TREANOR PUMPING OF CO INITIATED BY CO LASER EXCITATION

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An experiment is discussed in which CO can be excited up to energies of several electronvolts by the absorption of infrared radiation from a relatively low-power CO laser. Furthermore, experimental results are examined through kinetic modelling. In the experiment, the beam of an intracavity-chopped CO laser operating on all lines at 500 mW and containing a few milliwatts of the fundamental \( \nu = 1 \rightarrow 0 \) band component, is focused into an absorption cell containing a mixture of CO and Ar. The absorption of this infrared radiation is monitored by the optoacoustic effect. A second CO laser operating cw and capable of providing 8 W on all lines but not lasing on the \( \nu = 1 \rightarrow 0 \) band component, is then focused into the same volume in the absorption cell. With both lasers simultaneously focused into the absorption cell, strong fluorescence from the irradiated region is detected by a photomultiplier tube. Modulation of the signal intensity with time is observed, and indicates chemical destruction of the CO in the cell. An analysis and kinetic modelling calculation of this experiment shows that it is possible to excite CO up to high vibrational quantum numbers \( (\nu \gg 40) \) at gas temperatures up to 800 K by means of CO laser irradiation at the fundamental \( \nu = 1 \rightarrow 0 \) band component.

One source responsible for the fluorescence signal observed in the experiment is identified as the 4th positive \( A^ \Pi \rightarrow X^ \Sigma^+ \) spontaneous emission. Although the present kinetic model does not incorporate the chemical processes that may lead to the production of additional fluorescing species such as \( \text{C}_2 \), good agreement is obtained with the observed fluorescence signal characteristics.

1. Introduction

Interest in the details of the energy transfer kinetics of the CO molecule has prompted several investigations using optical pumping. This paper describes an experiment where gaseous CO is excited up to energies of several electron volts by the absorption of infrared radiation from relatively low power CO lasers with average powers of the order of a few watts. Such optical pumping excites the lowest vibrational levels of the CO ground electronic state \( (X^ \Sigma^+ ) \). Redistribution of vibrational energy in CO-CO collisions results then in substantial population of higher states by the Treanor pumping mechanism [1]. Subsequently, energy is transferred into low-lying excited electronic levels.

Successful experiments in optical pumping of solid phase [2] and liquid phase [3] with relatively low power CO lasers operating on the \( \nu = 1 \rightarrow 0 \) band component have been performed in the past. Optical pumping of gaseous CO has also been done successfully in the past [4]. Rich and Bergman [4] have shown that CO can be vibrationally pumped in a cool absorption cell irradiated by means of a supersonic flow CO laser operating cw on bands \( \nu = 3 \rightarrow 2 \) and higher, with a power of 220 W. The laser was not focused in their experiment. More recently, Cohn et al. [5] have shown that a CO laser of higher power (up to 820 W), operating on \( \nu = 5 \rightarrow 4 \) and higher band components, can pump gaseous CO in a cell only when an auxiliary electric discharge is used. The discharge produces a small initial population of \( \nu > 0 \) CO vibrational states. In the absence of the auxiliary discharge, no optical pumping of CO could be produced by this laser. It is evident therefore that the vibrational levels \( \nu = 2 \) and \( \nu = 3 \) must be substantially pop-
ulated before any significant collisional up-pumping could result from this CO laser irradiation. However, as discussed in this paper, up-pumping in gaseous CO can be achieved even at relatively low laser power levels, if energy is added to the CO molecule on the $v=1 \rightarrow 0$ band component. This band component does not always oscillate in the CO laser, but can be produced by different means [6-8]. The $v=1 \rightarrow 0$ band component in one of the lasers used in the experiment described in this paper is produced by $Q$-switching. Successful pumping is achieved even when gas translational temperatures reach several hundred kelvin.

This paper describes an experiment where CO is vibrationally excited up to high quantum numbers by means of simultaneous irradiation by two CO lasers. One laser is $Q$-switched so as to produce lasing on the fundamental $v=1 \rightarrow 0$ band component, while the other operates cw and lases on the $v=3 \rightarrow 2$ and higher bands. Fluorescence from the irradiated region is observed and detected with a photomultiplier tube. The resulting signal intensity is seen to be modulated. This experiment is also modelled and analysed in this paper. It is shown, as observed in the experiment, that it is possible to vibrationally excite gaseous CO initially at room temperature by using a $Q$-switched CO laser operating on the $v=1 \rightarrow 0$ band component. A possible explanation for the observed fluorescence signal and its modulation, is also given.

