Vibrational energy storage in high pressure mixtures of diatomic molecules

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Abstract

CO/N2, CO/Ar/O2, and CO/N2/O2 gas mixtures are optically pumped using a continuous wave CO laser. Carbon monoxide molecules absorb the laser radiation and transfer energy to nitrogen and oxygen by vibration–vibration energy exchange. Infrared emission and spontaneous Raman spectroscopy are used for diagnostics of optically pumped gases. The experiments demonstrate that strong vibrational disequilibrium can be sustained in diatomic gas mixtures at pressures up to 1 atm, with only a few Watts laser power available. At these conditions, measured first level vibrational temperatures of diatomic species are in the range $T_V = 1900–2300$ K for N2, $T_V = 2600–3800$ K for CO, and $T_V = 2200–2800$ K for O2. The translational–rotational temperature of the gases does not exceed $T = 700$ K. Line-of-sight averaged CO vibrational level populations up to $v = 40$ are inferred from infrared emission spectra. Vibrational level populations of CO ($v = 0–8$), N2 ($v = 0–4$), and O2 ($v = 0–8$) near the axis of the focused CO laser beam are inferred from the Raman spectra of these species. The results demonstrate a possibility of sustaining stable nonequilibrium plasmas in atmospheric pressure air seeded with a few percent of carbon monoxide. The obtained experimental data are compared with modeling calculations that incorporate both major processes of molecular energy transfer and diffusion of vibrationally excited species across the spatially nonuniform excitation region, showing reasonably good agreement. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Nonequilibrium vibrational kinetics of diatomic molecules has been a focus of attention for many years in gas discharge plasmas, molecular lasers, pollution control, upper atmosphere chemistry, and gas dynamic flows [1,2]. The rate of energy transfer between the vibrational molecular modes and the “external” modes of rotation and translation is, in particular, a determining process in many high enthalpy fluid environments (such as in supersonic nozzles and behind shock waves). Furthermore, the details of energy distribution among the quantum states within the vibrational modes is a key issue in nonthermal plasma chemical reactor design, in predicting radiation from
supersonic nozzle expansions, and in the design of a variety of molecular gas lasers [3]. This energy distribution is primarily controlled by vibration-to-vibration (V–V) energy exchange processes [4,5],
\[
AB(v) + CD(w) \rightarrow AB(v-1) + CD(w+1),
\]
which in a broad range of parameters are known to be much faster than vibration-to-translation (V–T) relaxation,
\[
AB(v) + CD \rightarrow AB(v-1) + CD.
\]
In Eqs. (1) and (2), AB and CD stand for diatomic molecules, \(v\) and \(w\) are vibrational quantum numbers. Near-resonance V–V exchange processes, such as \(E_v(AB) - E_{v-1}(AB) \approx E_{w+1}(CD) - E_w(CD)\) in Eq. (1), are of particular importance, since they can sequentially populate very high vibrational levels of the molecules [4,5], and thereby precipitate nonequilibrium chemical reactions, electronic excitation with subsequent visible and UV radiation, and ionization.

Methods of sustaining strong vibrational disequilibrium 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 (\(P \approx 1\) atm) and low energy loading per molecule because of rapid development of discharge instabilities [6,7]. In contrast to this, steady state optically pumped plasmas can be sustained at high pressures (up to 20 atm in CO–Ar mixtures) [8]. 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 [9–14], or CO with a frequency doubled CO\(_2\) laser [15]). On the other hand, the use of nonlinear absorption techniques, such as PUMP-DUMP [16], RELIEF [17], spontaneous Raman absorption [18], etc., allows only pulsed mode operation and makes energy addition to vibrational modes of homopolar molecules, such as N\(_2\) and O\(_2\), extremely inefficient.

These obstacles prevent development of new promising applications of vibrationally nonequi-

librium environments, including sustaining stable large-volume ionization in high pressure air and energy efficient high yield mode-selective chemical synthesis.

