Removal of trace CH_4 emissions by warm O_2 plasma is kinetically limited: Insights from modeling and experiments

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Supplementary Information

S.1 Rotational Raman Spectroscopy - Theory

We measure spontaneous Raman scattering spectra of N_2, O_2 and O, using a high-resolution grating of 1700 lines per mm. These spectra are fitted using Ramlab, an inhouse created method that calculates the expected rotational-vibrational Raman spectra, adapted from books from Long and Herzberg [1, 2].

Raman scattering only involves transitions between rotational and vibrational states, thus the energy is expressed as the sum of the rotational (E_r) and vibrational energy (E_v):

$$E = E_\mathrm{r}(v, J) + E_\mathrm{v}(v)$$

where v and J are the rotational and vibrational quantum numbers. Here, the rotational energy term for diatomic molecules is expressed as follows:

$$E_\mathrm{r}(v, J) = B_v J(J+1) - D1_v J^2(J+1)^2 + D2_v J^3(J+1)^3$$

where the rotational (B_v) and centrifugal distortion ($D1_v$ and $D2_v$) constants are a function of the vibrational quantum number. The vibrational energy term for diatomic molecules is expressed as followed:

$$E_\mathrm{v}(v) = \left(v + \frac{1}{2}\right)\omega_e - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e \gamma_e \left(v + \frac{1}{2}\right)^3$$

where ω_e is the harmonic vibration constant and $\omega_e x_e$ and $+\, w_\omega \gamma_e$ are vibrational anharmonicity constants. The calculation of the connected spectral line intensities is given by:

$$I \propto \tilde{\nu}_s^4 N_i \Phi(a^2, \gamma^2, \theta)$$

where $\tilde{\nu}_s$ is the wavenumber of the scattered radiation, N_i is the population density of the molecule for a given rotational-vibrational state and $\Phi(a^2, \gamma^2, \theta)$ depends on the polarizability tensors and orientation of incident and scattered radiation. The polarizability tensors, in their turn, depend on the Herman-Wallis factors ($F_a(J)$ and $F_\gamma(J)$) and the Placzek-Teller coefficients ($b_{J',J}$). The Herman-Wallis factors are calculated using the method given by Buldakov *et al.* [3], while the Placzek-Teller coefficients are given by Gaufres and Sportouch [4]**.** The state-specific population density is expressed by:

$$N_i = N_{tot}\frac{g_\mathrm{v}}{Q_v}\frac{g_n g_r}{Q_r}\exp\left[-\frac{hc}{k_B}\left(\frac{\tilde{E}_v}{T_v}+\frac{\tilde{E}_r}{T_r}\right)\right]$$

where N_{tot} is the species gas density, Q_v and Q_r are the vibrational and rotational partition functions, g_v, g_r and g_n are the vibrational, rotational and nuclear spin degeneracy, h is the Planck constant, c is the speed of light, $k_B$is the Boltzmann constant, $\tilde{E}_v$ and $\tilde{E}_r$ are the lower state vibrational and rotational energies (in m^{-1}) and T_v and T_r are the vibrational and rotational temperatures.

The position of the spectral lines is determined by the energy difference between lower and upper rotational-vibrational states:

$$\Delta E = E'^{(v,J)} - E''^{(v,J)}$$

S.2 Rotational Raman Spectroscopy – Fitting

In the fitting process, the theoretically expected Raman lines are calculated with the energy difference of the transition [5]. Following the method by Buldakov *et al.*, the intensity of the Raman lines is calculated by first calculating the absolute cross section of O, O_2 and N_2. However, due to the limited resolution of the spectrometer, spectral lines have a finite linewidth, which is chosen to be represented by Voigt functions. Using Rayleigh scattering, the Voigt line shape is determined to have a Gaussian width of 0.9432 cm^{-1} (w_g) and a Lorentzian width of 1.0310 cm^{-1} (w_l). It is also determined that the Gaussian follows the Doppler broadening temperature dependence, given by:

$$w_g = \sqrt{{w_{g,0}}^2 + \left(\frac{4\lambda}{c}\sqrt{\frac{2k_BT}{m}\ln 2}\right)^2}$$

For the O atom, two atomic transitions of value are found, one at 158 cm^{-1} (J=2→1) and one at 226 cm^{-1} (J=0→2) [6], which can be represented by two Voigt line shapes, whose absolute cross sections have a ratio of approximately 2.5:1 [7].

Further necessary constants can be found in Table 1.

Table 1: Spectroscopic data used for fitting the Raman spectrum of N_2, O_2 and O *[8, 9, 7]*.

