Nonequilibrium vibrational kinetics of carbon monoxide at high translational mode temperatures

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Recent experiments and analyses involving vibration-to-vibration (V–V) pumped carbon monoxide are presented. Pure CO, and CO–Ar mixtures, in a flowing-gas cell, are vibrationally excited by absorption of CO laser radiation. The pump laser is a slow-flow liquid-nitrogen wall-cooled device, which can be operated in either Q-switched or cw mode for these experiments. There is output down to the e=1–0 vibrational transition (Q-switched) or e=2–1 (cw). CO has been V–V pumped in these experiments to very high vibrational quantum levels, at partial pressures up to 65 Torr. The rotational/translational mode temperature has been measured by emission spectroscopy of rotationally resolved Swan bands of C2 formed from reaction of the V–V pumped CO. Measured rotational mode temperatures up to 1500 K have been achieved with strong V–V pumping. Low levels of ionization have been observed under these extreme pumping conditions. Results of time-resolved experiments exploring the kinetics are presented. These results are analyzed using a time-dependent kinetic master equation modeling code for the vibrational state kinetics.

1. Introduction

It has long been established that a special type of extreme thermodynamic disequilibrium exists in the vibrational energy modes of many low-temperature molecular plasmas. This disequilibrium occurs in environments for which the average energy of the vibrational modes is a significant fraction of the fundamental vibrational quantum and for which the heavy species translational mode energy is substantially less than the vibrational mode energy. Such conditions occur when the average energy of the vibrational modes is typically a few tenths of an electron volt per oscillator and the gas kinetic temperatures are of the order of several hundred Kelvin. With somewhat higher energy loading of the vibrational modes, the disequilibrium can be sustained at temperatures exceeding 1000 K, as will be shown in this paper. For such conditions, the vibrational quantum level populations of many diatomic and small polyatomic molecular gases are strikingly non-Boltzmann. This population distribution, when compared with a Boltzmann distribution corresponding to the same energy, is characterized by extreme overpopulation of the higher vibrational quantum states. Upper state populations may be many orders of magnitude greater than the populations of the corresponding Boltzmann distribution. Such nonequilibrium distributions are variously called "Treonar distributions", "vibration–vibration (V–V) pumped distributions", or "anharmonic pumped distributions", and have an extensive literature [1–3].

The nonequilibrium plasma conditions necessary to create V–V pumped distributions are pervasive in most collision-dominated electric glow discharges. Since many plasma chemical, ionic, and electronic energy transfer processes proceed from higher molecular vibrational states, the influence of this type of disequilibrium is critical, and its detailed considera-
tion is essential to predicting a variety of plasma chemical phenomena.

V-V nonequilibrium is also created in many supersonic flows of high enthalpy gases [4] and in the optical excitation of cool absorption cells [5–8], in addition to its creation in electric discharges. In absorption cells, the phenomenon has been observed in both solid [6,7] and liquid [8] phase materials, in addition to gases. At this writing, V-V pumped nonequilibrium and its effects have been detected in a variety of molecular systems, including N₂, CO, NO, H₂, D₂, HF, I₂, CO₂, H₂O, N₂O, and ¹³CH₃F [2,3]. Indeed, in the type of environments cited, it is usually difficult to inhibit the creation of a V-V pumped distribution for these small molecules.

Much of the research on V-V pumping effects has centered on their role in carbon monoxide gas lasers and closely related laser systems [9]. More general investigations in molecular discharge plasmas include the work of Capitelli and co-workers [10,11], the work of several Soviet groups [12–16], and studies at the Advanced Plasma Group at the USAF Aerospace Propulsion Laboratory [17,18]. The work of these groups provides strong evidence that V-V pumped nonequilibrium systems afford a major avenue to drive unique plasma chemical reaction paths and also afford a method to produce large populations of excited molecular electronic states in a collision-dominated, high-density plasma. The plasma chemical applications have, for example, great potential importance in microelectronics and detector fabrication processes [18] and in atomic-hydrogen power engineering [12]. The control of excited molecular electronic state populations has a corresponding potential for high-voltage switching applications and high-energy gas lasers [17,19–21].

A major difficulty in studying these V-V pumped processes in detail in electric discharges is that the relatively small fraction of rather high energy electrons can initiate many excited electronic state, ionization, and chemical processes, independently of the more dominant vibrationally excited state processes. It is difficult to determine the major energy storage and transfer paths in such a plasma in view of the large number of relatively minor plasma processes occurring. These minor processes contribute to the radiation signal from the plasma, often giving a misleading picture of the true energy partition in the environment. For this reason, the present study, at The Ohio State University and at Laboratoire d'Energetique Moleculaire et Macroscopique Combustion at Centrale Paris, centers on experiments in optically excited V-V pumped nonequilibrium gases. A carbon monoxide (CO) gas laser is used to excite the vibrational mode of diatomic molecules (CO and NO) in a reaction cell by resonant absorption of the laser radiation and subsequent redistribution of vibrational energy by V-V exchange collisions. In our experiments, conditions can be created such that the influence of free electron–molecule collision processes is negligible, and the major vibration-to-vibration, vibration-to-electronic, and chemical reaction channels can be conveniently studied. In the present paper, our recent results on V-V pumped CO are discussed; previous work with this technique has been published for both CO [5,22,23] and for NO [24].

2. Experimental

2.1. Apparatus

Fig. 1 shows the typical setup for the experiment, as used at Ohio State. The infrared and visible UV emission spectra of the observed molecules (CO and C₂) can be observed simultaneously as shown in the figure. At CNRS Centrale Paris only one port of the cell is used and the diagnostic apparatus is not the same; notably, a larger 1.15 m focal length SOPRA monochromator is used. This monochromator is equipped with an IR (4 μm) or UV (2500 Å) blazed grating so that the spectra emitted by the different molecules at different wavelength regions are recorded successively. As the pump laser is used in the cw mode only, the mechanical chopper is placed in front of the entrance slit of the monochromator. The lock-in amplifier is connected to a PC type microcomputer for further processing and display; the computer also drives the stepping motor of the monochromator, so that the spectrum can be recorded directly as a function of the wavelength.

The pump laser is a flowing-gas electric discharge CO laser, wall-cooled by a liquid nitrogen bath. The laser combines several features reported in the literature [25–29] for enhancing short-wavelength operation, i.e. forcing lasing on the lowest fundamental
vibrational band components, including $\nu = 1-0$. These features include: precollection of the laser gases before they are introduced into the discharge tube; pure helium gas injection at the tube ends to prevent absorption losses due to partially relaxed CO; small gas injectors which introduce the laser gases at sonic velocity into the tube and impart a swirling motion to the gases; a mechanical chopper to provide intracavity $Q$-switching; selectively coated laser mirrors; and optimization of the laser gas partial pressures and discharge operating current. With these features, the Ohio State laser, which has 1 m active discharge length, can produce 3 W average multiline power when lasing on $\nu = 1-0$ transitions, and up to 12 W multiline when $\nu = 2-1$ is the shortest wavelength lasing band component. The longest wavelength band component typically lasing is $\nu = 12-11$. The short wavelength operation is essential for optically exciting room temperature CO; if the shortest wavelength lasing band component is $\nu = 5-4$ or higher, it is impossible to initiate the CO vibrational excitation process. The Centrale Paris laser, which has a 1.64 m active discharge length, has mostly been operated in the cw mode for the present experiments, which have been conducted as discussed below, at powers up to 27 W. Fig. 2, taken from the Centrale Paris laser, shows the typical output spectrum from these lasers under 27 W cw conditions. Note that the rotational number of the lasing lines decreases with the vibrational band; this is a consequence of lasing-induced cascade [23].