The present paper discusses a new method of vibrational excitation of high pressure gases, including nitrogen and oxygen, by collision-dominated vibrational energy transfer of Eq. (1) from an infrared active species (carbon monoxide), optically pumped by resonance absorption of the CO laser radiation. This method combines the advantage of the use of an efficient gas laser with the capability of excitation of various species at high pressures, without using electron impact.

### 2. Experimental

#### 2.1. Emission spectroscopy

Fig. 1 shows a schematic of the experimental setup for the study of vibrational energy transfer in CO/Ar/N\(_2\)/O\(_2\) mixtures. A carbon monoxide laser is used to irradiate a gas mixture, which is slowly flowing through the pyrex glass optical absorption cell shown. The residence time of the gases in the cell is about 1 s. The liquid nitrogen cooled CO laser was designed in collaboration with the University of Bonn and fabricated at Ohio State. It produces a substantial fraction of its power output on the \(v = 1 \rightarrow 0\) fundamental band component in the infrared. The laser can operate at more than 100 W continuous wave (c.w.) power. However, in the present experiment, the laser is typically operated at 15 W c.w. broadband power on the lowest 10 fundamental bands, with up to \(\approx 0.3\) W on the \(v = 1 \rightarrow 0\) component. The output on the lowest bands (\(1 \rightarrow 0\) and \(2 \rightarrow 1\)) is necessary to start the absorption process in cold CO (initially at 300 K) in the cell. The quantum efficiency of the CO pump laser approaches 90%, with an overall efficiency of about 40%, which makes it the most efficient gas laser available. The present use of CO laser pumped absorption cells to study the V-V process is a further development of a technique with a considerable literature [9–14].

The emission spectroscopy measurements reported here are made at CO partial pressure of
2 Torr and total gas pressure of 100–130 Torr. At these conditions, the gas mixture is optically thick for the CO laser radiation. A substantial portion of the laser power (up to 5 W) is absorbed over the absorption distance of $L = 12.5$ cm. The Gaussian laser beam, which has a diameter of $\sim 0.5$ cm, does not have to be focused to provide substantial vibrational mode energy in the cell gases. However, in the present experiments it is focused to increase the power loading per CO molecule, providing an excitation region in the cell of $\sim 1$ mm diameter.

After the laser is turned on, the lower states of CO, $v \leq 10$, are populated by direct resonance absorption of the pump radiation in combination with the much more rapid redistribution of population by the intramode V–V exchange processes CO–CO (see Eq. (1)). These V–V processes then continue to populate the higher vibrational levels of CO above $v = 10$, which are not directly coupled to the laser radiation. At the same time, the intermode V–V exchange processes CO–N$_2$ and CO–O$_2$ also populate the low vibrational levels of nitrogen and oxygen molecules. In particular, rapid vibrational energy transfer from highly excited CO molecules to oxygen is facilitated by the near-resonance process

$$\text{CO}(v) + \text{O}_2(0) \rightarrow \text{CO}(v-1) + \text{O}_2(1), \quad v \sim 25$$

(3)

If the vibrational energy storage per N$_2$ or O$_2$ molecule becomes sufficiently high, the high vibrational levels of these molecules will also be populated by the intramode V–V exchange N$_2$–N$_2$ and O$_2$–O$_2$. It is well known [19] that until vibrationally excited molecules start producing rapid V–T relaxers in chemical reactions (such as N and O atoms, CO$_2$, etc.), the overall rate of V–T relaxation in the gas mixture remains slow. Therefore, a substantial fraction of the energy added to
the vibrational mode of CO by the laser remains stored in vibrational modes of N₂ and O₂.