This paper is organized as follows. The experiment is described in section 2, followed by a discussion of the governing equations for CO rate kinetics and a method of solution in section 3. The results of the numerical simulation of the experiment are given in section 4, culminating in the summary and conclusions in section 5.

2. Experiment

A schematic of the experimental setup is shown in fig. 1. Both liquid nitrogen cooled CO lasers are mounted on a single table. The gas flow of the $Q$-switched laser (henceforth referred to as laser I) is pre-cooled, and enters directly inside the cooled region of the gain tube. Such pre-cooling aids lasing on the lower vibrational transitions, and has been demonstrated earlier by Brechignac and Martin [7]. The uncooled regions near the ends of the gain tube are purged with He [6,7]. This gain tube is similar to the one described earlier by Lin et al. [9]. A conventional chopper wheel is used in the cavity of laser I in order to produce $Q$-switching, and can produce "open" and "closed" periods of the order of 1 ms. The average power is measured by placing a bolometer directly behind the output mirrors (represented as P1 and P2 respectively in fig. 1) of each of the lasers. Reflections from the Brewster windows are used for monitoring the spectral line distribution of either laser I or laser II, by passing the reflected beam through a 25 cm IR spectrometer (SPI). A liquid nitrogen cooled InSb element is used as an IR detector. In contrast to laser I, laser II has a much simpler gain tube without any pre-cooling or purging.

A PZT element is used in order to optimize for the P(12) transition of the fundamental band. The spec-

Fig. 1. A schematic of the experimental setup.
tral distributions of both laser I and laser II are shown in fig. 2. It can be seen that laser I has emission on bands from \( v = 1 \rightarrow 0 \) to \( v = 11 \rightarrow 10 \). Since only small CO concentrations are allowed into the gain tube of laser I in order to get short-wavelength lasing (i.e. lasing on \( v = 1 \rightarrow 0 \)), only 500 mW of total average power is obtainable from this laser. By contrast, laser II is capable of delivering 8 W cw on bands from \( v = 3 \rightarrow 2 \) to \( v = 11 \rightarrow 10 \) as shown in fig. 2. The time evolution of various bands in laser I (the \( Q \)-switched laser) is displayed in fig. 3, showing the cascading effect that is most pronounced in the \( v = 1 \rightarrow 0 \) emission.

The output beams of both lasers are focused via toroidal mirrors (represented by T1 and T2 in fig. 1).

![Diagram](image)

Fig. 2. The vibrational band distribution for lasers I (top) and II (bottom). The average power of the intracavity-chopped laser I is 0.5 W distributed over all bands shown. The intensity of the cw laser II can be as high as 8 W at the band distribution shown.
into an absorption cell containing a mixture of CO and Ar. The partial pressures of CO and Ar in the absorption cell are 10 and 80 Torr, respectively. The toroidal mirrors have different focal lengths (T1 has a focal length of 110 cm while T2 has a focal length of 185 mm) and can therefore be placed one behind the other. This provides the possibility of almost collinear focusing of both beams by conventional adjustment elements. Both a microphone and a multiplier are attached to the absorption cell. An additional spectrometer (denoted by SP2 in fig. 1) may also be used if desired, for spectral analysis of the fluorescence emanating from the irradiated volume.

As a first step, the optoacoustic signal produced by the periodically emitted radiation from laser I is optimized. A considerable amount of energy can be deposited into the vibrational modes of the CO molecules with even a low power laser. It is found however, that when the cw output from laser II is added simultaneously with the output from laser I, an enhancement of the optoacoustic signal results. This enhancement, depending on experimental conditions and on careful alignment of the focal areas, can be between a factor of 2 and a factor of 8 times higher.