Under $Q$-switched operation, the pulse-to-pulse broadband power output stability is quite good, with variations being less than $\pm 2.5\%$ over the entire pulse shapes. The long-time amplitude stability, over periods up to a few hours, is of the same magnitude as long as the liquid nitrogen level is maintained in the cooling baths. The single-line stability of the laser is poorer than the numbers just mentioned. For the present purposes of optically exciting the vibrational mode of the CO in the absorption cell, however, the broadband stability is the important parameter, and is quite satisfactory.

The development of a multiwatt, slow-flow, wall-cooled CO laser, providing a significant fraction of its output in the $\nu = 1-0$ and $\nu = 2-1$ band components, affords a novel opportunity to study V–V pumped gases. Relatively high pump laser powers are necessary to excite significant volumes of gas at pressures of several Torr and above. Most previous detailed spectroscopic studies of V–V pumped CO gas used large, supersonic-flow CO lasers [30], which were expensive to run for long times [5,22,31–32]. Except for the recent work of Urban et al. [23], other
attempts to excite V–V pumping in CO with a slow-flow laser required auxiliary discharge excitation [33]. The present experiments can be operated continuously, permitting sampling times of hours, if necessary.

After some preliminary studies done to test the efficiency of the pumping of CO by the infrared CO laser as a function of laser power, Q-switch and cw modes, Ar–CO gas mixture composition, pressure and flow rate through the cell, we decided to build two complementary setups. The details of the absorption cells are given in fig. 3. At Ohio State (fig. 3a) the cell is built to achieve CO pumping at low flowing rate, medium laser power and relatively low temperature, 300 to 700 K. The cell is a six-armed stainless steel cross (Varian Corp.) of 1.5 inch diameter tubing, permitting optical access on three axes. One or more of the six windows can be replaced by a flange for mounting diagnostic equipment, if desired. The cell has gas fill and purge ports and fittings for pressure measurements. It can be operated either with static gas fills, or in a flowing-gas mode; CO fills the entire volume of the cell. In the flowing gas mode the gas mixture flows in the direction of the incoming laser beam.

At Centrale Paris (fig. 3b), the cell makes it possible to run at the higher translational temperatures associated with a more powerful laser. The temperature can vary from 600 to 1500 K, as described later.
It is a four-armed stainless steel cross of 25 mm diameter tubing, allowing access in two perpendicular directions. The viewing axis is perpendicular to the direction of the laser beam. The output window on the laser beam is adjusted at Brewster’s angle in order to avoid reflection of the high-power laser beam back into the cell. The CO–Ar gas mixture is injected perpendicularly to both the optical axis of the laser and to the detection direction through a 4 mm diameter stainless steel tube. The mixture is extracted through a similar tube placed at 8 mm distance opposite the injector exit. A buffer gas (Ar) is injected by a third inlet to fill the entire cell and pumped out by the same tube as the CO–Ar mixture. With this arrangement CO is present and excited only in the 4 mm i.d. region located between the injection and the evacuation tubes. The pressure is measured in the injection tube, 2 cm before injection in the cell.

As shown, diagnostics include infrared and visible/ultraviolet monochromators, for emission spectroscopy. Steady-state signals are processed with lock-in amplifiers, and pulsed signals with a boxcar averager. The cw and average laser powers and laser pulse energies are measured with a Coherent Corp. “Labmaster” system. Laser pulse shapes are determined with a Molecron P5-00 ultra-fast pyroelectric detector. Modifications from this basic setup are noted in the discussions of specific measurements in the following sections.

2.2. Operation and energy flow channels

With this setup, the CO laser beam is focused by a 2.5 cm diameter, 20 cm focal length zinc selenide lens into the absorption cell. A mixture of CO and Ar is slowly flowing through the cell. As discussed subsequently, the partial pressures of the CO and Ar can be varied over a large range; a typical condition is a 1/9 CO/Ar volumetric ratio at 100 Torr total pressure, with a flow velocity of 1 cm/s. Under such conditions, the CO in the cell readily absorbs the laser energy into its lowest vibrational states, ν ≤ 12. Higher CO vibrational states, ν > 12, are populated by V-V exchange. One result of this V-V up pumping is immediately seen in the absorption cell: there is a quite intense blue light emission visible, centered at the focal point of the laser beam, and extending for approximately 2 to 3 cm along the optical axis. The diameter of this luminous region varies with the cell and laser conditions; it is of the order of 1 to 2 mm. This blue emission is due to visible band components of the C₂ Swan system, d³Π_u → a³Π_u. The C₂ is generated by chemical reaction of the V-V pumped CO. It has been observed and discussed in previous work using this excitation technique [5,22,23,31,32].

Fig. 4 is a simplified energy level diagram for CO, showing the ground electronic state, X ¹Σ⁺, the lowest excited electronic state, a³Π, and the lowest excited singlet state, A ¹II. Several additional triplet states with energies between those of the a³Π and the A ¹II states have not been shown. Some of the energy transfer mechanisms occurring in the cell are shown, based on both the present work and the previous studies referenced above. We show the primary excitation transitions, which involve resonance absorption of the laser radiation by the ν = 0–1 to ν = 11–12 fundamental infrared band components of the CO in

![CO potential energy diagram](image_url)

**Fig. 4.** CO potential energy diagram. Shown are the main energy transfer processes between the vibrational levels of the X ¹Σ ground state, the first excited singlet state A ¹II and the lowest triplet state a³Π.
the cell. Note that in the excitation of CO initially in equilibrium at 300 K, some laser output in the \(v=1-0\) or, at least, the \(v=2-1\) band component, is needed; levels above \(v=1\) are negligibly populated at this temperature, and hence do not absorb. In our case, if the laser does not operate cw on these lowest band components, \(Q\)-switching the laser can often force these components. \(Q\)-switching the laser created higher peak powers in the higher bands than in the cw case. With \(Q\)-switching, lasing-induced cascade can force gain in the lowest vibrational band components. Such use of \(Q\)-switching to achieve CO pumping in an optical absorption cell was first demonstrated by Urban et al., who discuss the phenomenon [23]. In the present experiments, if the laser is operating cw, with no lasing output in the lowest two band components, the cell gases will not absorb the laser radiation. However, it is usually possible to trigger the initial absorption by merely briefly blocking one laser mirror intracavity. The cascade induced by this \(Q\)-switch is sufficient to trigger absorption and the subsequent \(V-V\) up-pumping; the cell gases will continue to absorb in the steady state, until the laser beam is interrupted. We emphasize that the laser excitation mechanism is, indeed, resonance absorption. The focused laser fields are relatively weak. Strong absorption and subsequent \(V-V\) up-pumping occur with focused laser field intensities of only a few hundred W/cm\(^2\). The strongest fields in the present experiments are \(2.7 \times 10^5\) W/cm\(^2\), reached in some of the Centrale Paris studies. We believe that even with these intensities, negligible multiphoton absorption is occurring, given the low density of states in the CO molecular absorber.

Also shown in fig. 4 are the \(V-V\) pumping transitions, created when two CO molecules collide and exchange a quantum of vibrational energy. These processes are typically much more rapid than the rate of energy absorption from the excitation laser, and very much more rapid than \(V-T\) deactivating collisions or spontaneous radiative decay. As indicated in the figure, vibrational levels up to approximately \(v=40\) have been observed to be populated by the \(V-V\) process. It was first specifically noted by Farrenq et al. [34] in \(V-V\) pumped CO in an electric discharge that levels above \(v=42\) are not populated in the \(V-V\) pump. This same limit appeared to occur in previous optically excited experiments [23,31,32], despite the fact that the dissociation energy of the CO \(X^1\Sigma^+\) state is 11.09 eV and there are 40 additional bound vibrational levels above \(v=42\) in the Morse oscillator model of CO. This limit on the up-pump appears to be a consequence of rapid \(V-E\) transfer into the \(A^1\Pi\) state, which is approximately isoenergetic with \(v=41\). It should be emphasized, however, that the mechanism coupling the \(X^1\Sigma^+\) and \(A^1\Pi\) states has not yet been detailed. In any case, the CO \(A^1\Pi\) state rapidly radiates in the CO fourth positive UV emission bands (10 ns lifetime), effectively putting a cap on the \(V-V\) up-pump [22,23,31,32,34]. In the present experiments, emission from vibrational bands to \(v=40\) have been observed at Ohio State University (OSU) and to \(v=27\) at Centrale Paris. The highest significantly populated vibrational level has not yet been determined for either of these experiments.