When the laser is turned off, the vibrational levels are depopulated, again mainly by the V–V energy transfer, and the vibrational energy distribution approaches the Boltzmann distribution at the translational temperature. In the steady-state measurements reported in the present paper, the laser remains on all the time, so that a complete steady state is reached. Note that the vibrational energy stored in the diatomic molecules is constantly converted into heat both in V–V and V–T processes. However, the large heat capacity of the gases (including the vibrational modes), as well as conductive and convective cooling of the gas flow, allow us to control the translational/rotational mode temperature in the cell. Even in steady-state conditions, when the average vibrational mode energy of the CO would correspond to a few thousand degrees Kelvin, the temperature does not rise above a few hundred degrees. Thus a strong disequilibrium of energy can be maintained in the cell, characterized by very high vibrational mode energy and a low translational/rotational mode temperature. As discussed in Section 1, similar nonequilibrium conditions exist in a variety of rapid supersonic expansions, in glow plasma discharges, and in a number of other thermodynamic environments. The present setup allows us to study the energy transfer and kinetic processes in a closely controlled environment, without the complications of electron impact processes and instabilities, which occur in electric discharges, or the experimental difficulties of creating and controlling a supersonic flow.

As shown in Fig. 1, the population of the vibrational states of the CO in the cell is monitored by infrared emission spectroscopy. For this purpose, a Bruker Fourier transform (FT) IFS 66 spectrometer is used to record the spontaneous emission from the CO fundamental, first and second overtone bands through a window on the side of the cell. The emission spectra are recorded at both high spectral resolution of 0.25 cm⁻¹ and low resolution of 8.0 cm⁻¹. The translational–rotational temperature of the cell gases is determined from the rotational structure of the R-branch of the CO fundamental band 1 → 0.

### 2.2. Raman spectroscopy

To measure vibrational populations of N₂ and O₂ molecules in optically pumped gas mixtures, spontaneous Raman spectroscopy is used. Laser Raman diagnostics were performed by combining the CO laser beam and a pulsed Nd:YAG Raman pump laser beam using a 90° CaF₂ dichroic mirror, which transmits the CO laser, while reflecting the Nd:YAG laser (see Fig. 2). Raman spectra were obtained using the second harmonic output of the Nd:YAG laser in combination with an optical multichannel analyzer (OMA) detector. The Nd:YAG laser was focused coaxial to the CO pump laser and Raman scattering in a volume element approximately 0.100 mm in diameter and 2 mm in length was captured at 90°. A simple long wavelength pass (OG-570) colored glass filter was used to attenuate the elastic scattering at 0.532 μm and transmit the Stokes shifted scattering, which was in the range 0.570–0.615 μm. The OMA consists of a 1/4 m grating spectrometer with a micro-channel plate intensified CCD camera as the detector. The intensifier allowed a fast (~10 ns) gate so that spontaneous emission from the optically pumped gas, which was much brighter than the detected Raman signal, could be minimized. The signal was integrated for time duration in the range 1–10 min. The resolution of the spectrometer was sufficient to resolve individual Q-branch vibrational bands but could not resolve any rotational fine structure. The wavelength coverage enabled the capture of approximately 15 vibra-
tional bands simultaneously. Determining the complete N$_2$, O$_2$, and CO vibrational distributions required merging of three spectra, which were obtained sequentially with identical experimental conditions. More experimental detail can be found in our separate publication [20].

Note that inference of the vibrational level populations from Raman spectra requires knowledge of the Raman cross section dependence on the vibrational quantum number. For all 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 [21]. The measurements are made in CO/N$_2$ and CO/N$_2$/O$_2$ mixtures at total gas pressures of $P = 400$ Torr up to 1 atm, with 2–5% fraction of CO and up to 16% of O$_2$ in the cell.

