Temperature and vibrational distribution function in high-pressure diatomic gas mixture

Guofeng Lou1, Walter R Lempert2, Igor V Adamovich2 and William J Rich2

1 Department of Mechanical Engineering, University of Science and Technology of Beijing, Handian district, Beijing 100080, People’s Republic of China
2 Department of Mechanical Engineering, The Ohio State University, Columbus, OH 43210, USA
E-mail: lgf@me.ustb.edu.cn

Received 28 August 2008, in final form 10 December 2008
Published 20 February 2009
Online at stacks.iop.org/JPhysD/42/055508

Abstract
Temperatures and vibrational populations are investigated experimentally and numerically in a CO–N2–O2 gas mixture. By spatially resolved Raman Q-branch spectra measurement, the strong vibrational excitation was observed in the gas mixtures at a high gas pressure. Numerical calculation, which incorporates both major processes of molecular energy transfer and diffusion of vibrationally excited species across the spatially nonuniform excitation region, provides indepth perception of vibrational kinetics of these diatomic molecular gas mixtures and is verified by the experimental data. The results demonstrate that strong vibrational nonequilibrium for all diatomic species can be sustained by the optical pumping method with a focused CO laser in a relatively cold (300–400 K) molecular gas mixture up to one atmospheric pressure. However, the results also demand further investigations on determining accurate rates of the V–V exchange gas mixture such as for N2–O2.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The nonequilibrium phenomenon is common in nature. An understanding of the kinetic processes in this phenomenon is of great interest in many modern physics, chemistry and engineering research areas, such as gas discharge plasmas, molecular lasers, pollution control, upper atmosphere chemistry and gas dynamic flows [1, 2]. Vibrational kinetics that investigate the relaxation processes of molecular vibrational levels and their influence on the properties of molecular gas are a fundamental part of physical–chemical kinetics for the study of nonequilibrium molecular gases [3]. It is well known that the great difference in the rates among molecular energy modes (vibration, rotation and translation) and gaseous species for the relaxation to equilibrium allows the possibility of large energy storage in a molecular vibrational mode [4] or say strong vibrational nonequilibrium. Methods of sustaining strong vibrational nonequilibrium in gases include (i) rapid expansion in a supersonic nozzle, (ii) excitation of molecular vibrations in electric discharges and (iii) optical pumping by laser radiation absorption. The use of the first approach is difficult due to the short available test time, while the second approach is limited to fairly low pressures ($P \sim 1$ atm) and low energy loading per molecule because of rapid development of discharge instabilities [5, 6]. In contrast to this, steady state optically pumped plasmas can be sustained at high pressures (up to 20 atm in CO–Ar mixtures) [7]. The main problem with optical pumping, however, is that the use of efficient resonance absorption provides access only to a very few heteropolar molecules (such as CO and NO with a CO laser or CO with a frequency doubled CO2 laser [8–13]). On the other hand, the use of nonlinear absorption techniques, such as PUMP–DUMP [14], RELIEF [15] and spontaneous Raman absorption [16], allows only pulsed mode operation and makes energy addition to vibrational modes of homopolar molecules, such as N2 and O2, extremely inefficient. These obstacles prevent development of new promising applications of vibrationally
nonequilibrium environments, including sustaining stable large-volume ionization in high-pressure air and energy efficient high-yield mode-selective chemical synthesis.

In the research carried out at the Nonequilibrium Thermodynamics Laboratory at the Ohio State University, the optical pumping method with an efficient CO laser is used for vibrational kinetics investigation. The process referred to as ‘optical pumping’ consists of two distinct steps. Step one is the direct laser excitation of a suitable target species to a low vibrational level. In the CO mixture, the CO molecule is the target, which is directly excited to vibrational levels \( v < 10 \) by resonance absorption of laser radiation. The second step is the anharmonic collisional vibration-to-vibration (V–V) up-pumping process. The energy distribution is primarily controlled by V–V energy exchange processes [17]:

\[
\text{AB}(v) + \text{CD}(w) \rightarrow \text{AB}(v-1) + \text{CD}(w+1),
\]

which in a broad range of parameters are known to be much faster than vibration-to-translation (V–T) relaxation, which will limit the degree of vibrational excitation because of rates of V–T relaxation increase with the vibrational level (in some cases, coupling with the vibrational-to-electronic (V–E) relaxation):

\[
\text{AB}(v) + \text{CD} \rightarrow \text{AB}(v-1) + \text{CD}.
\]

In equations (1) and (2), AB and CD stand for diatomic molecules and \( v \) and \( w \) are vibrational quantum numbers. Near-resonance V–V exchange processes, such as \( E_v(\text{AB}) - E_{v-1}(\text{AB}) \cong E_{v+1}(\text{CD}) - E_w(\text{CD}) \) in equation (1), are of particular importance, since they can sequentially populate very high vibrational levels of the molecules (here, \( E_v \) and \( E_w \) stand for energy of \( v \)th or \( w \)th molecular vibrational levels) [17] and thereby precipitate nonequilibrium chemical reactions, electronic excitation with subsequent visible and UV radiation and ionization \( (v \sim 30) \), which may have many applications.

