On the accuracy of determination of gas rotational temperature from Raman spectra

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The role of vibrational-rotational interaction and centrifugal distortion in a molecule, as well as its polarizability anisotropy (for *Q* branch) in the accuracy of determination of the rotational temperature from Raman spectra is investigated. It is shown that neglect of these effects can give a noticeable systematic error in the temperature determination. Analytical equations are obtained for systematic errors of temperature determination in the case of using lines of the *O*, *S*, and *Q* branches for the vibrational bands $v \to v$, $v + 1$. The results obtained are illustrated with data on nitrogen and oxygen molecules as an example.

Introduction

Temperature is one of the important characteristics of a gas medium, and remote measurement of temperature is of interest for solution of a wide scope of basic and applied problems. Spectroscopic methods are usually used for this purpose. Many gas media, including the Earth's atmosphere, contain nitrogen and oxygen molecules, and therefore it is worth using just their spectra for determination of gas temperature. The zero dipole moment of these molecules makes gas temperature measurement by the methods of IR spectroscopy impossible, and this problem can be solved only using methods of Raman spectroscopy, among which the most widely used methods are of spontaneous Raman scattering (SRS) spectroscopy and coherent anti-Stokes Raman scattering (CARS). The SRS spectroscopy is largely used for diagnostics of vibrationally unexcited gas media,[1–4] while the CARS spectroscopy giving the far higher level of signal is also applied to temperature measurements in nonequilibrium luminous gas media, such as plasma and flame (see Refs. 5 and 6 and references therein).

In practice of determination of rotational temperature by the SRS and CARS methods simplified computational equations are used that ignore centrifugal distortion the interaction between vibrational and rotational levels of molecules. Besides, when the temperature is determined from *Q*-branch lines by the methods of CARS spectroscopy, polarizability anisotropy of molecules is ignored. The use of such simplified equations leads to a systematic error, which was found experimentally in Ref. 7. The aim of this work was to study this systematic error.

Systematic error in temperature determination

SRS technique. Because of low resolution of SRS spectrometers, determination of the gas rotational temperature T involves intensities of lines of only the *S*- and *O*-branches of the vibrational bands $v \to v$ (for single-component gases) and bands $v \to v + 1$ (for multicomponent gas mixtures).

The line intensity of the S ($J' = J + 2$) and O ($J' = J - 2$) branches in the SRS spectrum is determined by the equation[8]:

$$I_{vJ\to v'J'} = C\omega^4_{vJ\to v'J'} g_J b_{S,O}(J) F^{\gamma}_{vv'}(m)\times$$
$$\times\exp\left\{-\frac{hc}{kT}\left[B_v J(J+1) - D_v J^2 (J+1)^2\right]\right\}, \qquad (1)$$

where C is the constant independent of J; v and J are the vibrational and rotational quantum numbers; $\omega_{vJ\to v'J'}$ is the line frequency; g_J is the degeneracy factor due to nuclear spin; $b_S(J) = (J + 1)(J + 2)/(2J + 3)$ and $b_O(J) = J(J - 1)/(2J - 1)$ for the *S*- and *O*-branches, respectively; $F^{\gamma}_{vv'}(m)$ is the factor of vibrational-rotational interaction for the matrix element of the polarizability anisotropy,[9] in which $m = 2J + 3$ for the *S*-branch and $m = -2J + 1$ for the *O*-branch; B_v and D_v are the effective rotational constants. The simplified equation (1) is usually used when determining the rotational temperature from the SRS spectra, and it is supposed in it that $F^{\gamma}_{vv'}(m) = 1$ and $D_v = 0$. In such a case, the procedure of T determination is reduced to measurement of line intensities $I_{vJ\to v'J'}$ and solution,

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by the least squares method, of the system of linear (with respect to $J(J+1)$) equations of the form

$$\ln\left[\frac{I_{vJ\to v'J'}}{\omega^4_{vJ\to v'J'}\, g_J\, b_{S,O}(J)}\right] = A - \frac{hc}{k\tilde{T}} B_v J(J+1)\,, \qquad (2)$$

where A is a constant independent of J; $\tilde{T}$ is the resulting rotational temperature in this approximation. The use of simplified equation (2) leads to a systematic error in temperature determination $\Delta T = \tilde{T} - T$, whose value can be represented as

$$\Delta T \approx T R^{v}_{S,O}(J_{\max}) + T^2 S^{v,v'}_{S,O}(J_{\max})\,, \qquad (3)$$