3. Kinetic model and the V–V 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 is based on the master equation model described in detail in Ref. [10]; a significant upgrade is the incorporation of 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. The model evaluates the time-dependent vibrational level populations in CO–N$_2$–O$_2$–Ar mixtures excited by a laser beam

$$\frac{\partial n_{v,j}(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ rD_j \frac{\partial n_{v,j}(r,t)}{\partial r} \right] + (V-V_j) + (V-T_j) + \text{SRD}_{v,j} + (V-E_j) + \rho\text{PL}_{v,j} \frac{\partial n_{v,j}(r,t)}{\partial r} \bigg|_{r=0} = 0;$$

$$n_{v,j}(r,t)\bigg|_{r=\infty} = n_{v,j}(r,t)\bigg|_{r=0} = n_{v,j}(T_0) \quad v = 0, v_{\max}. \quad \text{(4)}$$

In Eqs. (4) and (5), $n_{v,j}(r,t)$ is the population of vibrational level $v$ of species $i$, $n_{v,j}(T_0)$ is the initial equilibrium population at $T_0 = 300$ K, $n_i = \sum_j n_{v,j}$ are the species concentrations, $r$ is the distance from the beam axis, $D_j$ and $\lambda$ are the diffusion and heat transfer coefficients, respectively, $\rho$ and $c_p$ are density and specific heat of the gas mixture at constant pressure. The rest of the notation is the same as in Ref. [10]: V–V, vibration–vibration term; V–T, vibration–translation term; SRD, spontaneous radiative decay (infrared); V–E vibration–electronic coupling; PL, laser pumping; HVR, gas heating by vibrational relaxation. The explicit expressions for these terms are given in Ref. [10]. The line-of-sight averaged vibrational populations are calculated as follows [22]:

$$n_{v,j}(t) = \int_0^\infty n_{v,j}(r,t) \, dr. \quad \text{(6)}$$

Eq. (6) takes into account both the effect of the decrease of the radiating volume and the increase of the steradiancy toward the focal point of the FT spectrometer collection optics, which compensate each other. The V–V rates for CO–CO, the V–T rates for CO–Ar, and the V–E energy transfer rates CO(X$^1\Sigma$) + CO $\rightarrow$ CO(A$^1\Pi$) + CO, used in the present model, were inferred from previous time-resolved optical pumping experiments [9,23]. The V–V rate parametrizations for CO–N$_2$, N$_2$–N$_2$, N$_2$–O$_2$, O$_2$–O$_2$, and N$_2$–O$_2$ are based on the results of the close-coupled trajectory calculations by Billing et al. [24–27]. Since the V–V rates for CO–O$_2$ are not available, they are evaluated by replacing the vibrational quantum, $\alpha_v$, and anharmonicity, $x_v$, of N$_2$ for those of O$_2$ in the CO–N$_2$ rate parametrization, keeping all other parameters the same (see Eqs. (A.5) and (A.9) of Appendix A and Table 1). 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 V–T rate parametrizations for CO–CO, N$_2$–N$_2$, and O$_2$–O$_2$ are also based on the results of calculations [24–27] (Table 2); 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 and by argon atoms 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 large uncertainty in prediction of chemical reaction rates of vibrationally excited molecules. The explicit analytic rate expressions used can be found in Appendix A.

The system of Eqs. (4) and (5) for 40 vibrational levels of CO, N$_2$, and O$_2$ is solved using a standard solver for stiff partial differential equations, PDECOL [28]. 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

$$I(r) = I_0 \left[ \frac{2}{\pi R^2} \exp \left(-2r^2/R^2\right) \right],$$

where $I_0$ are the incident line intensities in W, and the parameter $R = 0.56$ mm in the Gaussian intensity distribution across the focused laser beam is calculated by the code STRAHL developed at the University of Bonn [29,30]. The present code uses the spectroscopic data for the CO molecule [31] and accurate Einstein coefficients for spontaneous emission and absorption coefficients for the CO infrared bands [32] as inputs.

4. Results and discussion

4.1. Emission spectroscopy results

Under the conditions described in Section 2, a highly nonequilibrium distribution of vibrational energy is created in the cell. Fig. 3 shows the CO infrared emission from the CO–Ar mixture excited by the focused laser beam, as recorded by the FT spectrometer at a resolution of 0.25 cm$^{-1}$. The second overtone bands can be seen at the highest frequencies on the left ($v > 4300$ cm$^{-1}$), the first overtone bands dominate at the lower frequencies ($2250$ cm$^{-1} < v < 4300$ cm$^{-1$}), and the high frequency tail of the R-branch of the $v = 1 \rightarrow 0$ fundamental is the tall peak on the right. A long wavelength cut-off filter is used to prevent any more of the very intense fundamental band emission at frequencies $v < 1950$ cm$^{-1}$ from entering the instrument, and swamping the overall signal. While this resolution is approximately 1/10 the rotational spacing of the CO molecule, there is a dense array of individual vibrational–rotational lines, due to the overlapping of the various band components.