This paper presents our recent experiment and numerical calculation results on the vibrational excitation of high-pressure gas added air species, such as nitrogen and oxygen. In the gas mixture the vibrational energy is transferred from optically pumped infrared active molecules (CO) to \( \text{N}_2 \) and \( \text{O}_2 \) by the collision-dominated process of equation (1). It allows one to produce a strong vibrational excitation of \( \text{N}_2 \) and \( \text{O}_2 \). Using this method combining the advantage of an efficient gas laser may realize the vibrational excitation of various species at high pressures and low power budget large-volume air plasma.

2. Experiment

A schematic diagram of the optical cell and Raman instrumentation is illustrated in figure 1. Optically pumped gas mixtures are formed by focusing a continuous wave (cw) CO laser into a flowing Pyrex glass cylindrical cell of approximate dimensions 0.60 m long \( \times \) 0.050 m diameter. The total laser output power employed in these studies is approximately 10 W.

Raman spectral diagnostics were performed by combining the CO laser and the Nd : YAG/ArF probe lasers with a 45° CaF\(_2\) dichroic mirror. Q-branch Raman spectra were obtained using the Nd : YAG laser in combination with an optical multichannel analyzer (OMA) detector. The experimental instruments are described in detail in [18, 19].

Spontaneous Raman spectroscopy allows access to vibrational levels of homopolar molecules and thereby provides powerful diagnostics of a nonequilibrium gas mixture with nitrogen and oxygen. Vibrational level populations were inferred directly from the integrated intensity of each unresolved Q-branch band profile. For all the experimental data presented in this paper, we assume that the Stokes scattering cross sections scale as \( v + 1 \), which is rigorously true only for a harmonic potential. Uncertainty of the relative intensity in the experimental is estimated to be 10–20%. Uncertainty in the ratio of vibrational populations of levels \( v = 0 \) and \( v = 1 \), which is used to define effective vibrational temperatures of the species, is estimated to be 5% for \( \text{N}_2 \) and 7% for \( \text{CO} \) and \( \text{O}_2 \) [18]. The effective vibrational temperature of the species \( T_v \) used in this paper is defined from the ratio of vibrational populations of levels \( v = 0 \) and \( v = 1 \) and is given by the following formula:

\[
T_v = \frac{\theta_1}{\ln[n_0/n_1]},
\]

where \( \theta_1 \) is the energy of the first vibrational level and \( n_0, n_1 \) are relative populations of the vibrational levels \( v = 0 \) and \( v = 1 \).

