} times the intensity of the exciting source. Therefore, the use of an intense monochromatic light source such as a laser is ideal. Often the intensity of Raman signals is still a problem, and one wants to increase the power density by focusing the laser beam. However, strong focusing to small (2500 μm^2 , macro-Raman) or very small (1–100 μm^2 , micro-Raman) areas, necessary to obtain a sufficiently strong Raman signal, can result in damage or modification of the sample due to local heating. With respect to industrial applications on polymers, local heating can cause changes in morphology of the sample long before burning, thereby destroying the practical use of Raman spectroscopy in this particular field. The same applies to adsorbed species in the field of catalysis.

It is well known^{1–3} that by measuring both Stokes (S) and anti-Stokes (AS) lines one can determine the local temperature from the ratio of their intensities. With the use of optical fibers this method can also be used for contactless determination of local temperature in a reactor or extruder. In this paper, the results of temperature measurements by Stokes and anti-Stokes lines for industrial samples such as polyethylene, polypropylene, polyvinylchloride, and melamine will be presented with the use of a micro- and macro-Raman setup. We are not aware of any published work describing the practical use of the Stokes/anti-Stokes temperature determination

with regard to the industrial application of Raman spectroscopy.

In Fig. 1 the Stokes and anti-Stokes parts of the Raman spectrum of CCl_4 are shown. The intensities of the Stokes and anti-Stokes lines depend on the population of the ground and excited state of the specific vibrations. These populations are dependent on the temperature of the sample. If thermal equilibrium exists, the relative occupation of the ground and excited states can be derived from the Boltzmann distribution, $I_S/I_{AS} \propto \exp[h\nu_1/kT]$, where $h\nu_1$ is the energy gap between the excited and the ground state, and T is absolute temperature. The frequency dependence of the inelastic Stokes and anti-Stokes Raman scattering processes can, according to Hayes and Loudon,³ be described by

$$I_S \propto \nu_0(\nu_0 - \nu_1)^3 \quad (1)$$

$$I_{AS} \propto \nu_0(\nu_0 + \nu_1)^3 \quad (2)$$

where ν_0 = frequency of exciting laser beam, and $\nu_0 \pm \nu_1$ = frequency of Raman Stokes (– sign) and anti-Stokes (+ sign) band.

A combination of the Boltzmann distribution Eqs. 1 and 2 results in the following ratio of the Stokes and anti-Stokes Raman intensities:

$$\text{P.L.} \quad I_S/I_{AS} = \frac{(\nu_0 - \nu_1)^3}{(\nu_0 + \nu_1)^3} \exp[h\nu_1/kT]. \quad (3)$$

The Boltzmann distribution only holds for $kT \gg h\nu_1$. In general, Bose-Einstein statistics should be used. However, the difference between Boltzmann and Bose-Einstein distribution vanishes in the ratio I_S/I_{AS} (Eq. 3).

By measuring I_S/I_{AS} , one can determine the local temperature using Eq. 3. In Table I the calculated Stokes/anti-Stokes intensity ratios for different Raman shifts and temperatures are shown for excitation with the 514-nm line of an Ar^+ laser. The influence of temperature on the Stokes/anti-Stokes ratio is most significant for large Raman shifts. However, for these large Raman shifts the Stokes/anti-Stokes ratio is difficult to determine accurately because of the low intensity of the anti-Stokes line. The best choice for accurate determination of temperature is bands with a Raman shift of about 500 cm^{-1} .

If we assume excitation with 514 nm, application of the (incorrect) simplified expression for the dependence of the Stokes and anti-Stokes intensities as a function of frequency,^{1,2} $I_S \propto (\nu_0 - \nu_1)^4$ and $I_{AS} \propto (\nu_0 + \nu_1)^4$, yields deviations in the calculated temperatures ranging from 5 K for $\nu_1 = 20 \text{ cm}^{-1}$ to 15 K for $\nu_1 = 2000 \text{ cm}^{-1}$.

