Time-resolved Fourier transform infrared spectroscopy of optically pumped carbon monoxide

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Abstract

The paper discusses measurements of vibration-to-vibration (V–V) energy transfer rates for CO–CO using time-resolved step-scan Fourier transform infrared spectroscopy of optically pumped carbon monoxide. In the experiments, time evolution of all vibrational states of carbon monoxide excited by a CO laser and populated by V–V processes (up to \( v \approx 40 \)) is monitored simultaneously. The V–V rates are inferred from these data using a kinetic model that incorporates spatial power distribution of the focused laser beam, transport processes, and multi-quantum V–V processes. Although the model predictions agree well with the time-dependent step-scan relaxation data, there is variance between the model predictions and the up-pumping data, however. Comparison of calculations using two different sets of V–V rates with experimental spectra showed that the use of the semi-empirical V–V rates of DeLeon and Rich provides better agreement with experiment. It is also shown that the multi-quantum V–V rates among high vibrational quantum numbers, calculated by Cacciatore and Billing, are substantially overpredicted. The results provide some new insight into nonequilibrium vibrational kinetics, and also demonstrate the capabilities of the step-scan Fourier transform spectroscopy for time-resolved studies of molecular energy transfer processes and validation of theoretical rate models. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Nonequilibrium vibrational kinetics of diatomic and small polyatomic molecules has been the focus of attention for many years in gas discharge plasmas, molecular lasers, upper atmosphere chemistry, and gas dynamic flows [1,2]. The rate of energy transfer between the vibrational molecular modes \( AB(v) + AB(w-k) \rightarrow AB(v-k) + AB(w) \), and the “external” modes of rotation and translation is, in particular, a determining process in many high enthalpy fluid environments. The details of the actual distribution of energy among the vibrational quantum states is important in a more restricted range of problems, but is certainly key in non-thermal 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],
which for a broad range of parameters are known to be much faster than vibration-to-translation (V–T) relaxation,

\[
AB(v) + M \rightarrow AB(v - k) + M.
\]  

(2)

In Eqs. (1) and (2), AB and M stand for diatomic molecule and atom, respectively, \(v\) and \(w\) are vibrational quantum numbers, \(k\) is the number of quanta transmitted in a collision. The rates of the near-resonance V–V exchange processes of Eq. (1) among the high vibrational quantum levels \((v \sim w, v, w \gg 1)\) are of particular importance, since molecules on the high vibrational levels can also participate in nonequilibrium chemical reactions as well as produce electronic excitation and ionization. In particular, the vibration-to-electronic (V–E) processes, in which energy is transferred from highly vibrationally excited levels of the ground electronic state to a low-lying excited electronic state, with subsequent ultraviolet and visible band radiation, have been observed in optical pumping experiments in both CO \([6–8]\) and NO \([9,10]\). Ionization in collisions of two vibrationally excited CO molecules pooling their energies together has been studied in Refs. \([11,12]\). Predictive analysis of kinetics of these energy transfer processes, coupled to the high vibrational level populations, require precise knowledge of the V–V rates.

The present paper addresses recent measurements of the V–V rates in strongly vibrationally excited carbon monoxide (CO). The V–V rates for CO–CO have previously been measured using a variety of spectroscopic techniques (see Ref. \([6]\) and references therein), including experiments by Brechignac and co-workers \([13–15]\) and DeLeon and Rich \([6]\) who inferred the near-resonance V–V rates up to \(v \leq 29\) and \(v \leq 35\), respectively. The main advantage of the present study over the previous experiments is the use of time-resolved step-scan Fourier transform infrared (FTIR) emission spectroscopy. Step-scan Fourier transform (FT) spectrometers, such as the system used in the present study, have become available only relatively recently. These instruments provide the ability to record emission spectra in a broad wavelength range with high time resolution. The time resolution is limited by the response time of the detector system and data acquisition capabilities. In the present study, a fast response InSb detector with a high bandwidth DC preamplifier allows time resolution of up to a few nanoseconds. In other words, instead of measuring the time-dependent emission signal in a narrow wavelength range, the population of each radiating vibrational–rotational state can be monitored simultaneously. The step-scan technique requires a repetitively pulsed experiment, which is arranged in the present study; note that the technique could not be used for single-pulse experiments, such as in shock tunnels. An emission experiment is advantageous with this instrument, since absorption spectroscopy introduces noise complications from the incident absorption source. In addition, FT spectrometers provide throughput and multiplex advantages compared to conventional narrow-slit monochromators, improving the signal-to-noise ratio at high spectral resolution. Step-scan FT spectroscopy has been recently used to study energy transfer in vibrationally excited NO\(_2\) \([16,17]\).

Thus, in the present study, the time evolution of all vibrational states populated by the V–V processes up to extreme vibrational disequilibrium can be monitored simultaneously.