where $R^{v}_{S,O}(J_{\max})$ is the contribution due to centrifugal extension of a molecule ($D_v \neq 0$) for the S- and O-branches, respectively; $S^{v,v'}_{S,O}(J_{\max})$ is the contribution due to vibrational-rotational interaction ($F^{\gamma}_{vv'}(m) \neq 1$); $J_{\max}$ is the maximum value of the quantum number J, which limits the number of lines taken into account when processing experimental data. The explicit form of the functions $R^{v}_{S,O}(J_{\max})$ and $S^{v,v'}_{S,O}(J_{\max})$ for the N_2 and O_2 molecules is given in the Appendix. In deriving these functions, it was assumed that all lines of the S-branch with $J = 0$–$J_{\max}$ and all lines of the O-branch with $J = 2$–$J_{\max}$ are involved in processing.

CARS technique. High spectral resolution and high level of the signal in CARS technique allows the determination of the rotational temperature of the vibrationally nonequilibrium media as well through the use of not only lines of the S- and O-branches of vibrational bands $v \to v$, $v + 1$, but also the lines of the Q-branch of the bands $v \to v + 1$. Since different approximations are used for determination of the rotational temperature from the lines of the S- and O-branches and the lines of the Q-branch, let us consider the systematic errors arising in the cases of S- (or O-) and Q-branches separately.

The intensity of lines of the S- and O-branches in the CARS spectrum is described by the equation[10]:

$$I_{vJ\to v'J'} \sim \omega^4_{vJ\to v'J'}\left[g_J b_{S,O}(J) F^{\gamma}_{vv'}(m)\right]^2 \times$$
$$\times \exp\left\{-\frac{2hc}{kT}\left[B_v J(J+1) - D_v J^2 (J+1)^2\right]\right\}. \qquad (4)$$

In determining the rotational temperature, Eq. (4) is simplified, as in the SRS technique, by assuming $F^{\gamma}_{vv'}(m) = 1$ and $D_v = 0$, and the system of equations for the temperature takes the form

$$\ln\left[\frac{I_{vJ\to v'J'}}{\omega^4_{vJ\to v'J'}\, g_J^2\, b^2_{S,O}(J)}\right] = A' - \frac{2hc}{k\tilde{T}} B_v J(J+1)\,. \qquad (5)$$

In this case, the systematic error ΔT is determined by Eq. (3) as well.

Unlike the S- and O-branches, the equation for line intensity in the Q-branch has a more complicated form[10]:

$$I_{vJ\to v'J} \sim \omega^4_{vJ\to v'J}\, g_J^2 (2J+1)^2 \times$$
$$\times \exp\left\{-\frac{2hc}{kT}\left[B_v J(J+1) - D_v J^2 (J+1)^2\right]\right\} \times$$
$$\times\left[\langle v|\alpha|v'\rangle^2 F^{\alpha}_{vv'}(m) + \frac{4}{45}\frac{J(J+1)}{(2J-1)(2J+3)}\langle v|\gamma|v'\rangle^2 F^{\gamma}_{vv'}(m)\right]^2, \qquad (6)$$

where $m = J(J+1)$; $\langle v|\alpha|v'\rangle$ and $\langle v|\gamma|v'\rangle$ are vibrational matrix elements of the mean polarizability α and the polarizability anisotropy γ (Ref. 9), and $F^{\alpha}_{vv'}(m)$ is the factor of vibrational-rotational interaction for the matrix element of the mean polarizability.[9] To find the rotational temperature, Eq. (6) is simplified by assuming $F^{\gamma}_{vv'}(m) = 1$ and $D_v = 0$ and neglecting the term involving $\langle v|\gamma|v'\rangle$. Then the system of equations for determination of the rotational temperature takes the form (5), in which J' is replaced for J and $b_{S,O}(J)$ is replaced for $(2J + 1)$. In this case, the systematic error can be represented as

$$\Delta T \approx T R^{v}_{Q}(J_{\max}) + T^2 S^{v,v'}_{Q} + T^2 P^{v,v'}_{Q}(J_{\max}), \qquad (7)$$

where $R^{v}_{Q}(J_{\max})$ and $S^{v,v'}_{Q}$ are, respectively, the contributions due to the centrifugal extension of the molecule and the vibrational-rotational interaction, and $P^{v,v'}_{Q}(J_{\max})$ determines the contribution due to neglect of the polarizability anisotropy. The explicit form of the functions $R^{v}_{Q}(J_{\max})$, $S^{v,v'}_{Q}$, and $P^{v,v'}_{Q}(J_{\max})$ for the N_2 and O_2 molecules at $v' = v + 1$ is given in Appendix.