The CO vibrational distribution functions (VDF) inferred from such high resolution spectra using the standard technique [33], as well as theoretical line-of-sight averaged VDFs, are shown in Fig. 4 for two different gas mixtures, CO/Ar = 2/100 and CO/N$_2$ = 2/100, at $P = 100$ Torr. The theoretical VDFs have been calculated using the kinetic model discussed in Section 3. The measured translational–rotational temperatures for these two cases are $T = 600$ and 450 K, respectively. The distributions shown in Fig. 4 are the well-known “V–V pumped” distributions [4,5], maintained by the rapid redistribution of vibrational energy by the V–V processes, which pump energy into the higher vibrational levels. They are obviously extremely non-Boltzmann, and characterized by high population of the upper vibrational levels. Note that replacing argon with nitrogen in the cell somewhat reduces the measured CO vibrational level populations, since some vibrational energy is transferred from CO to N$_2$. This effect is somewhat less pronounced in the calculations (see Fig. 4), which suggests that the theoretical V–V rates for
CO–N₂ [24] used in the present calculations are underestimated. Fig. 4 also shows the calculated centerline CO and N₂ VDFs in the CO/N₂ mixture. One can see that carbon monoxide at the beam center is in extreme vibrational disequilibrium. Furthermore, modeling calculations suggest that nitrogen also becomes strongly V–V pumped by vibrational energy transfer from CO, as discussed in Section 3. Calculated radial distributions of the first level vibrational temperature $T_{V(CO)}$,

$$T_V = \frac{\theta_1}{\ln(n_0/n_1)}, \quad (7)$$

shown in Fig. 5, predict the centerline values of $T_V(CO) = 12,000 \text{ K}$ in the CO/Ar mixture, and $T_V(CO) = 8500 \text{ K}$, $T_V(N_2) = 2400 \text{ K}$ in the CO/N₂ mixture. In Eq. (7), $\theta_1$ is the energy of the first vibrational level of a molecule, and $n_0$ and $n_1$ are the populations of vibrational levels $v = 0$ and $v = 1$, respectively. The first level vibrational temperature defined by Eq. (7) is used throughout the remainder of the present paper. For comparison, the apparent first level vibrational temperatures of CO inferred from the line-of-sight...
averaged VDFs of Fig. 4 are $T_V(\text{CO}) = 3300$ and 2700 K, respectively. Fig. 6 plots the calculated CO distribution functions in the CO/Ar mixture at different distances from the laser beam axis. From Figs. 5 and 6, one can see that the optically pumped region is strongly nonuniform in the radial direction.