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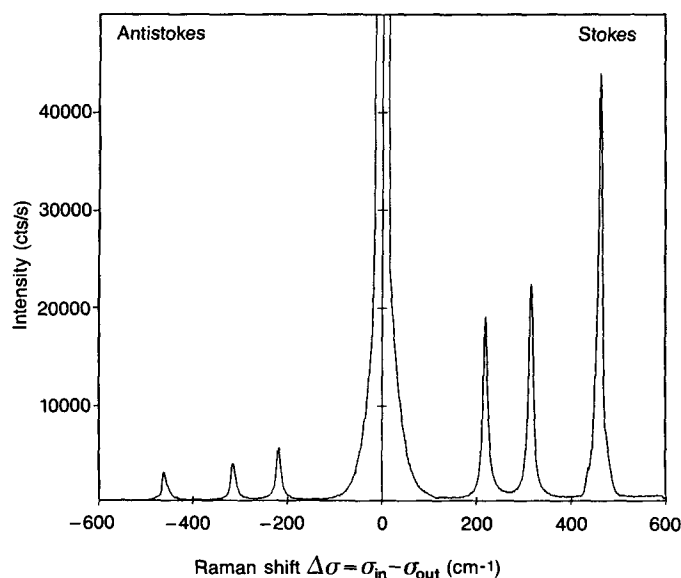


FIG. 1. The Stokes and anti-Stokes Raman spectrum of CCl_4 , taken at 295 K (514-nm Ar^+ line, 200 mW laser power).

EXPERIMENTAL

Samples. Cystine was obtained from Merck (p.a.); melamine, isotactic polypropylene, polyethylene foil, and polyvinylchloride were prepared at DSM Research.

Raman Spectrometer. Raman spectra were obtained with the use of a Ramanor HG2S spectrometer (Jobin Yvon) equipped with a cooled photomultiplier tube (Hamamatsu R943-02). An Ar^+ laser (Spectra-Physics, Model 2025) was used for excitation at 488, 496, 502, and 514 nm. Excitation at longer wavelengths was realized by means of a dye laser (Spectra-Physics, Model 375B) with the use of DCM (excitation at 650 nm) or Styryl 8 (excitation at 750 nm). An Anaspec 300-S laser filter was used to remove plasma lines present in the primary laser beam and interference lines in the beam originating from the dye laser. Samples placed in the macro-chamber were measured with the use of 90° scattering geometry and $f/2.2$ collection optics or were placed in the micro-Raman setup, which consisted of an Axioplan Zeiss microscope attached to the HG2S monochromator and specially adapted for Raman measurements.[†] In the Raman microscope a $20\times$ objective (Zeiss Epiplan Neofluar/0.50 Pol, $\infty/0$) was used. Before it entered the monochromator, the Raman light was depolarized by a quarter wave plate.

Power levels at the samples varied from 10 to 2000 mW. In the present paper, indicated power levels are all measured at the sample position, and intensities are based on peak maxima.

Heating of the Samples. First, the samples were heated by subsequently increasing the laser power at the sample. Second, as a check on the accuracy of temperature determination by Stokes and anti-Stokes Raman scattering

TABLE I. Stokes/anti-Stokes intensity ratios calculated according to Eq. 3 for different Raman shifts and temperatures, with the use of the 514-nm line of an Ar^+ laser.

Temperature (K)	Raman shift (cm^{-1})							
	20	50	100	300	500	1000	1500	2000
298	1.09	1.25	1.57	3.88	9.60	92.1	884	8475
323	1.09	1.23	1.51	3.47	7.96	63.4	504	4011
373	1.07	1.19	1.43	2.90	5.91	34.9	206	1214
473	1.06	1.15	1.31	2.27	3.93	15.4	60	237
573	1.05	1.12	1.25	1.94	3.01	9.1	27	82

intensities, samples contained in a capillary tube were placed in a Bruker ER4111 VT dewar system and subsequently warmed up by a flow of heated nitrogen gas while temperature was simultaneously monitored with a chromel-alumel thermocouple, which was placed downstream from the laser spot.