Results and discussion

The systematic error ΔT was calculated by the following scheme. First, we calculated the line intensities $I_{vJ\to v'J'}$ by Eqs. (1), (4) and (6) at a preset rotational temperature T, and then the values obtained were used for determination of the temperature $\tilde{T}$ through solution of the systems of linear equations (2) and (5) by the least squares method. The systematic error in temperature determination was calculated as $\Delta T = \tilde{T} - T$. Calculations of the line intensities $I_{vJ\to v'J'}$ involved the values of the polarizability invariants, Dunham constants (a_i), and spectroscopic parameters of the N_2 and O_2 molecules from Ref. 9.

Analysis of thus obtained ΔT values has shown that they are well described by Eqs. (3) and (7). The error in ΔT calculated by these equations does not exceed 1% for the bands $v \to v$ and 10% for the bands

$v \to v + 1$. Also it should be noted that the systematic error for all branches weakly depends on v (see equations in Appendix), and therefore the figures show the function ΔT ($J_{\max}$) only for the case $v = 0$. The contribution due to centrifugal extension, vibrational-rotational interactions, and polarizability anisotropy (for the Q-branch) to the systematic error are different for the bands $0 \to 0$ and $0 \to 1$, and therefore they are considered separately for each band.

Figure 1 depicts the functions ΔT ($J_{\max}$) calculated from the intensity distribution of rotational lines in the S- and O-branches of the vibrational band $0 \to 0$ of nitrogen for different gas temperature. In this case, the contributions of centrifugal extension and vibrational-rotational interaction to ΔT have comparable values and the same sign (positive) and do not exceed few degrees in the given temperature range.

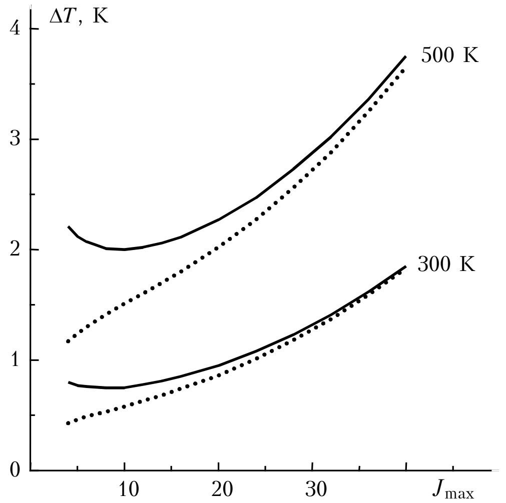

Fig. 1. Error in temperature determination from the lines of the S- and O-branches of the vibrational band 0–0 of SRS and CARS spectra of nitrogen: S-branch (solid curves) and O-branch (dashed curves).

The contribution due to centrifugal extension of a molecule increases following the square law with the increase of $J_{\max}$ and becomes significant only at large $J_{\max}$. The contribution due to the vibrational-rotational interaction is significant at all $J_{\max}$ values, and it is different for the S- and O-branches at small $J_{\max}$ and tends to a constant value as $J_{\max}$ grows. All these conclusions are valid for oxygen as well with the only difference, that the error for oxygen is roughly 1.5 times larger.

The systematic error ΔT for the vibrational band $0 \to 1$ is much larger (Fig. 2) than in the previous case and determined mostly by the contribution due to the vibrational-rotational interaction. A significant point in this case is that the contribution of the vibrational-rotational interaction for the S- and O-branches has opposite signs (see Appendix) and, as a consequence, ΔT also has opposite signs in the considered range of $J_{\max}$. Note that $\Delta T \approx -10$ K for the S-branch and $\Delta T \approx 10$ K for the O-branch that were measured experimentally[7] at $T \approx 300$ K for nitrogen ($J_{\max} = 14$) and oxygen ($J_{\max} = 23$) agree well with the calculated results (see Fig. 2).