Fig. 7 shows the experimental and the theoretical VDFs in CO/Ar/O$_2$ mixtures at different oxygen concentrations. One can see that the increase of O$_2$ partial pressure results in truncation of the CO VDF due to the V–V energy transfer from CO to O$_2$. However, even with 30 Torr of O$_2$ in the cell, CO is still V–V pumped up to the level $v \sim 20$. The model predictions do not fully reproduce the observed CO VDF fall-off at $v > 25$ (see Fig. 7) unless the V–V rates for CO–O$_2$ at high vibrational levels (see Eq. (3)), varied in the calculations, considerably exceed the gas kinetic collision frequency. We believe this discrepancy to be due to (i) possible contribution of a fast nonadiabatic (i.e. reactive) channel of the V–V exchange between highly excited CO and O$_2$, and (ii) the effect of rapid V–T relaxation of CO by O atoms, both not incorporated into the model. An indirect evidence of these effects is the CO$_2$ infrared spectrum observed in CO/Ar/O$_2$ mixtures (see Fig. 8). CO$_2$
radiation, which could not be detected in CO/Ar and CO/N\textsubscript{2} mixtures, is most intense at oxygen partial pressures of 0.1–1 Torr and becomes weaker as the O\textsubscript{2} concentration increases. CO\textsubscript{2} and oxygen atoms in the cell are likely to be produced in vibrationally stimulated chemical reaction CO\textsubscript{v}\textbullet + O\textsubscript{2}\textsubscript{w}\textbullet \rightarrow CO\textsubscript{2} + O. This scenario is consistent with the modeling calculations which predict strong vibrational excitation of diatomic species at the low O\textsubscript{2} partial pressures (see Fig. 9). For the conditions of Figs. 7 and 8, centerline first level vibrational temperatures are $T_{V}(\text{CO}) = 13,000$ K, $T_{V}(\text{O}_2) = 7000$ K and $T_{V}(\text{CO}) = 9500$ K, $T_{V}(\text{O}_2) = 3000$ K for 1 and 30 Torr of O\textsubscript{2} in the cell, respectively.

4.2. Raman spectroscopy results

Spontaneous Raman spectroscopy allows access to vibrational levels of homopolar molecules and thereby provides powerful diagnostics of nonequilibrium gases. It also gives an opportunity for comparing predictions of modeling calculations discussed in Section 4.1 with the experimental data. In the experiments described in Section

![Fig. 9. Calculated centerline vibrational distribution functions of CO and O\textsubscript{2} for the conditions of Fig. 7.](image)

2.2. Raman spectra of optically pumped CO, N\textsubscript{2}, and O\textsubscript{2} are recorded in the pressure range $P = 400$–760 Torr. Fig. 10 displays Raman spectra of these species measured in a CO/N\textsubscript{2}/O\textsubscript{2} mixture.

![Fig. 8. Low resolution (8.0 cm\textsuperscript{-1}) CO infrared spectra for the conditions of Fig. 7.](image)
at $P = 740$ Torr, with CO and O$_2$ partial pressures of 40 and 30 Torr, respectively. In these spectra, one can easily identify a few low vibrational levels of CO, N$_2$, and O$_2$. However, Raman vibrational spectra of CO in CO/N$_2$ mixtures also show multiple peaks corresponding to 38 first vibrational states of carbon monoxide, $v = 0 – 37$ [20]. This makes the inference of vibrational populations of all these levels possible, provided that the Raman cross sections for highly vibrationally excited molecules are known with reasonable accuracy. As discussed in Section 2.2, Raman spectroscopy is essentially a point measurement. This means that if the focused Nd:YAG laser is aligned along the axis of the CO pump laser (see Fig. 2), the Raman spectra would provide vibrational level populations in the vicinity of the centerline of the excited region.

Fig. 11 displays vibrational level populations of CO, N$_2$, and O$_2$ inferred from the Raman spectra such as shown in Fig. 10, at $P = 740$ Torr, with CO and O$_2$ partial pressures of 40 and 120 Torr, respectively. Fig. 12 shows vibrational level populations of CO and N$_2$ inferred from the Raman spectra of the optically pumped CO/N$_2$ = 3/100 mixture, at $P = 1$ atm. At these conditions, the incident CO laser power of 10–13 W was about the same as in the experiments discussed in Section 4.1, while the gas pressure in the cell was much higher (~1 atm vs. 100 Torr). Therefore vibrational energy loading per molecule in this second series of experiments is also much lower than in the first series. Indeed, the first level vibrational temperature of CO near the centerline, where vibrational disequilibrium is the strongest ($T_V = 2600–3000$ K, see Figs. 11 and 12), is in the same
range as apparent values inferred from the line-of-sight averaged CO VDF in emission spectroscopy measurements \((T_V = 2700–3300 \text{ K})\), see Figs. 4 and 7). In addition, one can see that the calculated centerline vibrational temperature of CO at \(P = 100 \text{ Torr}, T_V(\text{CO}) = 8500–12,000 \text{ K}\) (see Figs. 3 and 4) is much higher than its corresponding values calculated and measured at \(P = 1 \text{ atm}, T_V(\text{CO}) = 2600–3900 \text{ K}\) (see Figs. 11 and 12). In other words, vibrational disequilibrium becomes weaker at higher pressures. However, even at \(P = 1 \text{ atm}\) it remains very strong. This is consistent with modeling calculations, also shown in Figs. 11 and 12. Calculated centerline VDFs of the three diatomic species are in reasonable agreement with the data. Comparing the results of calculations in Figs. 11 and 12, one can see that addition of oxygen to optically pumped gases results in depletion of the high vibrational levels of CO, as has been also observed in the emission spectroscopy experiments (see Fig. 7). From Fig. 11 one can see that the model somewhat overestimates the first level vibrational temperature of oxygen. We believe this to be an indication of an additional energy sink from the vibrational mode of O₂, possibly due to V–T relaxation by O atoms.