Molecule	N_2	O_2	$O_{J=2\rightarrow1}$
Absolute Cross Section (Rot) (cm^2/sr)	1.64×10^{-29}	-	5.27×10^{-31}
Relative Cross Section to N_2 (Rot)	-	2.61	-

w_e (cm^{-1})	2358.62	1580.19	-
$w_e x_e$ (cm^{-1})	14.3444	11.98	-
$w_e y_e$ (10^{-2} cm^{-1})	-0.226	4.74	-
B_0 (cm^{-1})	1.99829	1.4376	-
B_e (10^{-2} cm^{-1})	1.74130	1.59	-
$D1_0$ (10^{-6} cm^{-1})	5.49723	4.839	-
$D1_e$ (10^{-8} cm^{-1})	-7.67491	-1	-
$D2_0$ (10^{-10} cm^{-1})	-3.02983	-1	-
$D2_e$ (10^{-11} cm^{-1})	-9.16227	-1	-
g_n (Odd J)	3	1	-
g_n (Even J)	6	0	-

In this procedure, the theoretical Raman spectra are calculated using absolute cross sections. However, because the spectrometer needs different exposure times during different measurements (to obtain a good signal, even at higher temperatures), calibrating for intensity is not easily done. Instead, the experimental data and the theoretical Raman spectra are normalized by dividing both spectra by their respective maxima. By doing this, we lose information about absolute concentrations, but we are still capable of measuring relative concentrations, as they depend on the final shape. This is done using the python module *lmfit*, which systematically changes the temperature, O atom, O_2 and N_2 molecule concentrations till a correct fit has been found. The complete fitting procedure has been stored online [10].

An example of an experimental spontaneous Raman spectrum is shown in Figure S1. Plotted in the same figure are the created fit, as well as the residual, which is defined as the measured signal minus the fit. The fit below was taken for atmospheric pressure, an O_2 flow rate of 20 SLM, no downstream injected synthetic barn air and a power of 700 W. In this case, all scattering is thus delivered by O atoms and O_2 molecules.

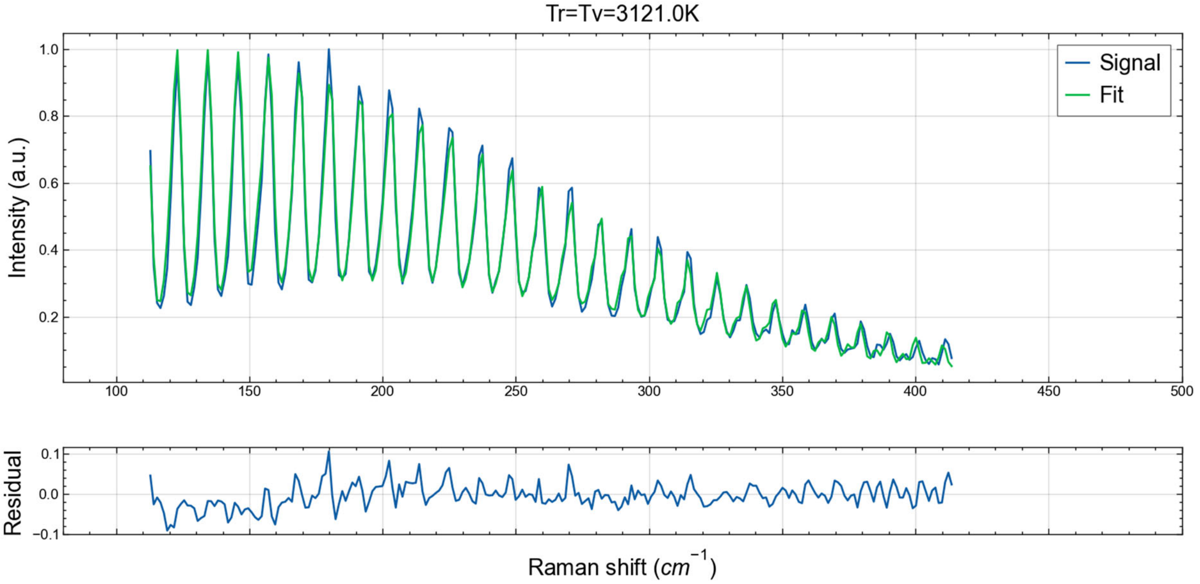

Figure S1. An example of an experimental spontaneous Raman spectrum, including the created fit. Also plotted is the residual, which is defined as the measured signal minus the created fit.

S.3 Rotational Raman Spectroscopy – Uncertainty

In the main paper, no error bars or uncertainties are given for the O atom fraction. The uncertainty on this parameter given by the fitting procedure (lmfit) is within 0.1 - 1% of the measured value. However, we believe this is unrealistically low, as the O atom fraction depends on the fitted temperature, which changes the overlapping O_2 molecule peak. More insight is obtained by plotting the fitted O atom fractions together with the expected values based on the temperature and thermal chemical equilibrium. Most values fall within 10% of the expectation, so we believe this is a more realistic estimate of the uncertainty. It's also noteworthy to mention that the O atom fraction uncertainty becomes smaller for higher temperatures, as the O atom peaks become larger with respect to the O_2 molecule signal.

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