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High-Temperature N_2-CARS-Thermometry

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Abstract. N_2-temperature measurements have been performed by coherent anti-stokes Raman scattering (CARS) up to more than 3200 K using a commercial heated graphite tube furnace. Surface radiation pyrometry served as the reference technique yielding good agreement between pyrometric and CARS-based temperature determination, resulting in an overall temperature uncertainty of ±80 K for a spectrum obtained at 1 bar and 3230 K.

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Spectroscopic temperature determination using Raman-active molecular rotational and vibrational transitions has gained increasing scientific attention for combustion studies. Several contributions in this feature issue document recent progress in this field, in particular applications of coherent anti-Stokes Raman scattering (CARS). It is the purpose of this communication to briefly discuss actual and potential limitations of this technique in the high-temperature regime exceeding 3000 K.

CARS-thermometry is based upon an experimental, usually computer-assisted evaluation of population differences of selected resonances of a rovibronic molecular manifold, such as the vibrational transitions in nitrogen (N_2). One may speculate that this procedure fails at elevated temperatures since the necessary population differences disappear. This is in fact the case for thermometry based upon pure rotational transitions [1, 2], but is, however, of no essential importance for vibrational transitions, such as the Q-branch thermometry of N_2. Next, molecular dissociation with increasing temperature may be considered as a potential problem. It is well known that at 5000 K only 2% of the molecules of hydrogen [3] remain thermally undissociated and hence are available for a spectroscopic technique employing molecular resonances. For the solution of thermometry tasks below 4000 K, both aspects related to the molecular nature of the gaseous species evaluated are less important. In this temperature range material stability, well-defined temperature conditions, and precise temperature calibration with other techniques are the major problems Tungsten-based devices can be used close to the melting point of this metal, 3683 K. In fact, an open centered single coil tungsten-filament was used in [4] to reach a N_2-temperature as high as 3467 K. Our studies have been performed with another source of high-temperature gases, a Massmann-type graphite tube furnace of an atomic-absorption spectrometer [5, 6]. This well-engineered, commercially available miniature oven can be conveniently operated for N_2-thermometry between 300 K and 3500 K, the decomposition temperature of graphite, using several programmable temperature routines. Serving as temperature references were both the temperature reading of the control unit of the resistively heated oven and independent temperature measurements of the inner surface of the graphite tube using an infrared pyrometer at a wavelength of approximately 900 nm. The small graphite oven, 28 mm long, with an internal diameter of 5.8 mm can be heated up within a few seconds, stays at a temperature of 3000 K for typically 10 s and can be cooled down to room temperature within 30 s, due to its water-cooled graphite contacts. The pyrometric measurements displayed excellent reproducibility for different operation cycles. The CARS sample volume was located at the longitudinal center of the tube near the wall, not far from the viewing area of the pyrometer. The CARS spectra were generated under stop-flow conditions in pure nitrogen at atmospheric pressure.

Figure 1 shows an example of an experimental high-temperature N_2 CARS-spectrum, displaying the first three vibrational bands. A 10 Hz repetition rate laser system (for details see [5, 6]) was used. Six measurement cycles each of 5 s duration were required in order to collect the 300 data points. The spectrum is normalized by dividing it by the Stokes-laser intensity distribution

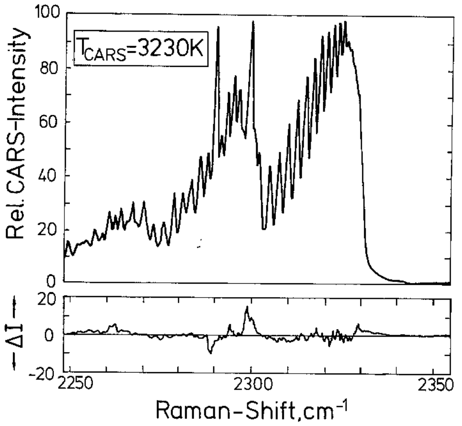

Fig. 1. Experimental N_2 CARS spectrum corrected for Stokes-laser intensity distribution. The lower panel indicates the difference $\Delta I = I_{ex} - I_{th}$ between experimental and theoretical spectra obtained by least-squares fitting and yielding a gas temperature of 3230 K

generated by a nonresonant interaction with argon replacing nitrogen within the graphite tube. The lower trace of Fig. 1 shows the difference

$$\Delta I = I_{ex} - I_{th}$$

between experimental spectrum and theoretical prediction. The least squares fit yields a CARS-temperature of 3230 K using all three bands. The pyrometer reading was 3160 K and the electrically preset oven temperature was 3200 K. Evaluating only the fundamental vibrational band, a CARS-temperature of 3250 K was obtained. This coincidence to within 20 K suggests the existence of thermal equilibrium between rotational and vibrational degrees of freedom. The CARS temperature evaluation code was developed at PCI Heidelberg. Collisional narrowing and cross-coherence are included as discussed in [7].

The intense luminosity and other incoherent and coherent emissions of the graphite furnace are a severe problem at temperatures above 3000 K. Accumulation of incoherent signal could be partially avoided by gating the diode-array detector for 500 ns. In particular, anti-Stokes fluorescence and electronically-enhanced wave mixing in the presence of the radical C_2 represent a major interference to N_2 CARS-thermometry using the 532 nm radiation of a frequency-doubled Nd:YAG laser [8]. Polarization techniques can reduce the incoherent contribution by a factor of two, but one may also use a three-color CARS process to shift the N_2 anti-Stokes spectrum around 473 nm into a region free of Swan bands [9].

Uncertainties in the pyrometric measurements, reproducibility in attaining the electronically preset apparatus temperature of 3200 K for the six successive runs leading to the spectrum of Fig. 1 and the remaining inaccuracies in the proper selection of the fit parameters of the theoretical spectrum add up to an overall precision of ±80 K for temperature measurements between 3000 and 3500 K. The good agreement of rotational and vibrational temperature to within 20 K is an indication of both thermal equilibrium and the absence of pump-induced population changes due to saturation phenomena [10].

The graphite tube furnace seems to offer considerable advantages as compared to other high-temperature sources. Its small volume combined with good line-of-sight optical access permits fast, efficient point-by-point gas temperature studies using convenient three-dimensional CARS-configurations permitting high spatial resolution. Its application is not restricted to N_2-thermometry only. As shown in [11] other gases of thermometric interest, such as hydrogen, can also be heated up to nearly 3500 K, and could also be buffered by another inert rare gas such as argon or neon. In principle, molecular nitrogen may serve as thermometer gas up to even higher temperatures: According to [12] even at 5000 K 96% of N_2 still remains undissociated and is hence available for Raman-type spectroscopic measurements.

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