2. Experimental setup

Fig. 1 shows a schematic of the experimental setup for the study of vibrational energy transfer in CO. A CO laser is used to irradiate a gas mixture of CO and Ar, which slowly flows through the shown pyrex glass optical absorption cell. The residence time of the gas mixture 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 (CW) power. However, in the present experiment, the laser is typically operated at 10 W CW broadband power on the lowest ten fundamental bands, with up to \(\sim 0.3\) W on the \(v = 1 \rightarrow 0\) component (Table 1). The output on the lowest bands (1 \(\rightarrow\) 0 and 2 \(\rightarrow\) 1) is necessary to
begin the absorption process in cold CO (initially at 300 K) in the cell.

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 amount of literature [6–11,18].

In the time-resolved experiments, intended to obtain a more precise measurement of the mechanism and rates of the V–V exchange processes, the laser beam is interrupted by a mechanical chopper, giving a nearly square wave input of laser power to the cell (Fig. 2). After the laser is turned on, the lower states, \( v \leq 10 \), are populated by direct resonance absorption of the pump radiation in combination with the much more rapid redistribution of population by the V–V exchange processes. The time-dependent transmitted laser pulse shapes are also shown in Fig. 2 for different CO partial pressures in the cell. The V–V processes then continue to populate the higher vibrational levels above \( v = 10 \), which are not directly coupled to the laser radiation. 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. The chopper is operated at a low frequency of 13 Hz with a low duty cycle of \( \approx 1/11 \), so that the laser pulse duration is 6.8 ms, and the time between the pulses is about 75 ms. The low duty cycle is deliberately chosen to allow complete vibrational relaxation between the laser pulses.

In the steady-state measurements, the laser remains on all the time, so that a complete steady state is reached. Note that the vibrational energy stored in the molecule is constantly converted into
heat both in V–V and V–T processes. However, the large heat capacity of the Ar diluent, 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 never rises above a few hundred degrees. Thus, a strong disequation of energy can be maintained in the cell, characterized by very high vibrational mode energy and a low translational/rotational mode temperature. 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 numerous electron impact processes 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 step-scan FT IFS 66 spectrometer with step-scan and rapid-scan capabilities 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 FT spectrometer can be used for recording of both steady-state and time-resolved spectra. Steady-state spectra are typically recorded in rapid-scan mode at a spectral resolution of 0.25 cm\(^{-1}\). In time-resolved measurements, a few hundred “time slices” are recorded in step-scan mode with a lower spectral resolution of 8.0 cm\(^{-1}\), and a time resolution ranging from 5 to 50 \(\mu\)s, thereby spanning a time period of a few ms to a few tens of ms.

The Gaussian laser beam, which has a diameter of \(~0.5\) 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 and accelerate the V–V up-pumping, providing an excitation region in the cell of \(~1\) mm diameter. The measurements reported here are made at the same Ar partial pressure of 100 Torr,

<table>
<thead>
<tr>
<th>Laser line</th>
<th>Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (\rightarrow) 0 P(15)</td>
<td>0.29</td>
</tr>
<tr>
<td>2 (\rightarrow) 1 P(15)</td>
<td>0.62</td>
</tr>
<tr>
<td>2 (\rightarrow) 1 P(16)</td>
<td>0.57</td>
</tr>
<tr>
<td>3 (\rightarrow) 2 P(14)</td>
<td>0.79</td>
</tr>
<tr>
<td>3 (\rightarrow) 2 P(15)</td>
<td>1.52</td>
</tr>
<tr>
<td>4 (\rightarrow) 3 P(13)</td>
<td>0.31</td>
</tr>
<tr>
<td>4 (\rightarrow) 3 P(14)</td>
<td>1.14</td>
</tr>
<tr>
<td>4 (\rightarrow) 3 P(15)</td>
<td>0.80</td>
</tr>
<tr>
<td>5 (\rightarrow) 4 P(13)</td>
<td>0.24</td>
</tr>
<tr>
<td>5 (\rightarrow) 4 P(14)</td>
<td>0.95</td>
</tr>
<tr>
<td>5 (\rightarrow) 4 P(15)</td>
<td>0.35</td>
</tr>
<tr>
<td>6 (\rightarrow) 5 P(12)</td>
<td>0.42</td>
</tr>
<tr>
<td>6 (\rightarrow) 5 P(13)</td>
<td>0.20</td>
</tr>
<tr>
<td>6 (\rightarrow) 5 P(14)</td>
<td>0.56</td>
</tr>
<tr>
<td>7 (\rightarrow) 6 P(12)</td>
<td>0.32</td>
</tr>
<tr>
<td>7 (\rightarrow) 6 P(13)</td>
<td>0.44</td>
</tr>
<tr>
<td>8 (\rightarrow) 7 P(12)</td>
<td>0.45</td>
</tr>
<tr>
<td>9 (\rightarrow) 8 P(11)</td>
<td>0.13</td>
</tr>
<tr>
<td>9 (\rightarrow) 8 P(12)</td>
<td>0.10</td>
</tr>
<tr>
<td>10 (\rightarrow) 9 P(10)</td>
<td>0.05</td>
</tr>
<tr>
<td>10 (\rightarrow) 9 P(12)</td>
<td>0.09</td>
</tr>
</tbody>
</table>
and at seven CO partial pressures varying from 0.5 to 3.5 Torr.