The observed optoacoustic signal indicates the IR-absorption process and subsequent VT relaxation. It shows that energy can be deposited into the vibrational modes of the CO molecules. It does not however, necessarily indicate the presence of VV transfer. Emission from excited states such as upper electronic levels or products appearing upon destruction of the CO molecule, would be needed to conclusively indicate the presence of VV pumping. This is why an IR-blind detector such as a multiplier is attached to the absorption cell (see fig. 1). Indeed, multiplier signals are observed even with only laser I operational.

It is found that both the peak intensity and time evolution of the multiplier signals vary with laser power. The effect of laser I on the multiplier signal is to produce sharply peaked signals. These multiplier signals are observed to get broader when laser II is simultaneously irradiated along with laser I, and also become increasingly broad as the intensity of the beam from laser II is increased. During the off period (i.e. while laser I, which is Q-switched, is in the "closed" period), the fluorescence was observed to vanish completely. A selection of multiplier signals for laser II operating at various power levels is shown in fig. 4.

Some additional experimental observations are worth reporting. First, the fluorescence intensity from the cell decreases with time, and can be restored to the previous conditions by renewing the CO–Ar gas mixture. This indicates the presence of a chemical reaction induced by the CO laser irradiation. Second, the fluorescence can not only be detected by the multiplier, but can also be seen by the naked eye (after slight adaptation) when laser II is on at the higher power levels (5 W and above, cw). Under this condition, one observes that the fluorescence from the irradiated region is sustained even with laser I turned off. This clearly indicates that once a high enough concentration of vibrationally excited CO is produced, VV transfer can itself trigger the excitation process.
In summary, vibrationally excited CO has been produced by triggering with a low power CO laser operating on the fundamental band. A direct inspection of the fluorescence from the irradiated region shows bluish emission, which may be caused in part by C$_2$ Swan bands [4]. This is consistent with the observed decrease of the signal amplitudes in the experiment, since the CO concentration would decrease due to chemical reaction. However, it will be shown in the subsequent sections that an important contribution to the observed fluorescence arises from the 4th positive A' Π→X' Σ$^+$ spontaneous emission. Since the spectral distribution of the fluorescence was not analyzed, it is not possible at this time to determine how much of the fluorescence was due to this spontaneous emission and how much was due to the C$_2$ Swan band emission. The results of this experiment indicate that it is more useful to emphasize vibrational band distribution rather than high output power for the generation of IR-pumped CO. Further, analysis indicates that the present pumping is occurring at a considerably higher gas translational temperature than that in the experiment of Rich and Bergman [4]. The following sections will focus on an analysis and computer simulation of the experiment just discussed.

3. Governing equations

Consider a mixture of CO in argon. The CO is assumed to exist in two electronic states, X' Σ$^+$ and A' Π. Each state contains a manifold of associated vibrational levels. Additional states exist (such as the a' Π for instance) and may be included, but for simplicity we will restrict ourselves to two. The rate equations describing the time evolution of the number density of each vibrational level of the ground state (X' Σ$^+$), upper electronic state (A' Π), and the diluent (argon in this case) may be written in the following vector form:

$$\frac{dn_i}{dt} = VV + VT + SRD + VE + PL,$$  

(1)

where VV is the net production due to vibration-vibration exchange, VT due to vibration-translation exchange, SRD due to spontaneous radiative decay, VE due to vibration-electronic exchange between X' Σ$^+$ and A' Π, and PL due to stimulated absorption and emission from an external pump laser. A description of eq. (1) and detailed rate expressions are given elsewhere [10–12], and will only be summarized here.

The Schwartz–Slawsky–Herzfeld (SSH) model is used to calculate the VT rate [11], and the VE term employs an analytical form based on a collision-induced near-resonance exchange mechanism [10]. The VV term is the sum of a long-range dipole–dipole Sharma–Brau term and a short-range SSH term [11]. An important feature of VV and VT rates is their strong dependence on the translational temperature. Increasing the translational temperature will result in an increase in VV rates between levels that are not in close resonance. If exchange among these levels is rate limiting, then the overall VV up-pumping increases. However, increasing the translational
temperature will increase the VT quenching as well. This will be shown to be important in understanding the observations of the experiment described in section 2, in sections 4 and 5. The radiative terms SRD and PL are computed from standard formulae [10]. The only loss mechanism for the A 1\(^{1}\Pi\) included in this model in addition to the reverse VE coupling with the resonant X 1\(^{1}\Sigma^{+}\) vibrational level, is the fast (10 ns) A 1\(^{1}\Pi\)→X 1\(^{1}\Sigma^{+}\) 4th positive radiative transition. Finally, the system of quasi-linear stiff equations (1) together with the initial conditions \(n_{i}(t=0)\) may be solved using Gear’s method [13]. The initial conditions \(n_{i}(t=0)\) are assumed to be given by the Boltzmann distribution corresponding to the given translational temperature. The simulation of the experiment described in section 2 will be discussed next.