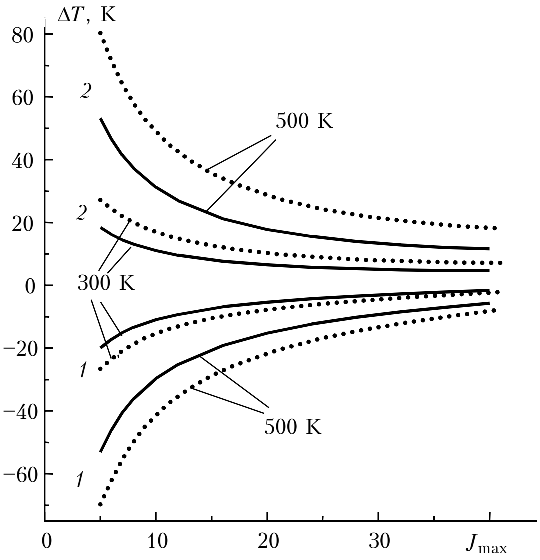

Fig. 2. Error in temperature determination from the lines of the S- and O-branches of the vibrational band 0–1 of the SRS and CARS spectra of nitrogen and oxygen: nitrogen (solid curves), oxygen (dashed curves); S-branch (*1*), O-branch (*2*).

The functions $\Delta T(J_{\max})$ calculated from the intensity distribution of lines in the Q-branch of the vibrational band $0 \to 1$ of nitrogen and oxygen for different temperature are depicted in Figs. 3 and 4.

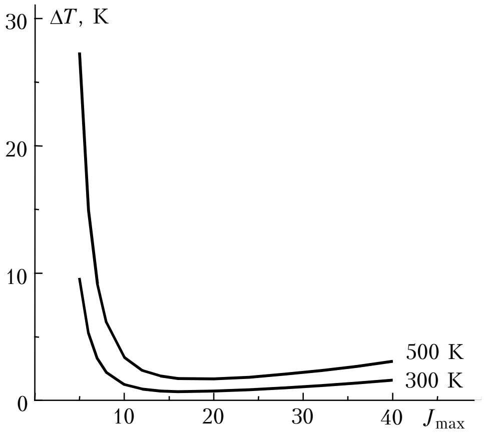

Fig. 3. Error in temperature determination from the lines of the Q-branch of the vibrational band 0–1 of nitrogen SRS and CARS spectra.

In this case, we can see the qualitatively different behavior of $\Delta T(J_{\max})$ for nitrogen and oxygen. Such a behavior of the function $\Delta T(J_{\max})$ is explained by the opposite sign of the term $P_Q^{v,v+1}(J_{\max})$, which gives the major contribution to ΔT at small $J_{\max}$. The contribution due to the vibrational-rotational interaction is small (1–2 K at $T = 500$ K) and independent of $J_{\max}$, while the contribution due to centrifugal extension of the molecule is significant only at high $J_{\max}$.

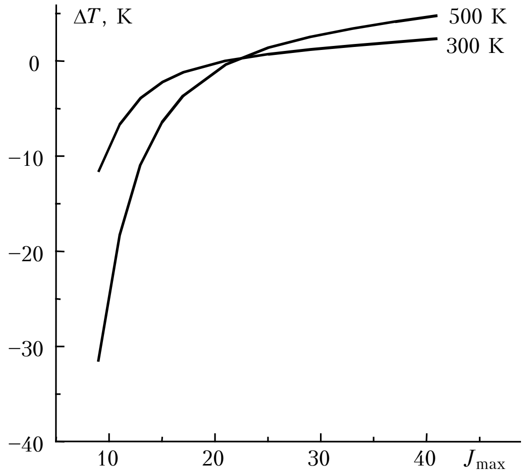

Fig. 4. Error in temperature determination from the lines of the Q-branch of the vibrational band 0–1 of oxygen SRS and CARS spectra.

Conclusion

Analysis of the results obtained has shown that the use of standard techniques for measurement of the rotational temperature can lead to marked systematic errors. Two methods can be proposed for determination of the rotational temperature without these errors. The first method consists in the use of complete equations for line intensities (1), (4), and (6), but in this case processing of experimental results becomes much more complicated. Another method is to use standard techniques for processing of experimental results and then take the systematic error into account using Eqs. (3) and (7). However, it should be kept in mind that the equations in Appendix were obtained for the particular case that processing involves all lines of a branch up to $J = J_{\max}$ inclusive. In other case, these equations should be derived anew.

