

Peak temperatures from Raman Stokes/anti-Stokes ratios during laser heating by a Gaussian beam

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The rise in temperature induced by heating a surface with a cw Gaussian laser is analytically related to the Raman Stokes/anti-Stokes intensity ratio measured by the same laser to induce the heating, for an idealized, though often experimentally-relevant, set of conditions. For a range of conditions, the peak temperature rise is actually twice that determined from this ratio if one were to assume a spatially uniform temperature rise. This shows that care must be exercised in determining temperature from Stokes/anti-Stokes ratios. © 2011 American Institute of Physics.
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Temperatures of structures can be determined from the Raman frequency, Raman linewidth, and the ratio of the intensities of the Stokes and anti-Stokes signals (the S/AS ratio).¹⁻⁴ This is relatively straightforward when the laser probes a region with uniform temperature. The interpretation of the Raman signals becomes more complex when the temperature profile changes much over the region probed by the laser. This is particularly true when the same focused TEM₀₀ Gaussian mode laser is used to both heat an absorbing medium and to probe it.²⁻⁴ Such laser heating includes intentional heating, for example of a substrate or film,²⁻⁴ or non-intentional heating, as that of a powder with low thermal conductivity.⁵ The expected S/AS ratio can be obtained by integrating the expected Stokes and anti-Stokes intensities for a calculated temperature profile for the probing beam, which propagates into the medium. It is shown here that under idealized, but sometimes experimentally relevant conditions, the peak temperature rise caused by a focused laser beam used both to heat the surface and to probe it by Raman scattering is exactly twice that determined from the measured S/AS ratio assuming a uniform temperature rise.

A fixed, cw laser with intensity profile varying as $\exp(-2r^2/w^2)$ impinging on an absorbing semi-infinite medium induces a temperature rise ΔT on the surface that is nearly spatially Gaussian at the center and decays as $1/r$ for $r \gg w$.^{6,7} It is assumed here that on the surface

$$T(r) = T_0 + \Delta T_{pk} \exp(-2r^2/w^2), \quad (1)$$

(i.e., the term in $1/r$ is neglected), where T_0 is the ambient temperature and ΔT_{pk} is the peak temperature rise, which occurs at $r=0$. (Because of thermal transport, this is clearly not exactly correct, as is addressed below.)

The rate of Stokes scattering is $R_S = A_S[n(\omega) + 1]$ and that for anti-Stokes scattering is $R_{AS} = A_{AS}n(\omega)$, where $n(\omega)$ is the number of phonons at frequency ω and equal to $1/[\exp(\hbar\omega/kT) - 1]$. So,

$$R_S = A_S/[1 - \exp(-\hbar\omega/kT)], \quad (2)$$

$$R_{AS} = A_{AS}[\exp(\hbar\omega/kT) - 1]. \quad (3)$$

The S/AS ratio $R' = R_S/R_{AS} = A'[(n(\omega) + 1)/n(\omega)] = A' \exp(\hbar\omega/kT)$, where $A' = A_S/A_{AS}$. A_S and A_{AS} include optical parameters, such as the Raman susceptibility, which depend on wavelength and temperature. Off resonance, the ratio A' is independent of T and very nearly equal to the third power of the ratio of Stokes-to-anti-Stokes photon frequencies;¹ it will be assumed to be independent of T here. Nearer resonance, assuming that A' has no dependence on material optical properties can lead to serious errors in determining T .¹ Probing a uniform temperature rise of $\Delta T_{pk,uniform}$ gives the ratio

$$R' = A' \exp[\hbar\omega/k(T_0 + \Delta T_{pk,uniform})]. \quad (4)$$

The medium is assumed to be very strongly absorbing, so the laser scatters from the medium very near the surface. Integrating the scattering rate from Eqs. (2) and (3) times the light flux over the surface and using Eq. (1) for the temperature profile, the Stokes and anti-Stokes signals are

$$R_S = \int_0^\infty f \{ A_S / [1 - \exp\{-\hbar\omega/k[T_0 + \Delta T_{pk} \exp(-2r^2/w^2)]] \} \exp(-2r^2/w^2) r dr, \quad (5)$$

$$R_{AS} = \int_0^\infty f \{ A_{AS} [\exp\{\hbar\omega/k[T_0 + \Delta T_{pk} \exp(-2r^2/w^2)]\} - 1] \} \exp(-2r^2/w^2) r dr, \quad (6)$$

where the factor f includes collection and other parameters that are the same for both.