RESULTS AND DISCUSSION

I_S/I_{AS} at Room Temperature. With low power levels in the macro-setup (100–200 mW on the sample) the Stokes/anti-Stokes intensity ratio was determined for samples of polypropylene, polyethylene, melamine, and cystine. Experimental and calculated data are collected in Table II. The calculated ratios were derived from Eq. 3, with the assumption of no heating. Experiments were performed in a well-conditioned room, $T = 295 \pm 0.5$ K. For most of the data presented in Table II, the experimental Stokes/anti-Stokes intensity ratios are about twice the calculated ratios. This difference between experimental and calculated ratios cannot be understood by assuming heating, because in that case experimental ratios should be smaller than calculated ratios. The measured Stokes/anti-Stokes intensity ratio is dependent on the excitation wavelength, as can be seen in Table III. Comparing excitation at 650 and 488 nm, the experimental and calculated Stokes/anti-Stokes intensity ratios are equal within experimental error. For excitation at 750 nm, the experimental ratio is smaller than the calculated ratio. Between 650 and 488 nm, the experimental ratios are larger than the calculated ones. This discrepancy can be understood by taking into account the efficiency of the gratings of the spectrometer and the

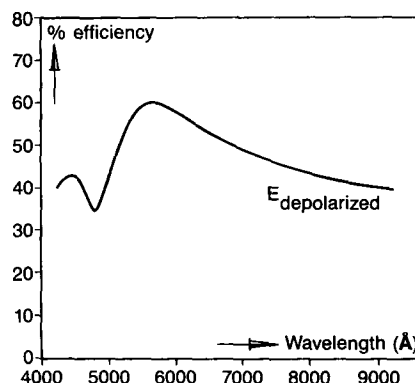


FIG. 2. Efficiency for depolarized light as a function of the wavelength for a Jobin Yvon concave holographic grating with 1600 gr/mm, optimized for 647 nm.

[†] A detailed description of the setup of our Raman spectrometer, the adaptation of the Zeiss microscope, and an improved macrochamber for accurate polarization measurements and improved collection optics will be submitted to the *Journal of Physics E: Scientific Instruments*.

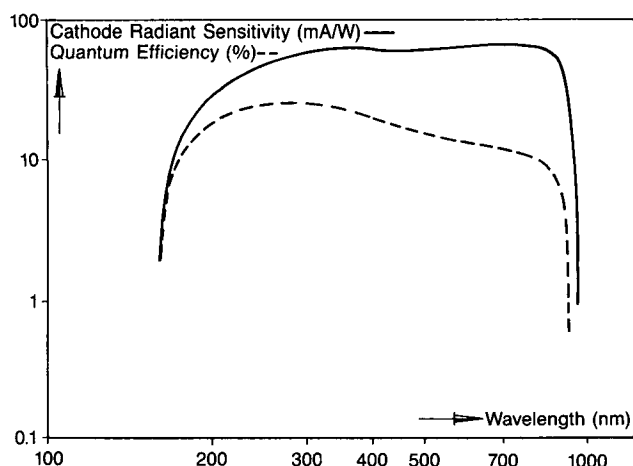


FIG. 3. Efficiency of the Hamamatsu R943-02 photomultiplier as a function of wavelength.

photomultiplier response as a function of wavelength. Around 500 nm, the efficiency of our gratings drastically changes (see Fig. 2). This effect must be squared because of the use of a double monochromator. If we take the 500 cm^{-1} cystine band, according to Fig. 2 the Stokes/anti-Stokes intensity ratio measured by excitation at 514 nm is too high, by a factor of $(58/45)^2 = 1.7$ times, resulting in a corrected experimental Stokes/anti-Stokes intensity ratio of 11, which is close to the calculated ratio of 10. As can be seen from Fig. 3, the change in the efficiency of the gratings around 488 nm is rather small and symmetric. Therefore, the measured and calculated ratios measured at 488 nm (see Table III) are quite close. The discrepancy for excitation at 750 nm can be understood by the decreasing efficiency of the gratings with increasing wavenumber around 750 nm and the quickly decreasing efficiency of the photomultiplier tube around 800 nm (see Fig. 4). The 500- cm^{-1} band of cystine is positioned at 780 nm if excitation at 750 nm is used. Finally, it must be stressed that the remaining discrepancies should not be interpreted as neglected warming-