Appendix

Functions $\boldsymbol{R^{v}}$, $\boldsymbol{S^{v,v'}}$, and $\boldsymbol{P^{v,v'}}$ for the N_2 molecule

$$R_S^{v}(n) \equiv R_Q^{v}(n) = \frac{2D_v}{7B_v}(3n^2 + 6n - 2),$$

$$R_O^{v}(n) = \frac{2D_v}{7B_v}\left(\frac{12n^4 + 99n^3 + 322n^2 + 523n + 393}{4n^2 + 22n + 33}\right);$$

$$S_S^{v,v}(n) = \frac{k}{hcB_v}\frac{\gamma'_e}{\gamma_e}\left(\frac{2B_e}{\omega_e}\right)^2\left[2 + 15\frac{(n+1)}{(2n+1)(2n+3)}\right],$$

$$S_O^{v,v}(n) = \frac{k}{hcB_v}\frac{\gamma'_e}{\gamma_e}\left(\frac{2B_e}{\omega_e}\right)^2\left[2 - 15\frac{(n+3)}{4n^2 + 22n + 33}\right],$$

$$S_S^{v,v+1}(n) = -\frac{30k}{hcB_v}\frac{\gamma_e}{\gamma'_e}\left(\frac{2B_e}{\omega_e}\right)\left[\frac{n+1}{(2n+1)(2n+3)}\right],$$

$$S_O^{v,v+1}(n) = \frac{30k}{hcB_v}\frac{\gamma_e}{\gamma'_e}\left(\frac{2B_e}{\omega_e}\right)\left[\frac{n+3}{4n^2 + 22n + 33}\right],$$

$$S_Q^{v,v+1} \cong \frac{2k}{hcB_v}\left(\frac{2B_e}{\omega_e}\right)^2\left[-\frac{3}{4}(1 + a_1) + \frac{\alpha''_e}{\alpha'_e}\right];$$

$$P_Q^{v,v+1}(n) \cong \frac{k}{hcB_v}\left(\frac{\gamma'_e}{\alpha'_e}\right)^2\frac{4}{(2n+1)^2(2n+3)^2}.$$

Functions $\boldsymbol{R^{v}}$, $\boldsymbol{S^{v,v'}}$, and $\boldsymbol{P^{v,v'}}$ for the O_2 molecule

$$R_S^{v}(n) \equiv R_Q^{v}(n) = \frac{D_v}{7B_v}\left(\frac{96n^4 + 678n^3 + 1247n^2 + 25n - 630}{16n^2 + 62n + 45}\right),$$

$$R_O^{v}(n) = \frac{D_v}{7B_v}\left(\frac{96n^4 + 1086n^3 + 4523n^2 + 8417n + 6300}{16n^2 + 118n + 225}\right);$$

$$S_S^{v,v}(n) = \frac{2k}{hcB_v}\frac{\gamma'_e}{\gamma_e}\left(\frac{2B_e}{\omega_e}\right)^2\left[1 + 30\frac{n+2}{16n^2 + 62n + 45}\right],$$

$$S_O^{v,v}(n) = \frac{2k}{hcB_v}\frac{\gamma'_e}{\gamma_e}\left(\frac{2B_e}{\omega_e}\right)^2\left[1 - 30\frac{n+4}{16n^2 + 118n + 225}\right],$$

$$S_S^{v,v+1}(n) = -\frac{120k}{hcB_v}\frac{\gamma_e}{\gamma'_e}\left(\frac{2B_e}{\omega_e}\right)\left[\frac{n+2}{16n^2 + 62n + 45}\right],$$

$$S_O^{v,v+1}(n) = \frac{120k}{hcB_v}\frac{\gamma_e}{\gamma'_e}\left(\frac{2B_e}{\omega_e}\right)\left[\frac{n+4}{16n^2 + 118n + 225}\right];$$

$$P_Q^{v,v+1}(n) \cong -\frac{k}{hcB_v}\left(\frac{\gamma'_e}{\alpha'_e}\right)^2\frac{4}{(16n^2 + 62n + 45)(2n+3)}.$$

Here $n \equiv J_{\max}$, B_e and ω_e are the rotational constant and harmonic frequency of molecular vibrations at the equilibrium internuclear separation R_e; $\gamma_e = \gamma(R_e)$, $\gamma'_e = R_e(\partial\gamma/\partial R)_{R_e}$; $\alpha'_e = R_e(\partial\alpha/\partial R)_{R_e}$, $\alpha''_e = R_e^2(\partial^2\alpha/\partial R^2)_{R_e}$. The functions $S_Q^{v,v+1}$ are identical for the N_2 and O_2 molecules.

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