The translational temperature in this series of experiments is evaluated from comparison of two Raman spectra of nitrogen, one with the CO laser on (e.g. see Fig. 10(a)), and the other with the laser turned off, i.e. in an equilibrium gas mixture at \(T_0 = 300 \text{ K}\). 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, \(\sigma_v \sim (v + 1)\), this allowed inference of the number density of N₂ molecules, as well as the translational temperature, on the centerline of the excited region,

\[
\frac{T}{T_0} = \frac{n_{N_2}(T_0, \text{non-excited})}{n_{N_2}(T, \text{excited})} = \frac{n_0}{\sum_v n_v} \frac{I_0}{\sum_v I_v/(v+1)}. \tag{8}
\]

Nitrogen spectra have been used for the temperature inference for two reasons, (i) in the present experiments it is the most abundant species (78–98% of the gas mixture), so that vibrationally stimulated chemical reactions are least likely to affect its concentration, and (ii) it has the fewest number of vibrational levels excited. From Eq. (8), the centerline translational temperature of the optically pumped gases for the conditions of Figs. 10–12 is inferred to be \(T \geq 500 \text{ K}\). Additional experiments [20] demonstrate that the rotational structure of the S-branch Raman spectra can also be resolved, which also allows estimating the translational–rotational temperature of the optically pumped gas, \(T < 600 \text{ K}\) [20].

These experimental results confirm the predictions of modeling calculations (see Section 4.1) and demonstrate that strong vibrational disequilibrium can be sustained by a c.w. CO laser in relatively cold molecular gas mixtures at atmospheric pressure. Among the numerous implications of this major result is the possibility of sustaining a cold stable plasma in atmospheric pressure air (with CO used as an additive). Associative ionization of carbon monoxide in strongly vibrationally excited CO/N₂, CO/Ar/O₂, and CO/Ar/NO mixtures has already been demonstrated in
our previous work [11,34,35]. The unconditional stability of these optically pumped plasmas is ensured by the absence of an external electric field and electron impact ionization. The present data (in particular, strong vibrational excitation of \( \text{O}_2 \)), suggest that oxygen might also play an important role in vibrationally stimulated ionization kinetics. In addition, high concentrations of vibrationally excited molecules in optically pumped air plasmas might also affect the electron removal rates, i.e. recombination and attachment. Discussion of these issues is beyond the scope of the present paper. Recent studies of rates and mechanisms of ionization, recombination, and electron attachment in optically pumped air plasmas, as well as their stability, are discussed in our separate publication [35].

Comparison of the experimental data with the modeling calculations provides insight into kinetics of vibrational energy transfer among diatomic species and energy transport in nonuniform optically pumped gases. However, the results suggest that the rates of V–V exchange for \( \text{CO}–\text{N}_2 \), and especially those for \( \text{CO}–\text{O}_2 \), are not known with sufficient accuracy. Further optical pumping experiments using complementary infrared and Raman diagnostics would allow inference of the rates of these key energy transfer processes.