3. Kinetic model and the V–V rate parametrization

To interpret the results of the measurements, we use a state-specific kinetic model of excitation and relaxation of optically pumped anharmonic oscillators in inhomogeneous media. It incorporates the effect of the laser power distribution profile and transport processes (diffusion and heat conduction) across the Gaussian laser beam, which become of crucial importance when the beam is focused [20]. The model evaluates the time-dependent vibrational level populations in gas mixtures excited
by a laser beam:
\[
\frac{\partial n_{v,i}(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r D_i \frac{\partial n_{v,i}(r,t)}{\partial r} \right] + VV_{v,i} + VT_{v,i} + SRD_{v,i} + VE_{v,i} + PL_{v,i},
\]
\[
\frac{\partial n_{v,i}(r,t)}{\partial r} \bigg|_{r=0} = 0,
\]
\[
n_{v,i}(r,t) \big|_{r=\infty} = n_{v,i}(T_0),
\]
\[
v = 0, v_{\text{max}}, i.
\]
In equations (4) and (5), \( n_{v,i}(r,t) \) is the population of the vibrational level \( v \)-species \( i \), \( n_{v,i}(T_0) \) is the initial equilibrium population at \( T_0 = 300 \text{ K}, n_i = \Sigma n_{v,i} \) are the species concentrations, \( r \) is the distance from the beam axis, \( D_i \) and \( \lambda \) are the diffusion and thermal diffusivity, respectively, and \( \rho \) and \( C_p \) are the density and the specific heat of the gas mixture at constant pressure. The rest of the notation is the same as in the paper of Flament et al [9]: VV, vibration–vibration term; VT, vibration–translation term; SRD, spontaneous radiative decay (infrared); VE, vibration–electronic coupling, mainly between \( X \Sigma^+ \) and \( A^1 \Sigma^+ \); PL, laser pumping; and HVR is the gas heating by vibration relaxation (both in VT and in nonresonance VV processes). The V–V rates for CO and the important vibration-to-electronic (V–E) energy transfer rates, used in the present model, were inferred from previous time-resolved optical pumping experiments [8, 19]. The V–V rate parametrizations for \( \text{N}_2—\text{N}_2, \text{O}_2—\text{O}_2 \) and \( \text{CO—N}_2 \) are based on the experimental results [21–23]. Since the experimental V–V rates for \( \text{CO—O}_2 \) and \( \text{N}_2—\text{O}_2 \) are not available, the V–V rate parametrizations for \( \text{N}_2—\text{O}_2 \) are based on the results of the close-coupled trajectory calculations by Billing [24]. The V–V rates for \( \text{CO—O}_2 \) are evaluated by replacing the vibrational quantum, \( \omega_v \), and anharmonicity, \( \chi_v \), of \( \text{N}_2 \) for those of \( \text{O}_2 \) in the \( \text{CO—N}_2 \) rate parametrization, keeping all other parameters the same (see equations (A5) and (A9) and table A2 of the appendix). The rationale for this assumption is that the near-resonance V–V exchange in both CO–N\(_2\) and CO–O\(_2\) collisions is primarily induced by the dipole–quadrupole interaction. The explicit analytic rate expressions used in this paper can be found in the appendix. Tables A1 and A2 of the appendix show the parameters used in the calculation. The V–T rate parametrizations for CO–CO, N\(_2—\text{N}_2\), and O\(_2—\text{O}_2\) are based on the results of calculations [24–26]; the remaining molecule–molecule V–T rates AB–M are considered to be independent of the collision partner M. Note that the V–T relaxation by molecules is not expected to play an important part in the vibrational energy balance, because at the relatively low gas temperatures involved these V–T rates are very slow. The present version of the model does not incorporate V–T relaxation on reactive atoms such as N and O, because of the very small concentration and the large uncertainty in the prediction of chemical reaction rates of vibrationally excited molecules. Processes such as associative ionization are not considered in the model because of the requirement of very high vibrational levels (∼30).

The set of equations (4) for 50 vibrational levels of CO, N\(_2\), and O\(_2\) are solved using a standard solver for stiff partial differential equations, PDECOL [27]. The solution is for stationary results, although a time-dependent model is used for solving the ‘stiff problem’. In the calculations, a 21-point nonuniform grid, with most points located near the laser beam axis, is used. The laser line intensity distributions are given by the equation \( I = I_0 \cdot \left[ 2/\pi R^2 \cdot \exp(-2r^2/R^2) \right] \), where \( I_0 \) is the incident line intensities in watts, and the parameter \( R = 1.0 \text{ mm} \) in the Gaussian intensity distribution across the focused laser beam is calculated by the code STRAHL developed at the University of Bonn [28]. The present code uses the spectroscopic data for the CO molecule [29] and accurate Einstein coefficients for spontaneous emission and absorption coefficients for the CO infrared bands [30] as inputs.

4. Results and discussion

As mentioned previously, the high-pressure mixture gas with air species, nitrogen and oxygen, is investigated in this paper. The results are obtained from a mixture of 30 Torr CO, 120 Torr O\(_2\), and 590 Torr N\(_2\). The Raman spectrum is measured and used to infer the vibrational population and the vibrational temperature as described in section 2. The CO pumping laser used to sustain the vibrational nonequilibrium of the gas mixture has a Gaussian intensity distribution across the focused laser beam. This causes the nonuniformity of the vibrational distribution function (simply the vibrational temperature) along the radius of the laser beam. Since Raman spectroscopy is essentially a point measurement (compared with the region of consideration), it can provide the local measurement of the vibrational distribution function in the vicinity of the centreline of the excited region. This measurement allows verifying the modelling calculation that incorporates both major processes of molecular energy transfer and diffusion of vibrationally excited species across the spatially nonuniform excitation region.