3. Kinetic model and the V–V rate parametrization

To interpret the results of both steady-state and time-resolved measurements, and to infer the V–V rates for CO–CO, 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. [18]; two significant upgrades are (i) incorporation of laser power distribution and transport processes (diffusion and heat conduction) across the Gaussian laser beam, and (ii) incorporation of the multi-quantum V–V processes (|k| > 1 in Eq. (1)). The model evaluates the time-dependent vibrational level populations in CO–Ar mixture excited by a laser beam:

\[
\frac{\partial n_v(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r D \frac{\partial n_v(r,t)}{\partial r} \right] + VV_e + VT_v + \text{SRD}_e + \text{VE}_v + \text{PL}_v,
\]

\[
\left. \frac{\partial n_v(r,t)}{\partial r} \right|_{r=0} = 0, \quad n_v(r,t)|_{r=\infty} = n_v(r,t)|_{r=0} = n_v(T_0), \quad v = 0, v_{\text{max}},
\]

\[
\rho c_p \frac{\partial T(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r \lambda \frac{\partial T(r,t)}{\partial r} \right] + \text{HVR},
\]

\[
\left. \frac{\partial T(r,t)}{\partial r} \right|_{r=0} = 0, \quad T(r,t)|_{r=\infty} = T(r,t)|_{t=0} = T_0.
\]

In Eqs. (3) and (4), \(n_v(r,t)\) is the population of the \(v\)th vibrational level of CO; \(n_v(T_0)\) is the initial equilibrium population at \(T_0 = 300\) K; \(n_{CO}\) is the CO concentration; \(D\) and \(\lambda\) are the diffusion and heat transfer coefficients, respectively; \(\rho\) and \(c_p\) are the density and specific heat at constant pressure, respectively. The rest of the notation is the same as in Ref. [18]: VV, vibration–vibration term; VT, vibration–translation term; SRD, spontaneous radiative decay (infrared); VE, vibration–electronic coupling; PL, laser pumping; HVR, gas heating by vibrational relaxation. The explicit expressions for these terms are given in Ref. [18] and will not be repeated here, with the exception of the V–V term, which in the presence of the multi-quantum processes is modified as follows:

\[
VV_e = \sum_{w,k} Q(v,w-k \rightarrow v-k,w)n_v n_{w-k} - \sum_{w,k} Q(v-k,w \rightarrow v,w-k)n_{v-k} n_w,
\]

\[
|\Delta k| \leq \Delta v_{\text{max}}.
\]

In Eq. (5), \(Q(v,w-k \rightarrow v-k,w)\) is the rate of V–V energy exchange. Since the flow velocity is quite slow, a few cm s\(^{-1}\), convective cooling in the energy equation (4) is neglected.

The objective of upgrading the model is to study the effects of nonuniform intensity distribution across the laser beam and vibrational energy transport by diffusion [19], as well as the multi-quantum energy transfer, on the excitation and relaxation processes.

The Gaussian intensity distribution across the laser beam results in a faster V–V pumping near the beam axis. Pump power is highest on the axis, and it is here where the vibrational level populations most rapidly reach steady state. There is slower excitation far from the axis, where pump power is less. The same qualitative scenario (i.e. faster relaxation near the axis) can be observed during the relaxation after the laser is turned off. This occurs because V–V exchange between two excited molecules is a nonlinear kinetic process with a rate proportional to the product of the two level populations. For example, \([dn_z/dt]_{\text{VV}} \sim Q_{\text{VV}}(1,1 \rightarrow 2,0)n_1 n_1\), and the first-order “time constant” \(\tau_{\text{VV}} \sim [Q_{\text{VV}}(1,1 \rightarrow 2,0)n_1]^{-1} \neq \text{const}\) is inversely proportional to \(n_1\), which tends to increase with the pump laser power density. Note that emission spectroscopy is essentially a line-of-sight measurement. The line-of-sight integration of the time-dependent signal by the spectrometer will create an impression that the high level populations rapidly rise and decay, because of the contribution of the central portion of the beam where the power density is high and kinetics is fast. The described effect does not appear in linear or quasilinear kinetic processes, such as V–T.
relaxation or V–V exchange with the ground vibrational state, \( v = 0 \). For these two cases, the first-order time constants, \( \tau_{VT} \approx [P_{VT}(1 \to 0)N]^{-1} \) and \( \tau_{VV} \approx [Q_{VV}(1,0 \to 0,1)n_0]^{-1} \), are indeed constant (\( n_0 \) changes fairly weakly during the excitation) and independent of the laser power.

Focusing of the laser beam is likely to reduce this effect due to the more rapid diffusion of vibrationally excited molecules across the narrow beam. However, a greater effect of diffusion when the beam diameter is reduced will further complicate the analysis. For example, previous time-resolved experiments [6,18] show that the typical rise and decay times for the infrared radiation from the high CO vibrational levels excited by the focused laser beam are of the order of a few milliseconds. On the other hand, simple estimates show that the characteristic time for diffusion of vibrational energy out of the excited volume is of the same order of magnitude: \( \tau_{\text{diff}} \approx R^2/D \approx 10 \) ms. Here, \( R \approx 1 \) mm is the focused laser beam diameter, and \( D \approx 1 \) cm\(^2\) s\(^{-1}\) is the diffusion coefficient of CO at \( P \approx 100 \) Torr. This results in a competition between the V–V energy transfer and energy transport by diffusion.