4. Computational results

In this section, the results from the solution of the governing equations of section 3 for the particular experiment described in section 2, are given. These results are presented as three cases. The first consists of a simulation of the case where the Q-switched laser (henceforth referred to as laser I) is turned on, while the cw laser (henceforth referred to as laser II) is off. The second case consists of both laser I and laser II being on, but laser II is on at 2 W average power with a focal area of 10\(^{-2}\) cm\(^{2}\). The third case is similar to case 2 but with the distinction that the laser II focal area is 10\(^{-3}\) cm\(^{2}\).

In this simulation, all laser lines are taken to have identical variations in time. This temporal variation is given by a normalized non-symmetric Gaussian envelope (i.e. different shapes on the rise and decay sides), which roughly covers the laser lines in the experiment,

\[
h(t) = (1/2) \left[ (t-t_{p})/\Delta t_{d} \right]^{2} \exp \left[ -\left( (t-t_{p})/\Delta t_{d} \right)^{2} \right],
\]

where \(t_{p}\) is the time at which the peak intensity occurs, \(\Delta t_{d}\) is the difference between \(t_{p}\) and the time at the full-width at half maximum of the rise portion, and \(\Delta t_{d}\) is the difference between \(t_{p}\) and the time of the full-width at half maximum of the decay portion. This profile is then repeated at 1 ms intervals corresponding to the Q-switching time used in the experiment. Fig. 5 displays the time variation of laser I as used in this simulation. The \(v=1 \rightarrow 0\) line shape of the experiment has been used to represent laser I in the simulation. The time variation of laser II is also roughly simulated by eq. (2) but with a long \(\Delta t_{d}\) (10 s) so that the cw shape may be modelled. The frequencies of the laser lines are also taken from experiment. A search on the frequencies of the rotation-vibration transitions is performed including the effect of pressure broadening, to determine overlaps between the pump laser spectrum and the CO X 1\(^{1}\Sigma^{+}\) absorption spectrum. The pump laser intensities are specified for the various vibrational transitions at the predominant P-branch \(J=12 \rightarrow J=11\) lasing transition. It has been found in this calculation that the CO excitation from the fundamental band is primarily due to resonance absorption on this P(12) line. Since both lasers were focused in the experiment, the focusing area is treated parametrically in this simulation. It must be emphasized that lasers I and II are treated as being independent, non-interacting sources. In other words, the radiation transport within the absorption cell is not modelled. Another effect that is not modelled in this simulation is chemistry (i.e. production of C\(_{2}\), C\(_{2}O\), etc.). This could be important when laser II is turned on since some part of the observed fluorescence signal may be due to C\(_{2}\) Swan emission, as seen in the earlier CO pumping experi-

![Fig. 5](image-url)

Fig. 5. The temporal variation of the normalized intensity of laser I line \(v=1 \rightarrow 0\) used in the modelling calculations
ments [4,12]. Two reactions that may be principally responsible for the initial production of carbon are

$$\text{CO} + \text{CO} (\alpha \Pi) \rightarrow \text{CO}_2 + \text{C}$$  \hspace{1cm} (3)

and

$$\text{CO} (\nu) + \text{CO} (\omega) \rightarrow \text{CO}_2 + \text{C}.$$  \hspace{1cm} (4)

Diatom carbon can be formed in subsequent reaction steps.