Also shown in fig. 4 is the \(a^3\Pi\) state. There is also some energy transfer into this state from the \(V-V\) pumped \(X^1\Sigma^+\) states; reaction from the \(a^3\Pi\) state is presumably a major channel for the production of the \(C_2\) that is observed in emission [3,5,22,23,31,32,34]. Unlike the transfer into the \(A^1\Pi\) state, however, transfer into the \(a^3\Pi\) state does not stop the \(V-V\) up-pump; the radiative lifetime of the \(a^3\Pi\) state is long (4 ms) and the chemical reaction and any other quenching channels are not sufficiently rapid to provide a major energy sink. Nevertheless, perturbation of the steady-state \(V-V\) pumped \(X^1\Sigma^+\) state vibrational populations due to this transfer have been observed in high-resolution FTIR spectroscopic studies in electric discharges [34].

Our previous studies of CO laser-excited, \(V-V\) pumped, gaseous CO have yielded data on the rates for some of these processes at moderate translational/rotational mode temperatures, below 370 K [22]. More recent work has indicated that the \(V-V\) up-pump can occur at higher temperatures, of the order of 800 K [23]. The present study independently confirms that the results of ref. [23] are at 800 K and extends the results to 1500 K translational/rotational mode temperature; strong up-pumping is still occurring at these surprisingly elevated temperatures. This is discussed further in section 4.
2.3. Translational/rotational mode temperature measurement

2.3.1. \( \text{C}_2 \) Swan emission – OSU

In contrast to the emission from electric-discharge-excited CO plasmas [35], there are few band systems emitting in the visible and near-ultraviolet wavelength regions from the vibrationally pumped gases in the present experiments. By far the strongest system at these wavelengths is the \( \text{C}_2 \) Swan system. Fig. 5 shows a typical spectrum from one sequence (\( \Delta \nu = 0 \)) of this band system. The R-branch of the \( v=0 \rightarrow 0 \) sequence is rotationally resolved; the closely spaced multiplet structure is not separated. The values of \( J' \) for each line are indicated in the figure. The radiative lifetime of the \( \text{C}_2 \) d \( \tilde{\Pi}_u \) state is sufficiently long (\( \mathcal{O}(1 \mu s) \)) to ensure that these states are rotationally equilibrated, and, therefore, the intensity distribution of these lines can be used to infer the rotational mode temperature. Under the entire range of operating densities in the absorption cell, rotational mode relaxation is sufficiently rapid to ensure that this temperature is equilibrated to the translational mode temperature and the CO rotational mode temperature. Fig. 6 shows the usual semi-logarithmic plot to determine this temperature, for the spectrum of \( \text{C}_2 \) Swan band component intensities. (□) Experimental. (—) Linear regression.

Fig. 5. The pump laser was operating at 7.5 W cw power and the gas pressures in the cell were 9 Torr CO and 51 Torr Ar. The gas temperature is inferred as 753 K. Over the range of cell temperatures in the present (OSU) experiments, the accuracy of this measurement is estimated to be ±50 K.

2.3.2. CO first overtone emission – Centrale Paris

At Centrale Paris, temperature measurements have been performed by fitting the CO first overtone emission. The cell is filled with Ar under a total pressure of 240 Torr, and pure CO is injected at the center of the absorption cell at a speed of 1 m s\(^{-1}\). The pump laser is operating at 27 W cw power. Fig. 7 shows a portion of the first overtone spectrum, which corresponds to emission from CO vibrational levels \( v=4 \) to 8. The apparatus function of the monochromator is a triangle with a half width at mid height (hwhm) of 1.3 cm\(^{-1}\), so that the lines of a given vibrational transition, which are distant about 4 cm\(^{-1}\), should be well separated. Nevertheless, the badly resolved rotational structure demonstrates that there is a significant overlapping of the different bands and gives evidence that the levels of high \( J \) are populated. This is confirmed by the large emission in the band heads and proves that the temperature is high.

In order to deduce the rotational temperature and the vibrational distribution, we make a fit of the ex-
Experimental spectra, as first suggested by Horn and Oettinger [36]: when assuming that the rotational mode is at equilibrium at the translational temperature $T$, the theoretical intensity of the emission is given by

$$I^m(\sigma) = \sum_{\text{all bands} \ (v=2)} N_v U_v(\sigma, T),$$

(1)

where $N_v$ is the total population of level $v$, $\sigma$ is the wavenumber, and $U_v(\sigma, T)$ results from the contribution of all the rotational lines within the band $(v, v-2)$ and is convoluted with the apparatus function. Under our experimental conditions, the line shape is a Voigt profile with hwhm of typically $10^{-2}$ cm$^{-1}$. Since this value is much smaller than the width of the spectrometer apparatus function ($1.3$ cm$^{-1}$), one can calculate $U_v(\sigma, T)$ by using Dirac lines; this leads to:

$$U_v(\sigma, T) = \sum_{J, J'} \sum_{v=2} \left( A^{vJ}_{v-2J} \frac{2J+1}{Q_v(T)} e^{-F_v(T)/kT} \right)$$

$$\times h \sigma^{v-J}_{v-2J} \tau_{\text{mono}} (\sigma - \sigma^{v-J}_{v-2J}),$$

(2)

with $J' = J+1$ for the P-lines and $J' = J-1$ for R-lines; $\sigma^{v-J}_{v-2J}$ is the wavenumber of the transition $(v, J) \rightarrow (v-2, J')$ [37], $A^{vJ}_{v-2J}$ is the Einstein coefficient for spontaneous emission [38], $F_v(J)$ is the rotational part of the energy of the level $(v, J)$ [37] and $\tau_{\text{mono}}$ is the apparatus function.

$N_v$ and $T$ are then deduced from the experimental spectra, sampled in $n$ points $(\sigma_i, I^\text{exp}(\sigma_i))$, by using eqs. (1) and (2) and by minimizing the quantity

$$\sum_{i=1}^n \left[ I^m(\sigma_i) - I^\text{exp}(\sigma_i) \right]^2.$$  

(3)

In order to solve this separable nonlinear least-squares problem ($N_v$ is a linear parameter and $T$ is a nonlinear one), we use a technique based on the theoretical developments by Golub and Pereyra [39]. This method, contrary to that of Horn and Oettinger [36] or De Benedictis et al. [40], has the advantage of being non-iterative and thus does not require an arbitrary assumption for the initial shape of the $N_v$ distribution.

Fig. 7 shows the experimental spectrum (EXP) and the calculated spectrum with the fitted values of $N_v$ and $T$ (TH). The discrepancies remain less than $5\%$, except in spectral regions where absorption lines of water vapor in the optical path coincide with emission lines of CO. The regions, like that between 4000 and 4160 cm$^{-1}$, where the absorption by laboratory air does not perturb the fitting procedure, are unfortunately too narrow to allow a correct determination of all the vibrational populations, but permit a reliable measurement of temperature. In the conditions
of fig. 7, the deduced temperature is 1500 K (± 100 K).

Recordings of experimental spectra between 3100 and 3300 cm\(^{-1}\) show that levels up to \(\nu=27\) are significantly populated. This efficiency of V–V pumping is remarkable when considering the high rotational temperature obtained in the present experiment.