The ratio of R_S and R_{AS} from these two equations is

$$R' = A' \frac{\int_{u_1}^{u_2} du / [1 - \exp(-1/u)]}{\int_{u_1}^{u_2} du / [\exp(1/u) - 1]}, \quad (7a)$$

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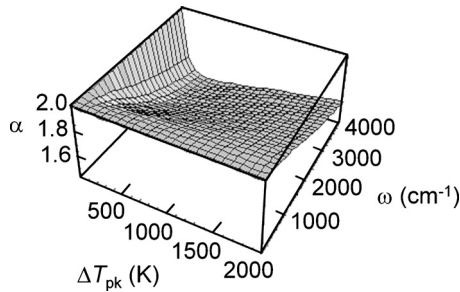


FIG. 1. The ratio $\alpha(=\Delta T_{pk}/\Delta T_{pk,uniform})$ vs the peak temperature increase ΔT_{pk} and phonon frequency ω .

$$=A' \left\{ 1 + (u_2 - u_1) / \int_{u_1}^{u_2} du / [\exp(1/u) - 1] \right\}, \quad (7b)$$

where $u = (k/\hbar\omega)[T_0 + \Delta T_{pk} \exp(-2r^2/w^2)]$, $u_1 = (k/\hbar\omega)T_0$, and $u_2 = (k/\hbar\omega)[T_0 + \Delta T_{pk}]$.

Call $u_1 = v - \delta$ and $u_2 = v + \delta$, where for now $v \gg \delta$ (small ΔT_{pk}). Then

$$R' = A' \exp(1/v) = A' \exp[2/(u_1 + u_2)], \quad (8)$$

$$= A' \exp[\hbar\omega/k(T_0 + \Delta T_{pk}/2)]. \quad (9)$$

Equating this with Eq. (4) gives

$$\Delta T_{pk} = 2 \Delta T_{pk,uniform}. \quad (10)$$

So, for these conditions the actual peak temperature rise is exactly twice that would be determined, $\Delta T_{pk,uniform}$, if the experimental S/AS ratio were analyzed assuming the intensity profile and temperature rise were spatially uniform.

Although Eq. (10) is valid only for small temperature rises for all phonon frequencies (as derived here) and for most temperature rises for lower phonon frequencies $\hbar\omega < \sim k(T_0 + \Delta T_{pk})$, $\Delta T_{pk,uniform}$ still severely underestimates ΔT_{pk} for other conditions (larger ω). Equating the numerically integrated Eq. (7) to $A' \exp[\hbar\omega/k(T_0 + \Delta T_{pk}/\alpha)]$ gives a range of $\alpha(=\Delta T_{pk}/\Delta T_{pk,uniform})$ from ~ 1.5 to 2.0 , for ω in the range $0-4000 \text{ cm}^{-1}$, as seen in Fig. 1. Note that for a given phonon frequency, α does not monotonically change with $T_0 + \Delta T_{pk}$, and attains a minimum value of α near a peak temperature change of 400 K . At the Si phonon frequency of 521 cm^{-1} (at room temperature), the variation in α is small,

$\sim 1.95-2.0$. As seen in Fig. 1, it may be better to use lower phonon frequencies to probe temperature because the variation of α with ΔT_{pk} is then small.

While Eq. (7) gives some significant insight, it is not exact due to the assumptions made. Neglecting the non-Gaussian $1/r$ decay for $r \gg w$ is likely not serious since few photons are incident there. Thermal conductivities that decrease (increase) with T , will narrow (broaden) the temperature profile, thereby increasing (decreasing) the difference between ΔT_{pk} and $\Delta T_{pk,uniform}$. Including beam propagation into the medium increases this difference. Changes in phonon frequency ω with T , do not affect this analysis much. More exact S/AS ratios (which will include all of these effects) can be obtained by using a finite-difference analysis of the temperature profile, coupled with laser beam propagation through the medium and Raman scattering. Even though the results of such calculations will depend on the details of the material system, the S/AS ratios obtained will largely agree with the analytic results presented here.

This analysis shows that care must be exercised in determining temperature from Stokes/anti-Stokes ratios during laser heating of semi-infinite substrates and of other media, such as multilayer film systems and systems with laterally defined microstructures.

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