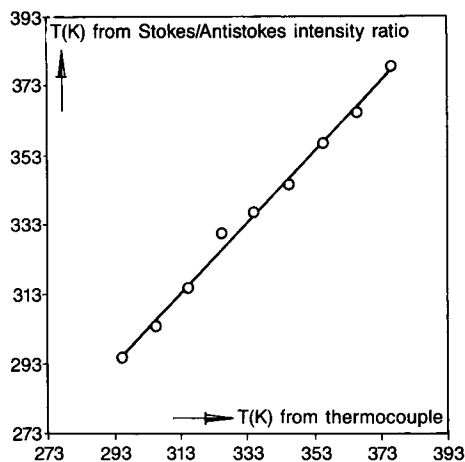


FIG. 4. Temperature determined with the use of the Stokes/anti-Stokes intensity ratio of the Raman 500- cm^{-1} band of cystine vs. temperature measured with a chromel-alumel thermocouple after the cystine sample positioned in a reactor has been heated with a stream of heated nitrogen. Raman measurement performed with 200 mW laser power on the sample, with the use of the 514-nm Ar^+ laser line and a resolution of 2 cm^{-1} .

TABLE II. Measured and calculated Stokes/anti-Stokes intensity ratios for several bands of polyethylene, isotactic polypropylene, melamine, and cystine. Excitation with the 514-nm Ar^+ line, 100–200 mW on sample.

Sample	Frequency (cm^{-1})	Stokes/anti-Stokes ratio measured	Stokes/anti-Stokes ratio calculated at 295 K
Polyethylene	1297	300	376
Polypropylene	400	11	6
	810	78	41
Melamine	380	10	6
	677	55	22
Cystine	500	19	10

up effects. Our knowledge of both the efficiencies of the gratings and the photomultiplier response as a function of frequency is too inaccurate to allow us to expect complete agreement. The best way to prove this is to start with very low laser power. Then, in first instance, increasing the laser power should not affect the I_S/I_{AS} ratio, i.e., the temperature.

Summarizing, the observed difference between the experimental and calculated Stokes/anti-Stokes Raman intensities results in the fact that experimental intensity ratios cannot be used directly to calculate the local temperature; they have to be corrected for differences in throughput of the spectrometer, including the detection system for different wavelengths unless they are used only for relative measurements.

Calibration of Stokes/Anti-Stokes Temperature Determination Using a Thermocouple. Heated nitrogen was made to flow along a tube with a cystine sample placed in the dewar system, and the temperature determined from the Stokes/anti-Stokes intensity ratio was compared with the temperature measured with a chromel-alumel thermocouple. In Fig. 4, the temperatures determined with the Stokes/anti-Stokes intensity ratio are compared with the temperatures measured with the thermocouple. It was assumed that the Stokes/anti-Stokes intensity ratio for the 500- cm^{-1} cystine band at 295 K was 19 (see Table II), implying that corrections for the efficiency of the gratings and for the response of the photomultiplier tube were systematically disregarded, which is justified for relative measurements. From the results in Fig. 4, it can be observed that the temperature determined with the Stokes/anti-Stokes intensity ratio is very close to the temperature in the dewar measured with the thermocouple. The difference between the temperature calculated from the Stokes/anti-Stokes intensity ratio and the temperature measured with the thermocouple is $+2.0 \pm 2.5$ K. One can understand that the temperature measured with the thermocouple is somewhat below the actual sample temperature because the thermocouple is placed downstream from the laser spot on the sample, which results in a lower temperature at

TABLE III. Stokes/anti-Stokes intensity ratios of a 500- cm^{-1} band for different excitation wavelengths.