Finally, three-dimensional semiclassical trajectory calculations of the V–V rates for CO–CO by Cacciatore and Billing [20] predict the rates of the near-resonance multi-quantum processes collisions involving exchange of two or more quanta (\( |k| \geq 2 \) in Eq. (1)) to be comparable with those of the single-quantum processes for high vibrational levels (\( v, w > 10 \) in Eq. (1)). This prediction is consistent with the results of the previous experiments [6], which inferred the near-resonance single-quantum V–V rates to be an order of magnitude greater than the gas kinetic collision frequency. This result might be attributed to the latent contribution of the multi-quantum processes, not accounted for in the kinetic model used.

All this suggests that the spatial power distribution, diffusion, and multi-quantum relaxation might well be significant factors in the present experiments.

In the present model, the rates of the energy transfer processes, except for CO–CO, V–V rates, are the same as described in Ref. [18]. The V–V rates are the remaining parameters in the model. Calculations that are only known with some uncertainty. Therefore, they are varied to provide better agreement with the experiment. In the calculations, two different sets of rates are used. In the first baseline series of modeling calculations, we used a V–V rate model based on the analytic parametrization suggested by Jeffers and Kelley [21], developed from the perturbation theory for the cross-sections, and correlated with the body of experimental data obtained in several previous measurements (see Ref. [6] and references therein). These rates constitute Set I (Fig. 3). This rate model is applicable only for single-quantum V–V exchange processes. The explicit V–V rate expressions used can be found in Appendix A. In the second series of calculations, we used an analytic nonperturbative theory of vibrational energy transfer [22–24] that provides a convenient parametrization of the results of the trajectory calculations by Cacciatore and Billing [20], considered to be the most reliable theoretical data available. This “forced harmonic oscillator” (FHO) theory takes into account the coupling of many vibrational states during a collision and is therefore applicable for multi-quantum processes. Since the
published set of the CO–CO rates [20] is somewhat incomplete, we have used the computer codes DIDIAV and DIDIEX developed by Billing [25,26] to extend the calculations up to $j = 6$, for the same CO–CO potential as used in Ref. [20]. The comparison of these rate data with the FHO parametrization, given in Appendix A, is shown in Figs. 3 and 4. These V–V rates constitute Set II.

In addition, the code DIDIEX was also used to calculate the rates of the asymmetric one-by-two quanta near-resonance V–V exchange process (Fig. 5):

$$\text{CO}(0) + \text{CO}(w) \rightarrow \text{CO}(1) + \text{CO}(w - 2),$$

$$w = 35–50.$$  \hspace{1cm} (6)

This process, incorporated in all subsequent calculations (using both sets of V–V rates), was suggested by Napartovich and co-workers to be very important in kinetics of high vibrational levels of CO [27]. Note that calculations of the rates of process (6) require the use of accurate CO spectroscopic constants [28]; otherwise, the quantum number at which the rate (6) reaches maximum can be shifted by a few levels.

We emphasize the necessity of the use of analytic parametrization for rate inference. Even if only transitions between adjacent quantum levels are incorporated in the time-resolved experiment analysis, there are potentially $40 \times 40$ specific rates involved for a pump up to $v = 40$. As is well known, deconvolution of all the specific rates from the time-dependent population measurements alone would require far greater accuracy than achieved in the present data. We therefore require theoretical models of the quantum number dependence of these rates, as discussed above, to greatly reduce the number of parameters involved.

The system of Eqs. (3) and (4) for 50 vibrational levels of CO is solved using a standard solver for stiff partial differential equations, PDECOL [29]. In the calculations, a 31-point nonuniform grid, with most points located near the beam axis, is typically used. The laser line intensity distributions are given by the equation $I_l(r) = 0.5(I_{in} + I_{th}) [2/\pi R^2 \exp(-2r^2/R^2)]$, where $I_{in}$ and $I_{th}$ are the incident and the transmitted line intensities in $W$, and parameter $R = 0.28$ mm in the Gaussian intensity distribution across the focused laser beam is calculated by the code STRAHL developed at
University of Bonn [30]. A synthetic spectrum code is then used to generate the model spectra. Rotational level populations are assumed to be in equilibrium with the translational temperature $T(r)$. Both the vibration–rotation level populations and the emission intensity are integrated along the optical path of the spectrometer (i.e. across the laser beam). The code uses the spectroscopic data for CO molecule [28] and accurate Einstein coefficients for spontaneous emission and absorption coefficients for the CO infrared bands [31] as inputs. As usual, the synthetic spectra are corrected for the blackbody-calibrated instrument response function.