2.3.3. \(\text{C}_2\) Swan emission – Centrale Paris

The rotational temperature has also been inferred from the R-branch of the \(\text{C}_2\) Swan \(\Delta \nu=0\) emission spectrum, as discussed in section 2.3.1. This leads to a temperature of 1450 ± 100 K, in very good agreement with that obtained from IR measurements. Fig. 8 shows the \(\text{C}_2\) Swan band emission spectra for these elevated rotational temperatures. It is important to note that, when the pump laser power is set to that used in OSU (6 W cw), the rotational temperature deduced from the \(\text{C}_2\) spectra is 660 ± 50 K. This value is in quite good agreement with the OSU measurements, given the different flow geometry.

2.4. Vibrational band emission measurements

The rate of the V–V up-pump is of considerable interest, in view of the high rotational/translational mode temperatures of the present experiments. Previous measurements of V–V exchange rates among high vibrational levels in CO have been at temperatures of 370 K and less [22]. In the OSU apparatus, the excitation laser was Q-switched with an intracavity chopper, and the response of the CO in the cell to the pulsed energy input was investigated. Fig. 9 shows the shape of the Q-switched laser pulse, when the laser was chopped with a 50% duty-cycle chopper at 200 Hz. Fig. 9a shows the entire pulse shape; pulse duration is 2.5 ms. The initial spike created by the cavity dumping is evident.

To investigate the rate of V–V up-pumping, the infrared monochromator was positioned at a wavelength centered on a preselected first overtone vibrational band component. The output of the InSb detector in the monochromator was directed to a gated boxcar averager. This infrared signal was monitored at selected time intervals during the laser excitation pulse. A 15 µs gate was typically used and 3000 pulses were averaged at each time interval. Fig. 9b shows an enlargement of the initial portion of the laser pulse and shows the 15 µs gate positioned at approximately 0.2 ms before the pulse.

Fig. 10 shows the time-dependent first overtone emission signal obtained by this means, with the monochromator centered at four selected wave-

![Fig. 8. \(\text{C}_2\) Swan bands, \(\text{d}^3\Pi_u \rightarrow \text{a}^3\Pi_u, \Delta \nu=0, -1, -2\) sequences, Centrale Paris experiment.](image-url)
Fig. 9. Q-switched laser pulse oscillograms. (a) Laser pulse shape observed with the fast pyroelectric detector. (b) Enlarged initial position of the laser pulse and 16 μs gate signal.

lengths. As indicated in the figure, the selected wavelengths correspond to the centers of the $v=4-2$, $v=19-17$, $v=35-33$, and $v=39-37$ band components. The cell conditions for these data are given in the figure. It is important to note that for these pulse conditions 100% modulation is not attained at any of the four selected wavelengths; the vibrational relaxation times, even when catalyzed by reaction products, are sufficiently long so that even the highest vibrational states monitored remain partially populated during the 2.5 ms laser-off period. This rather large vibrational heat capacity effect ensures relatively small fluctuations in the rotational/translational mode temperature during the pulse. The average rotational/translational mode temperature, measured by the C2 emission diagnostic discussed above, is 740 K. The sequential rise of each progressively higher band component can be seen; the rise times, of the
order of 0.1 ms, are in contrast to those observed in lower-temperature experiments [22]. These fast rise times are a consequence of the faster \( V-V \) rates at the present temperature.

Very high-energy loading of the vibrational mode can be obtained in these experiments, which permit \( V-V \) up-pump despite the high translational/rotational mode temperatures. Fig. 11 shows low-resolution first overtone emission spectra from the pumped CO for CO concentrations varying over two orders of magnitude. For these data, the cell gases are diluted by Ar; the Ar concentration is approximately constant at \( 3 \times 10^{18} \) cm\(^{-3} \). The centers of the vibrational band components are indicated in the figure. The maximum bandpass for this resolution is approximately 0.25 \( \mu \)m; this implies that approximately five adjacent vibrational states contribute to the emission at a given wavelength. Emission is measured to \( \approx 4.4 \) \( \mu \)m, at which wavelength the R-branch of the \( v=1-0 \) band component of the CO fundamental begins and swamps signal from the overtone, as can be seen. Air in the optical path causes significant H\(_2\)O absorption in the 2.4 to 2.8 \( \mu \)m region and significant CO\(_2\) absorption from 4.2 to 4.4 \( \mu \)m. The CO\(_2\) absorption and the overlap of the fundamental are particularly unfortunate diagnostic complications, since they prevent determination of the highest populated vibrational level from these low-resolution spectra. Nevertheless, it is evident that levels to at least \( v=40 \) are populated for all CO densities shown in the spectra of fig. 11.

For the data of fig. 11, the absorbed power decreased slightly with increasing number density, varying from 1.2 W at the highest CO concentration to 1.0 W at the lowest concentration. This near-constant absorbed power for the greatly varying number density implies that the vibrational mode energy loading per CO molecule is greatly increasing with decreasing concentration. This is confirmed by the emission spectra. It can be noted that, although the overall emission intensity can decrease with decreasing CO concentration, there is a marked increase in the relative population of the higher states with such decreasing concentration. For example, taking the ratio of the intensities of 2.40 and 3.25 \( \mu \)m implies an increase in \( n_{45}/n_4 \) of more than a factor of two as the CO density is decreased over the range shown.

![Graph](image-url)

**Fig. 10.** Time dependence of the first overtone emission (intensity normalized) after pulsed excitation for selected wavelengths, laser pulse duration of 2.5 ms. (■) 2440 nm (\( \sim v=4-2 \)); (△) 2975 nm (\( \sim v=19-17 \)); (○) 3850 nm (\( \sim v=35-33 \)); (•) 4200 nm (\( \sim v=39-37 \)).
2.5. Ionization measurements

It was proposed by Polack et al. [41] that an associative ionization mechanism involving vibrationally excited diatomic molecules could occur by the following scheme:

\[ \text{AB}(v_1) + \text{AB}(v_2) \rightarrow \text{AB} + \text{AB}^+ + e^- \]

if \( E(v_1) + E(v_2) > E_i \),

where \( \text{AB}(v) \) is the molecule in the \( v \)th vibrational state with energy \( E(v) \) and \( E_i \) is the ionization energy. The reverse of this reaction is a form of the well-known dissociative recombination mechanism which is a major mechanism controlling the electron concentration in many molecular plasmas [42]. The work of ref. [41] specifically studied \( \text{N}_2 \) plasmas, and a specific rate of the ionization of \( \text{N}_2 \) by this mechanism was inferred experimentally. A major difficulty in studying this process in an electric discharge plasma is that there are several ionization mechanisms operating in addition to eq. (4), and separation of this single-ionization process can be ambiguous. However, Achasov et al. [43] have done ionization measurements in the adiabatic supersonic nozzle expansion of shock heated \( \text{N}_2 \) and CO. As noted in section 1, such rapid expansions of high-enthalpy flows can create the requisite nonequilibrium conditions (high vibrational mode energy, low translational/rotational mode temperature) strongly favoring the \( \text{V-V} \) up-pump. This study, having been conducted in a discharge-free environment with negligible thermal ionization, clearly showed electron production in both \( \text{N}_2 \) and CO by mechanism of eq. (4). Electron concentrations several orders of magnitude above the concentration predicted by the Saha equilibrium were measured in the expansion.