Figures 2(a)–(c) show three-dimensional plots of the Raman intensity as a function of the wavelength and the radial position (in 250 μm intervals) for N\(_2\), CO and O\(_2\), respectively. It can be seen that significant vibrational excitation exists for all three diatomic species over a spatial diameter of order 2 mm. From the figure, it can be seen that there are more peaks for the spectrum curves in the centreline than for the curves on the side. To be shown more clearly, spectra at two positions, the centreline and the 1 mm side location, are drawn in figure 3 for three species. In the figure, the curves at the central position shows five nitrogen vibrational levels (\( v = 0–4 \)), seven CO vibrational levels (\( v = 0–6 \)) and seven excited vibrational levels (\( v = 0–6 \)) of oxygen. In contrast, the curves at the 1 mm side location only have two vibrational levels (\( v = 0–1 \)) for nitrogen, two for CO (\( v = 0–1 \)) and three for oxygen (\( v = 0–2 \)). It implies the variation of the vibrational distribution function...
Figure 2. Raman spectra as a function of the radial displacement from the centreline for N\textsubscript{2} (upper), CO (middle) and O\textsubscript{2} (lower), respectively. Vibrational distribution functions at the centreline.

Figure 3. Raman spectra for three species at the centre (lower) and at the location \( r = 1 \) (upper).

Figure 4. Radial dependence of vibrational temperatures and the translational temperature.

along the radius of the pumping laser. The variation, or say the nonuniformity, is not only determined by the energy distribution of the pumping laser beam but also affected by the energy transfer rates among the molecular energy modes of three species and the mass and energy diffusion processes. Although the vibrational distribution functions of all three species are non-Boltzmann and cannot be characterized by a single vibrational temperature, the spatial non-uniformity of vibrational distribution function is illustrated more explicitly in figure 4, which plots the effective vibrational temperatures of N\textsubscript{2}, O\textsubscript{2} and CO defined in equation (3) as a function of the radial position. The measured rotation–translation temperature is also shown in this figure. The translational temperature in this series of experiments is evaluated from the comparison of two Raman spectra of nitrogen, one with the CO laser on and the other with the laser turned off, i.e. in an equilibrium gas mixture at \( T_0 = 300 \) K. In the latter case, as expected, only the signal from \( v = 0 \) is measured. Since the Raman signal intensity, \( I_v \), is proportional to the product of the absolute population of a vibrational level, \( n_v \), and the
Raman cross section, $\sigma_{v \rightarrow v+1}$, this allowed the inference of the number density of $N_2$ molecules, as well as the translational temperature [20],

$$T = \frac{n_{N_2}(T_0, \text{non-excited})}{n_{N_2}(T, \text{excited})} = \frac{n_0}{\sum_v n_v} = \frac{I_0}{\sum_v I_v/(v+1)}.$$ (6)

It can be seen that while the translational temperature is approximately constant (300–400 K), the vibrational temperature of all diatomic species exceeds $\sim 1000$ K, over the spatial extent, and at the centre the vibrational temperature is much higher. The vibrational distribution function inferred from Raman spectra at the centreline is shown in figure 5. The modelling calculation results with the V–V rate parametrization of table A2 are also drawn in figures 4 and 5. Figure 6 shows the vibrational distribution function of the three species at 0.5 mm location. Although mainly the agreement of the calculated results with the experimental results is good, the difference may be easily found. Figure 4 shows that the calculated vibrational temperature of $O_2$ is different from the experimental data at the central position. And figure 5 also shows the difference between the calculated data and the experimental data for the relative population of $O_2$. As described in section 3, the lack of experimental data about the V–V rates of $CO$–$N_2$ and $N_2$–$O_2$ causes the uncertainty in determining the rate parameters in equations (A5), (A9). And the processes, which are not included in modelling such as V–T relaxation on reactive atoms, may cause the difference.

Briefly, compared with experimental data, the agreement is good. Both calculated and experimental results show the interspecies V–V energy exchanging results in the nonequilibrium vibrational population distributions of three diatomic species at atmosphere pressure. The good agreement verifies the modelling calculation. However, it also implies that more experimental research is needed on the V–V rates of various gas species.

5 Conclusions

Temperatures and vibrational populations are investigated experimentally and numerically in the $CO$–$N_2$–$O_2$ gas mixture. By spatially resolved Raman Q-branch spectra measurement strong vibrational excitation has been observed in gas mixtures up to atmospheric pressure. Modelling calculation provides in-depth perception of vibrational kinetics of these diatomic molecular gas mixtures. The agreement is good between the calculated and the experimental data after the rate modification. Both experimental and calculated results demonstrate that strong vibrational nonequilibrium for all diatomic species can be sustained in a relatively cold molecular gas mixture up to one atmosphere pressure by the optical pumping method with a relatively low intensity CO laser. However, the results also demand further investigations on the rates of V–V interspecies exchange of the gas mixture.