4. Results and discussion

4.1. Steady-state measurements

Under the conditions described in Section 2, with the laser left on, a highly nonequilibrium distribution of vibrational energy is created in the CO in the cell. The second overtone, first overtone, and part of the fundamental emission from CO excited by the focused laser beam is shown in Fig. 6, 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 being recorded by the detector, 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 vibrational population distribution functions (VDF) inferred from such high-resolution spectrum using the standard technique [32] are shown in Figs. 7 and 8 for different CO partial pressures. Typically, the vibrational level populations for $v < 30$ are inferred with the accuracy of a few percent, while for $v \geq 30$ the accuracy becomes somewhat worse, up to 20–30%. The translational/

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3 U. Sterr, W. Ertmer, University of Bonn, Germany, private communication.
rotational temperatures at these conditions, inferred from the rotationally resolved R-branch of the 1 → 0 fundamental band with the accuracy of ±10 K, are also shown in Fig. 8. The distributions shown in these figures 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. Although there are more than 80 bound vibrational levels in the CO ground electronic state, only the lowest 40 levels are populated by the V–V process. Note that V–V pumping of CO above \(v \sim 40\) has not been achieved in the previous experiments with vibrationally excited CO [6,8,11,18,33–35] in a broad range of translational temperatures \(T = 90–700\) K, regardless of available pumping power. This includes measurements in electric discharges and in laser absorption cells (both in gas and in liquid phase).

The reason for this persistent termination of the up-pumping has been discussed in the literature for some time [6,8,27,33–36]. The three most likely kinetic processes responsible for this effect are (i) asymmetric one-by-two quanta near-resonance V–V exchange (6) [27], (ii) near-resonance V–E energy transfer from \(v \sim 40\) of the ground electronic state, \(X^1\Sigma\), to the low levels of the excited electronic state \(A^1\Pi\),

\[
\begin{align*}
\text{CO}(X^1\Sigma, v \sim 40) + \text{CO} & \rightarrow \text{CO}(A^1\Pi, v \sim 0) + \text{CO} \\
\text{CO}(A^1\Pi) & \rightarrow \text{CO}(X^1\Sigma) + hv \\
\text{CO}(A^1\Pi) + M & \rightarrow \text{CO}(X^1\Sigma) + M
\end{align*}
\]

(7)

suggested in Ref. [6] based on the measurements of time-resolved radiation from CO fourth positive electronic bands \(A^1\Pi \rightarrow X^1\Sigma\), coupled with the population of \(v \sim 35\), and (iii) rapid V–T relaxation on the products of vibrationally induced chemical reactions initiated by the process,

\[
\text{CO}(v) + \text{CO}(w) \rightarrow \text{CO}_2 + C,
\]

(8)

such as C, C₂, C₂O, etc. (vibrationally induced chemistry was first observed in optically pumped CO in Ref. [37]). Finally, both theoretical calculations of the V–T rates for CO–CO [20] and measurements of the V–T rates CO–Ar at high vibrational levels [38] show them to be far too slow to affect the vibrational level populations at \(v \sim 40\), especially at the low temperatures of \(T = 100–300\) K. Note that dramatic increase of the state-specific vibrational relaxation rates above a threshold vibrational quantum level, induced by chemical reactions or intermolecular electronic coupling, has also been previously observed in NO \((v > 14)\) [39], \(O_2 (v > 26)\) [40], and NO₂ (vibrational energy greater than 10,000–12,000 cm⁻¹) [41].

To analyze the effect of these processes on the observed up-pumping termination, we calculated the steady-state distributions when turning processes (6) and (7) on and off separately, for both sets of V–V rates discussed in Section 3. The results are summarized in Figs. 7 and 8. First, calculations using the V–V rates of Set I show that the asymmetric V–V exchange (6) truncates the VDF at higher quantum numbers than observed in
the experiment, i.e., at $v \sim 45$, where the asymmetric V–V rate reaches maximum (Fig. 5). Replacing process (6) by V–E energy transfer (7) predicts VDF truncation in satisfactory agreement with the low temperature data (Fig. 7). However, as the CO partial pressure and the translational temperature both increase, the experimental VDF crashes at the lower quantum numbers than predicted using the near-resonance V–E transition (7) (Fig. 8).

These results are consistent with the studies of the V–E energy transfer in CO by Wallaart and co-workers [8]. First, Wallaart et al. concluded that the measured steady-state populations of CO(A′I, $v = 1$–11) best correlate not with the ground state level $v = 40$ but with $v = 33$, and therefore suggested a more complicated multi-step mechanism of CO(A′II) population via mediation of the triplet electronic states with excitation energies between 7 and 8 eV. In addition, their measurements of the CO(A′I) populations via time-resolved measurements of the CO(A′I) concentrations, $n_{CO(A')} = 10^7$–$10^8$ cm$^{-3}$, lead us to conclude that the maximum power removed by both radiation and collisional quenching of the A state, is $n_{CO(A')}E_A/\tau \sim 10^{-5}$–$10^{-4}$ W cm$^{-3}$, which is negligible compared with the absorbed laser power of 2 W. Here, $E_A = 8$ eV is the excitation energy of the A state, and $\tau \sim 10^{-8}$ s is its radiative lifetime, which at $P = 100$ Torr is comparable with the collisional lifetime. On the other hand, in our previous paper [19], we have shown that an energy sink at the level $v_a \sim 40$ that cuts off the V–V pumped VDF with the Treanor minimum at $v_0 \sim 10$ must remove a much larger fraction of the power added to the vibrational mode of the oscillator, $[1 - x_e(v_a + v_0)]/(1 - 2x_ev_0) \sim 80\%$, the other 20\% being removed by the V–V exchange. These estimates demonstrate that regardless of the details of kinetics of the V–E transition $X^3Σ \rightarrow A^1Π$, it is unlikely to be responsible for the up-pumping truncation at the conditions of experiments [8] ($T = 700$ K), since it apparently does not remove enough power from the vibrational mode of CO. We note, however, that the CO(A′II, $v$) populations measured in Ref. [8] might conceivably be underestimated due to the strong self-absorption of the CO fourth positive bands.