The present experiment also shows ionization in CO by the mechanism of eq. (4). For these ionization measurements, two parallel brass plate electrodes were placed in the absorption cell. One plate was on each side of the luminous region of the \( \text{V-V} \) pumped gas, centered on the focal point of the laser beam. The total plate separation was 2 cm; each plate was a \( 1 \times 2 \) cm rectangle. The long dimension of the plates was along the laser beam axis. A dc voltage was applied to these electrodes. Under all cell operating conditions in which significant \( \text{V-V} \) pumping was produced, a current could be drawn through the gas with moderate voltages applied; the voltages were much below the breakdown threshold for the cell gases. Currents were measured with a microampere-
meter. Fig. 12 shows typical voltage–current characteristics for one experiment. For this case, the CO/Ar concentration ratio was 4/69, and the cell pressure was varied from 60 to 500 Torr. The laser power was 5.1 W cw. From the measured currents, the electron concentration can be estimated from

$$n_e = I/A_e u_e,$$

where $I$ is the measured current, $A_e$ is the estimated collection area, and $u_e$ is the electron drift velocity for the applied $E/N$. The electron densities calculated from eq. (5) are in the range of $10^7$ to $10^8$ cm$^{-3}$ for a plasma area of 0.1 cm$^2$, for the data of fig. 12.

The measured currents, though small, can definitely be correlated with the volume ionization created by the laser excitation, via the mechanism of eq. (4). The possibility of photo-ionization of the plates, by UV radiation from excited CO electronic states (fig. 4), was excluded by surrounding the active pumped region in the cell by a 1 cm diameter UV grade quartz tube. Negligible currents could be drawn at all applied voltages with this arrangement. Some checks were also made for the possibility of an easy ionizable impurity creating electrons by ionizing collisions with highly vibrationally excited CO. Measurements with ultra-high purity CO and with liquid nitrogen trapping of the test gases before the cell did not show substantially lower ionization.

Finally, some preliminary experiments were performed to examine the response of the current to the pulsed operation of the laser. Fig. 13a is an oscillogram of the laser pulse, taken with the fast photodiode, and the current response. The modulation of the population of vibrational level $v=22$ was simultaneously monitored in these experiments by use of a narrow bandpass filter centered at 3.05 μm. This response is shown in fig. 13b. In all cases, the rise in the current was subsequent to the rise in $v=22$ emission. The plasma decays after the laser pulse with times of the order of a few milliseconds. This is unexpectedly rapid when compared to known associative recombination times for CO molecular plasmas [44]. The presence of an impurity which is a strong electronattacher is suspected. As discussed in ref. [44], iron pentacarbonyl, Fe(CO)$_5$, generated during storage of the CO test gas in a steel cylinder is suspected. Further experiments with traps to eliminate electron-attaching impurities are planned.

3. Kinetic modeling

A master equation kinetic model has been previously developed and applied to V–V pumping exper-
iments in CO and NO [22–24]. The earlier work on CO has been used to correlate experiments at temperatures below 370 K [22] and led to specific V–V rate model expressions valid over a temperature range 150 \( \leq T \leq 370 \) K and a vibrational quantum number range 0 \( \leq \nu \leq 35 \). This rate expression is also in agreement with the experiments and model rates of Powell [45], which includes some data to 500 K.

The previous model has been further developed and applied to the present experiments. A major question is whether the V–V rate expressions, obtained from lower-temperature data, are valid for the present elevated temperatures. We have applied the model to two of the experimental cases discussed in the previous section: the steady-state experiment at 1500 K (section 2.3) and the \( Q \)-switched pulse experiment at 740 K (section 2.4).

The numerical results presented in this section were obtained with a computer program which integrates the full set of kinetic equations describing the vibrational level populations in each electronic state as a function of time. Rapid integration of some seventy vibrational level equations relies upon efficient “stiff” equation integration routines [46,47].

3.1. Equations

A description of the master equation kinetic model employed in the present study has been given previously [22–24]; therefore only a brief summary is included here. The time dependence of each vibrational level in up to two coupled electronic manifolds is expressed as a sum of five rate processes:

\[
\frac{dn_{i\nu}}{dt} = VV_{i\nu} + VT_{i\nu} + SRD_{i\nu} + VE_{i\nu} + PL_{i\nu},
\]

\( i = 1, 2, \nu = 0, 1, ..., (v_{\text{max}})_i \), (6)

where \( n_{i\nu} \) (also written \( n_i(\nu) \)) is the number density of molecules \( i \) in vibrational quantum level \( \nu \), in cm\(^{-3}\); \( i = 1, 2 \) represents the ground state and one electronically excited state of CO, respectively; and \( (v_{\text{max}})_i \), is the highest level included in the vibrational manifold, where \( (v_{\text{max}})_i < 80 \). Allowance is also made for an inert diluent, which in the present case is argon. The translational and rotational modes of the system are assumed to be in equilibrium at temperature \( T \).

On the right-hand side of the above equation \( VV_{i\nu} \) is the vibration–vibration exchange rate, \( VT_{i\nu} \) is the vibration–translation exchange rate, \( SRD_{i\nu} \) is the spontaneous radiative decay rate, \( VE_{i\nu} \) is the vibration–electronic exchange rate, and \( PL_{i\nu} \) is the absorption and stimulated emission rate due to the CO pump laser. In our calculations the VV term is the sum of a long-range dipole–dipole Sharma–Braun term and a short-range impulsive Schwartz–Sawsk–Herfeld (SSH) term [48]. The VT rate used is a modified SSH model [49,50]. The VE term employs an analytical form based on a collision-induced near-resonance exchange mechanism [24]. Appendix A gives the actual VV, VT, VE, SRD and PL expressions used.
3.2. Input values

All the parameters needed in the calculation of the VV, VT, VE and SRD rates are given in tables 1 and 2. Table 2, in particular, gives the spontaneous electronic radiative transition rates from the electronic excited A 1Π state of the electronic ground level of CO. The spectroscopic parameters used in the computation of PL are given in table 3. These parameters are directly taken from Huber and Herzberg [51].

The input values characterizing the experiment are the temperature, the gas partial pressures in the cell, and a precise description of the laser pulse, which includes the power, the focus, the shape and the wave-

<table>
<thead>
<tr>
<th>Species \ VT</th>
<th>A_k</th>
<th>B_k</th>
<th>C_k</th>
<th>Θ_k/Θ' (K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-CO</td>
<td>-15.23</td>
<td>280.5</td>
<td>-549.6</td>
<td>45.6 10⁻²</td>
</tr>
<tr>
<td>CO-Ar</td>
<td>10.38</td>
<td>0.0</td>
<td>0.0</td>
<td>1.335 10⁻³</td>
</tr>
<tr>
<td>Species \ VV</td>
<td>S_k (K⁻¹)</td>
<td>L_k (K)</td>
<td>b_k (K)</td>
<td>Θ_k/Θ' (K⁻¹)</td>
</tr>
<tr>
<td>CO-CO</td>
<td>1.64 × 10⁻⁶</td>
<td>1.6142</td>
<td>40.36</td>
<td>45.6 10⁻²</td>
</tr>
<tr>
<td>Species \ VE</td>
<td>C_νν</td>
<td>S_νν (cm²/s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO-CO</td>
<td>5.49 × 10⁻²</td>
<td>9.94 × 10⁻¹³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Species \ SRD</td>
<td>U*</td>
<td>A¹⁰ (1/s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>4</td>
<td>30.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2
Spontaneous electronic radiative transfer rates, Frank-Condon factors A^νν_{CO(A 1Π→CO(X 1Σ⁺)} (1/s)