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Appendix A

Nomenclature

\( T \) translational temperature
\( \omega_{ei} \) and \( x_{ei} \) vibrational quantum and anharmonicity of the species \( i \), respectively
\( v, w \) vibrational quantum numbers

\( P_{ij}^{v-v} \) rate coefficient of V–T relaxation of the species \( i \) from level \( v \) to level \( v-1 \) by the species \( j \), \( \text{cm}^3 \text{s}^{-1} \)

\( \tau_{ij} P \) vibrational relaxation time of the species \( i \) by the species \( j \) times pressure, \( \text{atm} \text{\mu s} \)

\( Q_{ij}(v,v-1 \rightarrow v-1,w) \) rate coefficient of V–V exchange between the species \( i \) and \( j \), \( \text{cm}^3 \text{s}^{-1} \)

\( Z \) gas-kinetic collision frequency, \( \text{cm}^3 \text{s}^{-1} \)

A.1. V–T rate parametrization

\[
P_{ij}^{v-v-1} = P_{ij}(T) \frac{v}{1-x_{ei}v} F(\lambda_{ij}^{v-v-1}),
\]

\[
F(\lambda) = \frac{1}{2} \left( 3 - e^{-2\lambda/3} \right) e^{-2\lambda/3},
\]

\[
\lambda_{ij}^{v-v-1} = 2^{-3/2} \sqrt{\frac{C_{ij}}{T}} |\Delta E|,
\]

\[
\Delta E = \omega_{ei} (1 - 2x_{ei}v),
\]

\[
P_{ij}(T) = \frac{10^{-7} kT}{(\tau_{ij} P) F(\lambda_{ij}^{v-v})(1 - \exp(-\omega_{ei}/T))},
\]

\[
\tau_{ij} P = \exp(A_{ij} + B_{ij} T^{-1/3} + C_{ij} T^{-2/3}) \text{ \text{atm} \text{\mu s}},
\]

A.2. V–V rate parametrization

\[
Q_{ij}(v,v-1 \rightarrow v-1,w) = Z \left( S_{v-1,w}^{v-1} + L_{v-1,w}^{v-1} \right) e^{-\Delta E/2T}
\]

\[
\Delta E = \omega_{ei} (1 - 2x_{ei}v) - \omega_{ej} (1 - 2x_{ej}v),
\]

\[
S_{v-1,w}^{v-1} = S \cdot T \frac{v}{1-x_{ei}v} \frac{w}{1-x_{ej}w} F(\lambda_{i,j,v-1,w}^{v-1-1}),
\]

\[
F(\lambda) = \frac{1}{2} \left( 3 - e^{-2\lambda/3} \right) e^{-2\lambda/3},
\]

\[
\lambda_{v-1,w}^{v-1} = 2^{-3/2} \sqrt{\frac{e}{T}} |\Delta E|,
\]


\[ L_{w-1,w} = \frac{L}{T} \left( \frac{g^{w-1}}{g^{1.0}} \right)_{i} \left( \frac{g^{w-1}}{g^{1.0}} \right)_{j} \exp \left( -\frac{\Delta E_{2}^{2}}{bT} \right) \]  

(A.8)

\[ \left( \frac{g^{w-1}}{g^{1.0}} \right)_{i} = \left( \frac{a + 1}{a + 3 - 2v} \right)^{2} \times \frac{v(a + 2 - 2v)(a + 4 - 2v)}{a(a + 3 - v)} \]

\[ a = 1/x_{e}, \]  

\[ Z = 3 \times 10^{-10}(T/300)^{1/2} \text{ cm}^{3} \text{ s}^{-1}. \]  

(A.9)

A.3. \( \nu-E \) rate \( CO(\nu^{j}) + M \rightarrow CO(\nu^{j}) + M \)

\[ k_{\nu-E} = 10^{-12} \text{ cm}^{3} \text{ s}^{-1}. \]

References