Quite obviously, chemical reactions such as Eq. (8) can truncate the V–V pumped distribution only if the reaction rate coefficient, $k_r$, is comparable with the near-resonance V–V rate that sustains the VDF at $v \sim 40$, $k_r \sim Q_{VV} \sim 10^{-10}$ cm$^3$ s$^{-1}$. This gives an unrealistic reaction rate $k_r n_{CO(w)} n_{CO(w)} \sim 10^{-10} \times 10^{14} \times 10^{14} = 10^{18}$ 1 cm$^{-3}$ s$^{-1}$, or $\sim 100$ Torr CO per second. We therefore tentatively suggest that the VDF cutoff at $v < 40$ can be at least partially attributed to the fast V–T relaxation of CO on the products of chemical reaction (8). This mechanism may be most prevalent at the higher cell temperatures. At the same time, previous experimental data (in particular, the VDF crash at $v \sim 40$ observed at cryogenic temperatures $T = 90–100$ K [33–35], when the V–T relaxation becomes extremely slow) still suggest that the V–E transition (8) might also play a role in the VDF truncation at low temperatures.

Returning to the discussion of Fig. 7, we note that calculations using the V–V rates of Set II demonstrate a similar although somewhat weaker effect of processes (6) and (7) on the VDF at $v \sim 40$–45. In addition, the slope of the VDF calculated using Set II V–V rates becomes much steeper than in the experiment (Fig. 7). Varying $\Delta v_{max}$ in the calculations showed that this occurs due to a rapid increase of the multi-quantum V–V rates at high vibrational quantum numbers, even though the rates of the single-quantum processes of Set II are somewhat slower than those of Set I (Figs. 3 and 4). It therefore appears that Set II substantially overpredicts the multi-quantum V–V rates at the high $v$'s.

Before we proceed with the discussion of the time-resolved measurements, we tentatively conclude that the use of the rates of Set I together with the V–E process (7) instead of the asymmetric V–V exchange (6) provide better agreement with the low-temperature steady-state data. We would like to emphasize that, apparently, the details of the VDF truncation kinetics, which are still not well understood, have little effect on the vibrational populations at $v < 40$ (Fig. 7). This fact allows inference of the V–V rates from the time-resolved measurements. Finally, Fig. 9, which shows the VDFs and the values of the first level vibrational temperature,
4.2. Time-resolved measurements

Fig. 10 shows a typical time-resolved step-scan spectrum obtained in the experiment. In this three-dimensional projection, emission intensity in arbitrary units is on the vertical axis, frequency in cm$^{-1}$ is on the horizontal axis, and the diagonal axis is the time in microseconds. The overtone bands (Section 4.1) are used as the primary diagnostic to infer the vibrational state populations, as the gas is optically thin on all these transitions. The resolution here is 8 cm$^{-1}$, so that the rotational line structure is not resolved, although the individual vibrational band component structure is clearly seen. The time resolution is 50 $\mu$s here, and every spectrum obtained at these intervals is being displayed. The broadband structure visible at $t = 0$ is the blackbody background, subtracted in the subsequent analysis. The laser is switched on at $t = 0$, reaches its steady state intensity in about 200 $\mu$s, and is switched off at $t = 6.6$ ms (Fig. 2). In addition to the low time resolution spectrum shown in Fig. 10, a 5 $\mu$s time resolution spectrum is taken for each CO partial pressure to better resolve the initial 2 ms stage of the up-pumping after the laser is turned on. For each step-scan CO emission spectrum, a time-dependent laser
spectrum was also measured; the time-dependent transmitted laser power obtained from these laser spectra is shown in Fig. 2.

Figs. 11 and 12 display slice-by-slice comparisons between the experimental and the synthetic spectra using the model described in Section 3 and the first set of the V–V rates. Although the spectra are shifted along the y-axis for illustrative purpose, they are shown in the same scale. In this experiment, the CO partial pressure is 3.5 Torr. One can see that although the model is in very good agreement with the time-resolved relaxation data (Fig. 12), it fails to reproduce the time-dependent spectra during the excitation (Fig. 11, only two synthetic spectra at \(t = 0.45 \) ms and \(t = 4.45 \) ms are shown). Basically, the model predicts much faster laser radiation absorption and the CO up-pumping after the laser is turned on, so that the V–V pumped distribution reaches the steady state within a few hundreds of microseconds instead of a few milliseconds (Fig. 11). The same kind of disagreement between theoretical and experimental excitation spectra has been also observed at other CO partial pressures.