<table>
<thead>
<tr>
<th>ν</th>
<th>w</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>1.387×10⁴</td>
</tr>
<tr>
<td>1</td>
<td>2.785×10⁴</td>
</tr>
<tr>
<td>2</td>
<td>2.648×10⁴</td>
</tr>
<tr>
<td>3</td>
<td>1.586×10⁴</td>
</tr>
<tr>
<td>5</td>
<td>2.142×10⁴</td>
</tr>
<tr>
<td>7</td>
<td>1.075×10⁴</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Species</th>
<th>Spectroscopic constants (in 1/cm except ν)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(X 1Σ⁺)</td>
<td>ν_max = 55, ω_u = 2169.8, ω_u,ν = 13.288, T_e = 0.0</td>
</tr>
<tr>
<td>CO(A 1Π)</td>
<td>ν_max = 10, ω_u,ν = 1518.24, ω_p,ν = 19.4, T_e = 6.5 × 10⁴</td>
</tr>
<tr>
<td>Species</td>
<td>PL rate parameters (in 1/cm except d)</td>
</tr>
<tr>
<td>CO(X 1Σ⁺)</td>
<td>ω_u,ν = 1.0511 × 10⁻², ω_p,ν = 5.74 × 10⁻², ω_p,d = 9.83 × 10⁻²,</td>
</tr>
<tr>
<td></td>
<td>ω_u,d = 3.166 × 10⁻⁴, B_u = 1.9313, a_u = 1.75 × 10⁻²,</td>
</tr>
<tr>
<td></td>
<td>χ_u = 5.487 × 10⁻², D_u = 6.12 × 10⁻⁸, β_u = 9.666 × 10⁻⁹,</td>
</tr>
<tr>
<td></td>
<td>d_{CO-CO} = 5.119 × 10⁻⁸ cm, d_{CO-Ar} = 5.0 × 10⁻⁸ cm,</td>
</tr>
<tr>
<td></td>
<td>σ_{CO-CO} = 3.75 × 10⁻⁸ cm</td>
</tr>
</tbody>
</table>
lengths used. These input values are given for each application of the code (see below). The beam focus is a significant input parameter that is not directly measured in the experiment and is therefore treated parametrically in these model calculations.

3.3. cw case

We first apply the code to the calculation for the cw experiments. The cell conditions are: $P_{CO}=24$ Torr, $P_{Ar}=216$ Torr. The wavelengths and spectral power distribution of the excitation laser are listed in table 4 (see also the spectrum in fig. 2). For these conditions, the calculation was begun with the gases initially in a 1500 K equilibrium state. Eq. (6) was integrated until steady state was achieved for the vibrational populations. The calculation was done for two focal diameters, 3.0 and 1.00 mm. Fig. 14 shows the calculated steady-state distribution for these two cases. As can be seen, the model rates predict strong pumping to $v=35$ for the 3 mm focus and to $v=40$ for the stronger 1.0 mm focus. The value 1.0 mm is the focal diameter estimated for the experiments of section 2.3.

![Fig. 14. Kinetic modeling calculation: predicted steady-state vibrational population densities of the V--V pumped CO for two different focal diameters (power densities) of the laser beam, for $T=1500$ K.](image)

<table>
<thead>
<tr>
<th>Frequency lines</th>
<th>rotational numbers</th>
<th>% of power</th>
</tr>
</thead>
<tbody>
<tr>
<td>vibrational number</td>
<td>P15</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>P16</td>
<td>3.3</td>
</tr>
<tr>
<td>V(3–2)</td>
<td>P14</td>
<td>5.2</td>
</tr>
<tr>
<td>V(4–3)</td>
<td>P15</td>
<td>3.9</td>
</tr>
<tr>
<td>V(5–4)</td>
<td>P13</td>
<td>3.4</td>
</tr>
<tr>
<td>V(6–5)</td>
<td>P14</td>
<td>9.3</td>
</tr>
<tr>
<td>V(7–6)</td>
<td>P13</td>
<td>1.0</td>
</tr>
<tr>
<td>V(8–7)</td>
<td>P14</td>
<td>16.5</td>
</tr>
<tr>
<td>V(9–8)</td>
<td>P13</td>
<td>4.6</td>
</tr>
<tr>
<td>V(10–9)</td>
<td>P11</td>
<td>14.8</td>
</tr>
<tr>
<td>V(11–10)</td>
<td>P10</td>
<td>3.4</td>
</tr>
<tr>
<td>V(12–10)</td>
<td>P11</td>
<td>2.1</td>
</tr>
<tr>
<td>V(13–11)</td>
<td>P12</td>
<td>10.5</td>
</tr>
<tr>
<td>V(14–12)</td>
<td>P11</td>
<td>5.2</td>
</tr>
<tr>
<td>V(15–13)</td>
<td>P10</td>
<td>2.1</td>
</tr>
<tr>
<td>V(16–14)</td>
<td>P12</td>
<td>0.6</td>
</tr>
<tr>
<td>V(17–15)</td>
<td>P10</td>
<td>3.5</td>
</tr>
<tr>
<td>V(18–16)</td>
<td>P11</td>
<td>0.4</td>
</tr>
<tr>
<td>V(19–17)</td>
<td>P11</td>
<td>0.7</td>
</tr>
<tr>
<td>V(20–18)</td>
<td>P11</td>
<td>1.5</td>
</tr>
<tr>
<td>V(21–19)</td>
<td>P10</td>
<td>0.3</td>
</tr>
<tr>
<td>V(22–20)</td>
<td>P10</td>
<td>0.5</td>
</tr>
</tbody>
</table>

3.4. Q-switched case

This case models the pulsed experiment of section 2.4, the results of which are given in fig. 10. The cell conditions are: $P_{CO}=6.14$ Torr, $P_{Ar}=103.9$ Torr, $T=740$ K. The laser Q-switched at 200 Hz, with a 50% chopper, giving a 2.5 ms pulse duration with a 2.5 ms off-period. The model pulse shape closely approximates the experimentally measured shape of fig. 9. Note that the laser pulse intensity starts to decrease at 2 ms. The simplifying assumption is made that each lasing spectral line has the same temporal dependence as the total power pulse shape of fig. 9. The total laser power is 2.2 W. Results are calculated for a range of power densities, W/cm², corresponding to varying focal diameters. The solution is started from initial conditions for the cell gas in equilibrium at 740 K. The calculation is continued until there is no pulse-to-pulse variation in the vibrational state populations. Figs. 15 and 16 show the predicted first overtone radiative intensities from four vibrational
levels, $v=4, 19, 35$ and $39$. The intensity is calculated from

$$I_v = (E_v - E_{v-2}) A_{v,v-2} n_v,$$

(7)

where $I_v$ is the intensity from vibrational level $v$, $E_v$ is the energy of this level, and $A_{v,v-2}$ is the Einstein coefficient. Fig. 15 shows these intensities for a power density of 22.0 W/cm$^2$ and Fig. 16 for the lower density of 2.2 W/cm$^2$. The calculated intensities have been referenced to a common zero and then normalized. It can be seen that at the higher power density, the radiative intensity follows the shape of the excitation laser pulse (Fig. 15). The lower power density case, for which the laser excitation rates ($PL_{e\nu}$) are much smaller than the V–V rates ($VV_{i\nu}$) for all levels, does not reflect the shape of the pump pulse and the intensities are in reasonable correspondence with the experimental intensities of Fig. 10.

4. Discussion and conclusions

V–V pumping of vibrational nonequilibrium is generally regarded as a low-temperature phenomenon. It is certainly true that some of the most extreme nonequilibrium vibrational population distributions created by this mechanism have been observed in solid and liquid CO [6–8]. Nevertheless, the key criteria for such disequilibrium are [2]:

(a) The translational temperature must be less than the characteristic vibrational exchange mechanism is dominant: $T < \theta_{\text{char}}$, where $\theta_{\text{char}} = h \nu / k$.

(b) The vibrational “temperature” parameter $\theta^*_v$ must be at least a considerable fraction of the characteristic vibrational temperature if there is to be any significant influence of the excited vibrational states:

$$\frac{\theta^*_v}{\theta_{\text{char}}} \approx [\ln(n_0/n_1)]^{-1} = O(1).$$

(8)

(c) The ratio of the vibrational temperature parameter $\theta^*_v$ to the translational temperature must be considerably greater than one: $\theta^*_v/T > 1$.