Excitation wavelength (nm)	750	650	514	502	497	488
Measured Stokes/anti-Stokes	5	9	19	15	12	10
Calculated Stokes/anti-Stokes	9.2	9.4	9.8	9.9	9.9	9.9

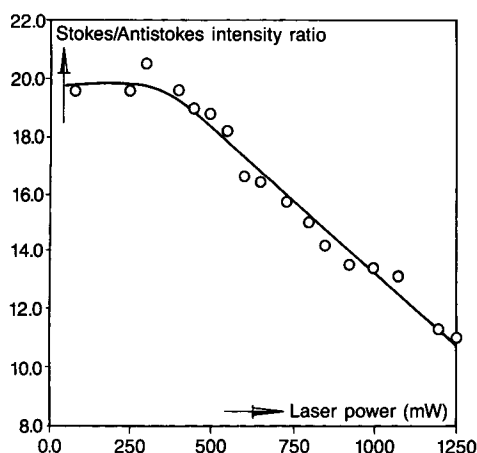


FIG. 5A. Measured Stokes/anti-Stokes intensity ratio of the 500-cm⁻¹ cystine band as a function of the laser power at the sample (514-nm Ar⁺ line, resolution 2 cm⁻¹).

the position of the thermocouple (see experimental section for description of setup).

From these measurements one can conclude that by using the Stokes/anti-Stokes intensity ratio one can determine temperature within 2 K.

Heating of Cystine by the Laser Beam. We studied the heating of a cystine sample by means of the Stokes/anti-Stokes intensity ratio for the 500-cm⁻¹ band of cystine. Results are shown in Fig. 5. It can be clearly seen that laser powers above 350 mW (at the sample) cause local heating of the cystine sample. Using a laser power at the sample of 1200 mW caused an increase of the local temperature of about 100 K. Further increase of the laser power caused burning of the sample. The sample showed inhomogeneity; the power at which burning started was not the same at all positions. At some places, burning has already started with a laser power of ~500 mW (also see section on micro-Raman spectroscopy).

Stokes/Anti-Stokes Intensity Ratio to Monitor Heating of Some Industrial Samples. For some polyethylene foils (about 30 μm thick) the Stokes/anti-Stokes intensity ratio of the 1060-cm⁻¹ Raman band was used to determine whether heating took place with the use of 500, 1000, 1500, and 2000 mW of laser power on the samples. The

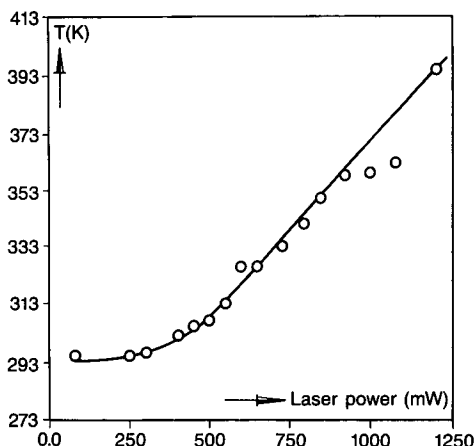


FIG. 5B. Temperature calculated from the Stokes/anti-Stokes intensity ratios, shown in Fig. 5A, assuming a Stokes/anti-Stokes intensity ratio of 19 for 295 K, as a function of the laser power at the sample.

TABLE IV. Stokes/anti-Stokes intensity ratios for the C-Cl stretching bands (600–700 cm⁻¹) of polyvinylchloride as a function of the used laser powers. Resolution 8 cm⁻¹, Ar 514 nm line. In this case Stokes/anti-Stokes intensity ratios are based on peak areas because of the rather broad signal and relatively high background. No corrections were made for grating and photomultiplier efficiency effects.