Appendix

Notations.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>translational temperature</td>
</tr>
<tr>
<td>$\omega_{ei}$ and $x_{ei}$</td>
<td>vibrational quantum and anharmonicity of the species $i$, respectively</td>
</tr>
<tr>
<td>$v, w$</td>
<td>vibrational quantum numbers</td>
</tr>
<tr>
<td>$P_{ij}^{w,v-1}$</td>
<td>rate coefficient of V–T relaxation of the species $j$ from level $v$ to level $v-1$ by the species $i$, cm$^{-3}$s$^{-1}$</td>
</tr>
<tr>
<td>$\tau_{ij}P$</td>
<td>vibrational relaxation time of the species $i$ by the species $j$ times pressure, atm$\mu$s</td>
</tr>
<tr>
<td>$Q_{ij} (v, w-1 \rightarrow v-1, w)$</td>
<td>rate coefficient of V–V exchange between the species $i$ and $j$, cm$^{-3}$s$^{-1}$</td>
</tr>
<tr>
<td>Z</td>
<td>gas-kinetic collision frequency, cm$^{-3}$s$^{-1}$</td>
</tr>
</tbody>
</table>
Table A1. Parameters used in the V–T rate expressions (equations (A1)–(A4)).

<table>
<thead>
<tr>
<th>Species</th>
<th>$c_{ij}$</th>
<th>$A_{ij}$</th>
<th>$B_{ij}$</th>
<th>$C_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO–M</td>
<td>0.25</td>
<td>−15.23</td>
<td>280.5</td>
<td>−549.6</td>
</tr>
<tr>
<td>N₂–M</td>
<td>0.25</td>
<td>−12.54</td>
<td>258.9</td>
<td>−390.9</td>
</tr>
<tr>
<td>O₂–M</td>
<td>0.25</td>
<td>−13.50</td>
<td>205.0</td>
<td>−295.0</td>
</tr>
</tbody>
</table>

Table A2. Parameters used in the V–V rate expressions (equations (A5)–(A9)).

<table>
<thead>
<tr>
<th>Species</th>
<th>$S$</th>
<th>$L$</th>
<th>$c$, $K$</th>
<th>$b$, $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO–CO</td>
<td>1.64e-6</td>
<td>1.614</td>
<td>0.456</td>
<td>40.36</td>
</tr>
<tr>
<td>N₂–N₂</td>
<td>1.0e-7</td>
<td></td>
<td>0.120</td>
<td>80.12</td>
</tr>
<tr>
<td>O₂–O₂</td>
<td>2.5e-6</td>
<td></td>
<td>0.25</td>
<td>80.05</td>
</tr>
<tr>
<td>CO–N₂</td>
<td>3.0e-8</td>
<td>0.15</td>
<td>0.185</td>
<td>87.67</td>
</tr>
<tr>
<td>N₂–O₂</td>
<td>1.0e-8</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO–O₂</td>
<td>3.0e-8</td>
<td>0.15</td>
<td>0.185</td>
<td>87.67</td>
</tr>
</tbody>
</table>

$V$–$T$ rate parametrization.

$$p_{ij}^{v,v-1} = p_{ij}(T) \frac{v}{1 - x_{ei}} F(\lambda^{v,v-1}_{ij}), \quad (A1)$$

$$F(\lambda) = \frac{1}{2} \left( e^{-\lambda} \right) \lambda^{-3/2} \left( \frac{c_{ij}}{T} \right) |\Delta E|, \quad (A2)$$

$$\Delta E = \omega_{ei}(1 - 2x_{ei})v - \omega_{ij}(1 - 2x_{ej})v, \quad (A3)$$

V–$V$ rate parametrization.

$$Q_{ij}(v, v - 1 \rightarrow v - 1, w) = Z(S_{w-1,w}^{v,v-1} + L_{w-1,w}^{v,v-1}) e^{-\Delta E/2T}, \quad (A5)$$

$$\Delta E = \omega_{ei}(1 - 2x_{ei})v - \omega_{ij}(1 - 2x_{ej})v, \quad (A6)$$

$$S_{w-1,w}^{v,v-1} = S \cdot T \left( \frac{w}{1 - x_{ei}v} \right) F(v_{w-1,w}^{v,v-1}), \quad (A7)$$

$$L_{w-1,w}^{v,v-1} = T \left( \frac{g_{v,v-1}^{w,1}}{g_{v,v}^{w,1}} \right)^2 \left( \frac{g_{w-1,w}^{v,v-1}}{g_{v,v}^{w,1}} \right)^2 \exp \left( -\frac{\Delta E^2}{k^2bT} \right), \quad (A8)$$

$$Z = 3 \times 10^{-10} \left( T/300 \right)^{1/2} \text{cm}^3 \text{s}^{-1}. \quad (A9)$$

References