It can be seen from this that if the vibrational mode energy loading is sufficiently high, pumping will occur even if the translational mode temperature is a sizable fraction of the characteristic vibrational temperature, $\theta_{\text{char}}$, which is 3.120 K for CO. This is what is occurring in the present experiments. The focused, multimode laser excitation powers provide sufficient vibration mode energy loading to create V–V up-pumping even at translational/rotational mode temperatures up to approximately $\theta_{\text{char}}/2$.

A related issue is the rate of the V–V up-pump. The laser is directly coupled only to the lowest vibrational states, $v \leq 12$. Indeed, at initiation of the V–V pump,
beginning with 300 K CO, there is significant energy absorption only into levels \( v = 1 \) and 2. Higher states, up to at least \( v = 35 \), are populated by the V–V pumping mechanism. It is important to note that for most of the approach to the steady-state nonequilibrium vibrational population distribution the dominant rates are relatively near-resonant processes [23]. For such processes, the specific V–V rate constant, \( Q_{k_{2-1}}^{n} \) (see appendix A), has \(|v-w|\) a small integer. These rates are quite rapid and increase with increasing vibrational quantum number. Both the long-range and short-range processes contribute to the overall rate; the total rates increase rapidly with increasing translational mode temperature. The present specific rate model, as detailed in appendix A, gives pumping times in good agreement with experimental time-dependent emission measurements to translational temperatures of 750 K.

The final feature of the present experiments is the observation of ionization accompanying the production of strongly V–V pumped nonequilibrium distributions. The ionization, although slight, is clearly a consequence of the high-level vibrational excitation of CO. The rapid plasma decay after the laser pulse suggests, as we have noted, that a strongly attaching impurity is present in the cell gases, which is likely to be Fe(CO)₅. Further experiments with trapping of this impurity will be conducted; it is probable that with the removal of impurity attachers, the steady-state electron concentration will be much higher than is measured here. We note, however, that the present low electron concentrations ensure that molecule-electron collision processes cannot have a significant influence on the basic energy transfer processes studied in these experiments.

In conclusion, the high rotational/translational mode temperature at which extreme vibrational disequilibrium can be produced in CO has implications for the chemistry of those plasma reactors using CO and those using N₂, which has a characteristic vibrational temperature and long V–T relaxation times similar to CO. Such plasma reactors include both CO₂/H₂O reactors for H₂ production [12] and N₂/ SiH₄ reactors for silicon deposition [18]. Despite the high rotational/translational mode temperature which can exist in such reactors, V–V pumped nonequilibrium processes can control the reaction kinetics.

Acknowledgement

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Program is gratefully acknowledged. We also wish to thank R. DeLeon, J.M. Hartmann, D. Straub, M. Grassi and J. Hiltner for many helpful discussions and for assistance in the conduct of the experiments.

Appendix A

We introduce \( n_{i,v} \), the number density of the primary species \( i \) in vibrational state \( v \), in part/cc; \( n_{j,w} \), the number density of the secondary species \( j \) in vibrational state \( w \), in part/cc; \( n_i = \sum_v n_{i,v} \), the total number density of species \( i \), in part/cc; and \( n_T = \sum_i n_i \), the total number density of the mixture. In the following, we use the internal energy of molecule \( i \) in vibrational level \( v \) of species \( i \) (in cm\(^{-1}\)): \( E_{iv} = T_{iv} + \omega_v (v + \frac{1}{2}) - \omega_v x_v (v + \frac{1}{2})^2 \), where \( T_{iv} \) (in cm\(^{-1}\)) is the electronic energy and where \( \omega_v \) (in cm\(^{-1}\)) and \( x_v \) (dimensionless) are the spectroscopic constants (fundamental vibrational frequency and anharmonicity, respectively) for molecule \( i \) (see table 3).

A.1. Vibration–translation term

The VT term of eq. (6) is written as

\[
V_{VT} = \sum n_i \left[ P_{ij}^{w+1,v} [n_{i,v+1} - \exp(-\Delta E^w/kT)] n_{j,w} \right] - P_{ij}^{w,v-1} [n_{i,v} - \exp(-\Delta E^w/vT)] n_{j,w-1}] ,
\]

where \( P_{ij}^{w,v-1} \) is the rate constant (in cm\(^3\)/s) of the V–T transition:

\[
X_i(v) + X_j(w-1) \rightarrow X_i(v) + X_j(w) .
\]

\( X_i(v) \) refers to species \( i \) in vibrational state \( v \). The rate constant can be expressed as follows [22,52]:

\[
P_{ij}^{w,v-1} = P_{i,j}^0(T) \frac{v}{1-x_v} \frac{1}{kT} \frac{\Delta E^w}{kT} \exp\left(-\frac{\Delta E^w}{kT}\right) .
\]

\( P \) is a function given by [49]:

\[
F(\lambda) = \frac{1}{4} (3 - e^{-2\lambda/3}) e^{-2\lambda/3} ,
\]

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

\( \Delta E \) is the energy difference (in J) between the products and the reactants in the V–T transition; \( \Theta_{ij} = \hbar c \omega_v / k \) is the vibrational characteristic temperature of species \( j \), where \( c \) is the speed of light (in cm s\(^{-1}\) in all the appendix); \( \Theta_{ij} = 16 \pi \mu_i c^2 \omega_j^2 / k \) is in K [52] where \( \mu_j \) is the reduced mass (in kg) and \( l = 0.2 \times 10^{-10} \) m is the range parameter.

In the rate constant expression, \( P_{ij}^0(T) \) is a coefficient which allows fitting to experimental relaxation time data. It is expressed (in cm\(^3\)/s) as:

\[
P_{ij}^0(T) = \frac{10^{-7}(1-x_v)kT}{(\tau_{ij})F_{ij}^0[1-\exp(-\Theta_{ij}/T)]}
\]

Here \( \tau_{ij} \) is the vibrational relaxation time in atm \( \mu \) (10\(^{-7}\) J s cm\(^{-3}\)) and is given by:

\[
\ln(\tau_{ij}) = A_{ij} + B_{ij} T^{-1/3} + C_{ij} T^{-2/3} .
\]

\( A_{ij} \), \( B_{ij} \) and \( C_{ij} \) are chosen in order to fit the experimental data (see table 1).

A.2. Vibration–vibration term

The VV term, including only the single-quantum transitions, is written as:

\[
VV_{i,v} = \sum_{j,w=0}^{n_{\text{max}}} \left\{ Q_{i,j}^{w+1,v} [n_{i,v+1} n_{j,w}] - \exp(-\Delta E^w/vT) n_{i,v} n_{j,w+1} \right\} - Q_{i,j}^{w,v-1} [n_{i,v} n_{j,w}] - \exp(-\Delta E^w/vT) n_{i,v-1} n_{j,w+1} \right\} ,
\]

where \( Q_{i,j}^{w,v-1} \) is the rate constant (in cm\(^3\)/s) of the V–V transition:

\[
X_i(v) + X_j(w-1) \rightarrow X_i(v-1) + X_j(w) .
\]

The rate constant is the sum of two terms, the first being the contribution of the short-range interactions, and the second the contributions of the long-range forces due to dipole–dipole interaction. The rate is expressed as [22]:

\[
Q_{i,j}^{w,v-1} = Z_{ij} (S_{i,j}^{w,v-1} + L_{i,j}^{w,v-1}) e^{-\Delta E / kT} ,
\]

\[
Z_{ij} = 400 \pi \sigma_{ij}^2 \sqrt{n_k T / 2 \mu_{ij}} ,
\]

where \( Z_{ij} \) is the collision number in cm\(^3\)/s and \( n \sigma_{ij}^2 \) is the cross section in cm\(^2\) (see table 3).