Fig. 13 displays the slice-by-slice comparison with the relaxation data at \(P = 0.5\) Torr. The scale in this figure is different from the scale used in Figs. 11 and 12 (the emission intensity is roughly proportional the CO partial pressure). However, all time slices within each figure are still shown in the same scale.

It is disappointing that the model is at variance with the time-resolved excitation data. Note that varying the adjustable parameters in the Set I parametrization or the use of Set II had not resulted in substantial improvement of the agreement. This fact, as well as good agreement of the model with the relaxation data in a wide range of CO partial pressures (Figs. 12 and 13), suggests that the observed slow up-pumping is not related to the V–V rates. On the other hand, the time dependence of the absorbed laser power (e.g. shown in Fig. 2), and therefore the overall rate of CO up-pumping were found to be very sensitive to the laser spectrum. We therefore believe that the observed slow excitation is due to the following
two effects. First is the laser “line hopping” (i.e. laser output power change on individual lines) detected in the time-resolved laser spectra, which is significant even though the total laser power remains fairly stable (Fig. 2). Second is the fast V–T relaxation on the chemical reaction products, which is the “bottleneck” at the first stage of excitation when the rate of the V–V process that triggers the up-pumping, \( \text{CO}(1) + \text{CO}(1) \rightarrow \text{CO}(0) + \text{CO}(2) \), is comparable with that of the V–T relaxation, \( \text{CO}(1) + \text{M} \rightarrow \text{CO}(0) + \text{M} \). Since the V–T relaxation rates for CO–CO and CO–Ar are extremely slow, relaxation on reaction products may change the effective rate of the V–T relaxation by several orders of magnitude, thereby delaying the onset of the up-pumping. We plan to verify these assumptions in our on-going time-resolved experiments on optical pumping of NO [42]. In these experiments, a stable single-line CO laser is used, while the rapid self-relaxation NO–NO is the dominant V–T process with well-known rates [39], so there should be much less uncertainty in the up-pumping delay. Finally, even though achieving better agreement with the experimental excitation

Fig. 13. Time-resolved CO emission spectra during relaxation: \( P_{\text{CO}} = 0.5 \) Torr. (—) experiment; ( - - - ) calculations using Set I of the V–V rates. Time slices shown in the legend are top to bottom.

Fig. 14. Time-resolved CO emission spectra during relaxation: \( P_{\text{CO}} = 0.5 \) Torr. (—) experiment; ( - - - ) calculations using Set II of the V–V rates. Time slices shown in the legend are top to bottom.
conclusion of Section 4.1 that calculations by Cacciatore and Billing substantially overpredict the multi-quantum V–V rates among the high vibrational quantum numbers. Note that recent semiclassical calculations by Coletti and Billing [43], where a more accurate potential energy surface has been used, also predict somewhat lower values of the V–V rates.

Fig. 15 displays the time-dependent VDFs for the conditions of Fig. 12, i.e. relaxation at $P_{\text{CO}} = 3.5$ Torr (solid lines). It shows that the relaxation occurs through a succession of distributions with long plateaus, known to be dominated by near-resonance V–V exchange [4,5]. Another well-pronounced feature is the development of a total population inversion at a late stage of the relaxation process, for $v > 10$, created by the diffusion of the vibrationally excited molecules out of the beam region (compare with the steady-state VDFs at large distances from the beam center shown in Fig. 9). Fig. 15 also shows that the calculated vibrational level populations drop by a factor of 20–100 during the relaxation, i.e. that the experimental step-scan data cover a substantial portion of the entire relaxation process. Dashed lines in Fig. 15 show the vibrational distributions calculated assuming a spatially uniform excited region and neglecting diffusion. The latter calculation starts from a VDF that is close to the line-of-sight integrated VDF predicted by the model incorporating nonuniformity and diffusion, and the V–V rates are the same in both cases. Qualitative difference between these two calculations can be easily seen. Relaxation in a nonuniform region occurs much faster because of the higher vibrational populations near the beam axis (see discussion in Section 3 and Fig. 9). The vibrational level populations calculated without nonuniformity and diffusion drop by only a factor of 4 and 5, which is inconsistent with the step-scan relaxation spectra (Fig. 12). Also, in this calculation the total population inversion does not form. This clearly shows the importance of taking into account spatial nonuniformity of the excited region as well as the transport processes.

Parametric calculations using the rates of Set I, where we replaced the V–E transfer (7) by the asymmetric V–V exchange (6) showed that both the VDF for $v < 40$ and the synthetic spectra shown in Figs. 12 and 13 are primarily influenced by the V–V rates, and only weakly sensitive to the rates of other energy transfer processes. Finally, varying the adjustable parameters for Set I shown in Appendix A showed that their values chosen in Ref. [6] provide the most consistent agreement with the step-scan relaxation spectra for $P_{\text{CO}} = 0.5–3.5$ Torr.