Laser powers (mW) on sample	I_S/I_{AS} ratio (based on peak areas)
33	44
45	42
70	47
105	46
120	44
140	44
160	40
180	44
210	47
240	Burned

measured Stokes/anti-Stokes intensity ratios were 265, 260, 270, and 220, respectively. This indicates that only above 1500 mW did some heating occur. For such thin films, most of the laser light just passes the sample, and high laser powers can be applied.

Heating of polyvinylchloride can induce thermal and photochemical degradation.^{4,5} In Table IV the Stokes/anti-Stokes intensity ratio for a PVC sample as a function of laser power is shown. Up to the power where the sample started to burn (240 mW) there were no indications from the Stokes/anti-Stokes intensity ratio that the sample was warming up. The power at which burning starts also differs for different positions on the sample. At some places, burning has already started at 20 mW; at other places, it does not occur before 250 mW power on the sample. These observations indicate that chromophoric impurities in the sample are the reason for burning. Once such an impurity in the sample is positioned in the laser beam, it absorbs much light and the sample starts to burn. With an increase in the laser power, the laser spot also increases in size, chromophoric impurities coming into the laser beam and causing burning of the sample.

Application of the Stokes/Anti-Stokes Temperature Determination in Micro-Raman Spectroscopy. Stokes/anti-Stokes intensity ratios were also used to study heating of a cystine sample with the micro-Raman setup using a 20× objective. The temperature of the cystine sample as a function of the laser power on the sample is shown

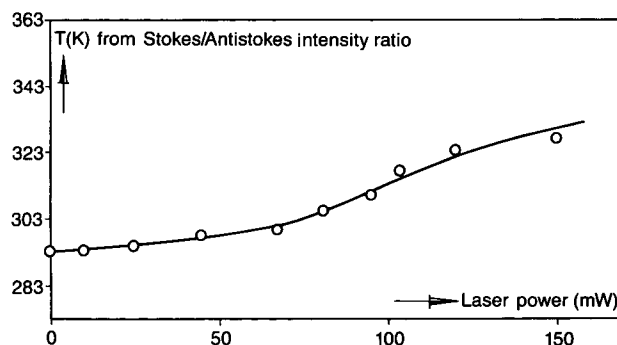


FIG. 6. Temperature at laser spot, calculated from Stokes/anti-Stokes intensity ratios, as a function of the laser power on a cystine sample. The spectra were measured with the use of the microscope with a 20× objective and 4 cm⁻¹ resolution.

in Fig. 6. Temperature starts to increase at a lower power level than in the macro-chamber experiment (compare Fig. 6 and Fig. 5b). Heating has already started at 20 mW and is more than 10 K for 50 mW, whereas for the Raman measurements in the macro-chamber the heating starts at about 350 mW. For the macro-chamber the diameter of the laser spot on the sample is about 50 μm ; with the use of the microscope with the 20 \times objective the laser spot is about 5 μm . Therefore, in the micro-Raman setup the power density at the same power level is 100 times larger than in the macro-chamber. However, serious heating only started at a power level about seven times lower than that for the case of the macro-chamber. At the maximum power available on the sample (150 mW; the power delivered by the laser in this case was 3500 mW) the sample did not burn. With a focus of the laser beam on another place, the sample has already started to burn at much lower power levels (80 mW) without any preceding sign of warming up. This response is probably due to impurities or small dust particles that are absorbing, heating, and subsequently burning without heating of the cystine itself.

Finally, studying polyethylene fibers, we were able to conclude from experimentally determined Stokes/anti-Stokes ratios that no heating occurred with the use of incident powers (focused onto 4 μm^2) up to 60 mW on the sample.

SUMMARY

The Stokes/anti-Stokes intensity ratios can be used to measure local heating of the sample due to the exciting laser beam. This is a useful tool in order to monitor unwanted local heating that induces modifications of the sample while the Raman signal is being recorded. This approach particularly applies to the case of micro-Raman spectroscopy, where the laser beam is highly focused on the sample. In a number of cases, however, we found that no observable heating took place before the sample suddenly began to burn.

ACKNOWLEDGMENT

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