The dimensionless short-range contribution is given by [52]

\[
S_{i,j}^{w,v-1} = S_{i,j}^0 T \frac{v}{1-x_v} \frac{w}{1-x_w} F_{i,j}^{w,v-1} \lambda_{ij}^{w,v-1} .
\]
$F(\lambda)$, $\lambda$, and $\Delta E$ have the same definitions as above. The dimensionless long-range contribution is given by [53]:

$$L_{0,0}^{n,n-1} = \frac{L_0}{T} \left( \frac{g_{i,0}^{n,n-1}}{g_{i,0}^{n,n-1}} \right)^2 \left( \frac{g_{i,0}^{n,n-1}}{g_{i,0}^{n,n-1}} \right)^{-2} \exp \left( -\frac{\Delta E^2}{k^2 T} \right).$$

$S_{ij}^0$ (in $K^{-1}$), $L_0^0$ (in $K$) and $b_{ij}$ (in $K$) are empirical parameters matched to experimental data (see table 1), and

$$\left( \frac{g_{i,0}^{n,n-1}}{g_{i,0}^{n,n-1}} \right)^2 = \frac{(a_i + 1)^2 \nu(a_i + 2 - 2\nu)(a_i + 4 - 2\nu)}{a_i(a_i + 3 - \nu)},$$

where $a_i = 1/x_n$.

### 3.3 Vibration-electronic term

The collision-induced V–E terms are retained only here:

$$VE_{e,v} = n_T \sum_{j=1}^{N_{\text{max}}} \sum_{w=0}^{N_{\text{max}}} S_{j,0}^{n,w}$$

$$\times \left[ \frac{n_{j,w} + n_{j,v}}{} \exp \left[ -\frac{hc(E_{j,v} - E_{j,s})}{kT} \right] \right],$$

where $S_{j,v}^{n,w}$ is the rate constant (in cm$^{-1}$/s) for the collision induced vibration-to-electronic transition:

$$X_v(v) + X_S(w) + X.$$  

$X_v(v)$ and $X_S(w)$ are two electronic manifolds of the same species. Their vibrational states are $v$ and $w$, respectively. It is assumed that collisions can induce the transition from $X_v(v)$ to $X_S(w)$ when the energies of these molecules are very close. The rate constant is modeled with a Gaussian function of the energy defect; the width and the maximum of the Gaussian rate are empirical parameters,

$$S_{j,v}^{n,w} = S_{\text{VE}} \exp \left[ -\frac{\Delta E}{C_{\text{VE}} \hbar \omega_v} \right] \exp \left( -\frac{\Delta E}{kT} \right).$$

The vibrational spectroscopic constant, $\omega_v$, is taken to be the larger of the constants for the two electronic states involved. The adjustable parameters are $S_{\text{VE}}$ (in cm$^{-1}$/s) and $C_{\text{VE}}$ (dimensionless). In the case of $CO(X^1\Sigma^+) \rightarrow CO(A^1\Pi)$ transfer, values of these parameters were obtained by fitting kinetic rate models to V–V up-pumping experiments in optical cells [22–24]. The range of validity of the resonance model above remains to be determined, in detailed state-resolved experiments. The value of these parameters are indicated in table 1.

### A.4. Spontaneous radiative decay term

The spontaneous radiative transfer term is written as

$$SRD_{\lambda,s} = SRVD_{\lambda,s} + SRED_{\lambda,v},$$

where

$$SRVD_{\lambda,v} = \sum_{k=1}^{n^*} \left( \delta_{\lambda}^{*} \right)_{n^*,k} n_{\lambda,k} - \delta_{\lambda}^{*} n_{\lambda,v}$$

is the radiative transition between vibrational levels with the same electronic state, using the Einstein coefficient [54]:

$$\frac{A_{\lambda}^{n^*,u}}{A_{\lambda}^{*}} = \frac{1}{(a_i - 2)(a_i - 3) u(v - u) \prod_{q=0}^{n^* - 1} (b_q - v + q)},$$

with $b_v = a_v - 2\nu - 1$, and $\nu^*$, $A_{\lambda}^{*}$ (in s$^{-1}$) given in table 1; and where

$$SRED_{CO(X^1\Sigma^+),v} = \sum_{w=W_{\text{max}}}^{W_{\text{min}}} \sum_{v=W_{\text{max}}}^{W_{\text{min}}} A_{CO(A^1\Pi),CO(X^1\Sigma^+),v}$$

and

$$SRED_{CO(A^1\Pi),v} = -n_{CO(A^1\Pi),u} \sum_{w=W_{\text{min}}}^{W_{\text{max}}} A_{CO(A^1\Pi),CO(X^1\Sigma^+),v},$$

using the Frank–Condon factors $A_{\lambda}^{n^*,u}$ (in s$^{-1}$) given in table 2.

### A.5. Stimulated emission/absorption term

The stimulated emission/absorption term is written [24]

$$PL_{A^1\Pi,CO(X^1\Sigma^+),v} = 0.$$
\[ P_{L_{COX+1,0}} = (T_{v+1,0}n_{v+1} - T_{v,0}n_v) \]
\[ -(T_{v+1,0}n_{v+1} - T_{v,0}n_v) , \]
where \( T_{v+1,0} \) and \( T_{v,0} \) are the rate constant (in 1/s) of the PL term [24]:
\[
T_{v+1,0} = \frac{1}{8\pi kT} \left( \frac{c}{\nu_{v+1,0}} \right)^3 A_{v+1,0} B_{v+1} \sum_{j} I_{j}(t) \\
\times \left[ \sum_{j=0}^{\text{max}} (J+1)Q_{v}^{R}(\nu_{j}) \exp \left( -\frac{hc}{kT}F_{j,v+1} \right) \right],
\]
\[
T_{v,0} = \frac{1}{8\pi kT} \left( \frac{c}{\nu_{v,0}} \right)^3 A_{v,0} B_{v} \sum_{j} I_{j}(t) \\
\times \left[ \sum_{j=0}^{\text{max}} (J+1)Q_{v}^{R}(\nu_{j}) \exp \left( -\frac{hc}{kT}F_{j,v} \right) \right],
\]
and \( \nu_{v+1,0} = c(E_{v+1} - E_{v}) \) (in 1/s) is the band center frequency, \( I_{j}(t) \) is the pulse height (in W/cm²), \( B_{v} = B - \alpha_{v}(\nu_{v} + \frac{1}{2}) + \gamma_{v}(\nu_{v} + \frac{1}{2})^2 \) (in 1/cm) is the vibrational constant, and the Lorentzian line shape factor is written (in s) [55]
\[
Q_{v}^{R}(\nu_{j}) = \frac{1}{2} \frac{\Delta \nu_{c}}{\pi} \frac{1}{(\nu_{j} - \nu_{v}^{PR})^2 + (\Delta \nu_{c}/2)^2} ,
\]
where
\[
\Delta \nu_{c} = 10^2 \sum_{k} n_{k} d_{CO_k}^{2} \sqrt{kT/\pi \mu_{cO_k}}
\]
(in 1/s) is the pressure-broadened line width, \( d_{CO_k} \) being the optical collision diameter (in cm) and where
\[
\nu_{v+1,0}(J) = \nu_{v+1} + c(F_{j,v+1} - F_{j,0})
\]
(in 1/s) is the center of the absorbing line, with
\[
F_{j,v} = B_{v}J(J+1) - D_{v}[J(J+1)]^2
\]
the rotational–vibrational contribution (in 1/cm) and \( D_{v} = D_{v} + \beta_{v}(\nu_{v} + \frac{1}{2}) \) the rotational constant (in 1/cm). All the different parameters are given in table 3.

**References**