The time-resolved measurements discussed in this section are made at translational temperatures fairly close to room temperature. Indeed, from Fig. 16, which shows the temperature change at the beam axis during the excitation and relaxation, one can see that the maximum temperature rise at $P_{\text{CO}} = 3.5$ Torr is about 100 K. However, good agreement between the steady-state data and the modeling calculations for $v < 30$ in the temperature range $T = 400–730$ K (Fig. 8) shows that the Set I rate parametrization is also applicable at these temperatures. As has been discussed in Section 4.1, the difference between the calculated and
the experimental VDF’s at \( v > 30 \) in Fig. 8 is due to the effect of the processes unrelated to the V–V exchange.

5. Summary

In the present paper, time-resolved step-scan FTIR of optically pumped CO is used to study the kinetics of vibrational energy transfer processes (primarily V–V exchange) in strongly vibrationally nonequilibrium CO. Time evolution of all vibrational states populated by the V–V processes up to extreme vibrational disequilibrium is monitored simultaneously. The V–V rates are inferred from these data using a kinetic model that incorporates the pump laser spatial power profile and transport processes, and allows incorporation of multi-quantum V–V processes. The model predictions agree well with the step-scan relaxation spectra.

Comparison of calculations using two different sets of V–V rates with experimental spectra showed that the use of the V–V rates of Set I provides better agreement with experiment. It is also shown that the multi-quantum V–V rates of Set II (i.e. analytic parametrization of semiclassical trajectory calculations by Cacciatore and Billing) are overpredicted at high vibrational quantum numbers.

These results provide new insight into nonequilibrium vibrational kinetics, and also demonstrate the capabilities of the time-resolved step-scan FT spectroscopy for studies of molecular energy transfer processes and validation of theoretical rate models.

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Appendix A

A.1. DeLeon–Rich single-quantum V–V rate parametrization (Set I) [6,18]

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

\[
\Delta E = 2a_c x_e (v - w),
\]

\[
S_{v-1,w}^{v,v-1} = S(T) \frac{v}{1 - x_e v} \frac{w}{1 - x_e w} F(\lambda_{v-1,w}^{v,v-1}),
\]

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

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

\[
L_{v-1,w}^{v,v-1} = L(T) \left( \frac{g_{v,v-1}^{v,v-1}}{g_{v,v-1}^{v,v-1}} \right)^2 \left( \frac{g_{w-1,w}^{w-1,w}}{g_{w-1,w}^{w-1,w}} \right)^2 \exp \left( -\frac{\Delta E^2}{bT} \right).
\]
(\frac{g^{e-1}}{g^{1.0}})^2 = \left( \frac{a + 1}{a + 3 - 2v} \right)^2 \times \frac{v(a + 2 - 2v)(a + 4 - 2v)}{a(a + 3 - v)}, \quad a = 1/x_e.

Gas-kinetic collision frequency, \( Z = 3 \times 10^{-10} \) (\( T / 300 \))\(^{1/2} \) cm\(^3\) s\(^{-1}\).

Parameters: short-range interaction \( S(T) = 4.93 \times 10^{-4} \) (\( T / 300 \)) cm\(^3\) s\(^{-1}\), \( c = 0.456 \) K\(^{-1}\); and long-range interaction \( L(T) = 5.37 \times 10^{-3} \) (300/\( T \)) cm\(^3\) s\(^{-1}\), \( b = 40.36 \) K.

A.2. FHO parametrization of Caciottoli–Billing \( V-V \) rates (Set II) [20,24]

\[ Q(v, w - k \rightarrow v - k, w) = \frac{\left( S_{w-k,w}^{e-k} \right)^k}{k! \left( 1 + \frac{3}{2} \frac{v + w - k}{k+1} \right)^{k+1}} + \frac{\left( L_{w-k,w}^{e-k} \right)^k}{k! \left( 1 + \frac{3}{2} \frac{v + w - k}{k+1} \right)^{k+1}}, \]

\[ S_{w-k,w}^{e-k} = S(T) \left( \frac{v!}{(v-k)!} \frac{w!}{(w-k)!} \right)^{1/k} F(\lambda_{w-k,w}), \]

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

\[ \lambda_{w-k,w}^{e-k} = 2^{-3/2} \sqrt{c |\Delta E| / k}, \]

\[ L_{w-k,w}^{e-k} = L(T) \left( \frac{v!}{(v-k)!} \frac{w!}{(w-k)!} \right)^{1/k} \times \exp \left( - \frac{(\Delta E/k)^2}{kb\sqrt{T}} \right), \]

\[ \Delta E = 2k\omega_x x_\tau (v - w). \]

A.3. Asymmetric \( V-V \) rate parametrization (used with both \( V-V \) rate sets) [24]

\[ Q(0, w \rightarrow 1, w - 2) = Z(S_{w-2,w}^{1.0} + L_{w-2,w}^{1.0})x_\tau (w - 1) / 2, \]

\[ S_{w-2,w}^{1.0} = S(T)F(\lambda_{w-2,w}^{1.0}), \]

\[ L_{w-2,w}^{1.0} = L(T) \exp \left( - \frac{\Delta E^2}{kb\sqrt{T}} \right). \]

\( S(T), L(T), c, b, \) and \( F(\lambda) \) are the same as in Appendix A.2.

References