First, let us consider the case where laser I is on and laser II is off (hereafter referred to as case 1). Laser I is assumed to be focused to an area of $10^{-3}$ cm$^2$, which is a lower bound according to an estimate for the actual experimental conditions. The cell gases were initially at room temperature prior to interaction. However, the translational mode temperature in the focal volume can rise due to heating by VT and VVT relaxation processes. This temperature rise can be computed as done by Schmalzl and Capitelli [14]. However, since the irradiated volume is not known, we treat the translational temperature and focal area parametrically. Calculations were made at 300, 500, 750 and 850 K. Figs. 6–8 show the calculated amplitude of the excited A $\Pi$ electronic state population versus time for 500, 750 and 850 K. It can be noted that the amplitude modulation in the A $\Pi$ population (defined as maximum number density divided by minimum number density, at periodic state) increases from $\approx 2$ at 300 K to $\approx 70$ at 850 K. This strong dependence of the modulation of the A $\Pi$ population will be discussed in detail in section 5.

In the second case, the translational temperature is fixed at 850 K, laser II is on at 2 W average power,
and the focal area of laser II is $10^{-2}$ cm$^2$. The resulting time variation of the total A'II population for this case, is shown in fig. 9. As can be seen, the modulation for this case is approximately 39.

Finally, for case 3 where the translational temperature is 850 K, and laser II is on at 2 W with a focal area of $10^{-3}$ cm$^2$, the A'II modulation is approximately 5. This is shown in fig. 10.

The three cases just described show the effects of varying translational temperature and focal area of laser II. Additionally, the time variation of the laser I line shape was also changed to the shape corresponding to the $v=3\rightarrow2$ band (in the abovementioned three cases, the time variation of the $v=1\rightarrow0$ band was used as the temporal variation of laser I). The result at a translational temperature of 850 K was that the A'II population pulses were slightly wider, and followed the decay side of the chosen $v=3\rightarrow2$ band more closely. This was found to be different at lower translational temperatures, where the laser pulse shape had no significant effect on the shape of the temporal variation of the A'II population.

Fig. 9. The total A'II population versus time for a translational temperature of 850 K. This is case 2, with laser I on and laser II on at 2 W with a focal area of $10^{-2}$ cm$^2$.

Fig. 10. The total A'II population versus time for a translational temperature of 850 K. This is case 3, with laser I on and laser II on at 2 W with a focal area of $10^{-3}$ cm$^2$.

5. Summary and conclusions

Several important facts regarding the experiment described in section 2 may be noted and highlighted:

(1) When only the Q-switched laser (laser I) is on, the observed fluorescence signal indicates a rapid rise and rapid fall with characteristic times less than 0.1 ms. Moreover, the modulation of the observed signal indicates that the population of the radiating species must vary by at least an order of magnitude over the period of the Q-switching time. The rapid rise and decay times (less than 0.1 ms) serve to eliminate the possibility of C$\,$ Swan emission via the reaction given by eq. (4), since this reaction has a characteristic time longer than 0.1 ms. However, the reaction given by eq. (3) and the 4th positive A'II $\rightarrow$ X $^3\Sigma^+$ radiative emission have characteristic times small enough to produce the observed response. The reaction rate constants for computation of these characteristic times is discussed by several authors [15–18]. It is difficult for this case, to account for such a strongly modulated signal based on chemiluminescent reaction alone. The 4th positive A'II $\rightarrow$ X $^3\Sigma^+$ radiative transition (10 ns lifetime) appears to be the only source that can provide a short enough response time together with high modulation, consistent with the observed signal.

(2) Both laser I and laser II were focused onto the absorption cell containing the non-flowing CO/Ar gas mixture. Our estimates indicate that the local translational temperature in the irradiated volume (from
which the fluorescence was observed) is significantly above room temperature.

(3) The photomultiplier signal time variation bears close resemblance to the $\nu = 1 \rightarrow 0$ band of laser I, when only laser I is on. However, this signal time variation is broader when laser II (operating on the wider $\nu = 3 \rightarrow 2$ bands and higher) is turned on at 2 W. The signal shape then broadens and more closely resembles the $\nu = 3 \rightarrow 2$ band of laser I, at least on the decay side.

(4) The magnitude of the fluorescence signal increases with increasing power on laser II.

The experiment described in section 2 has been modelled. Some quantities required for this simulation that were unavailable (such as translational temperature and laser focal areas) have been varied parametrically. Of these, the translational temperature governing the VV and VT exchange rates, has been identified as the key parameter. By varying the translational temperature, it has been shown that the amplitude of the total $A \ ^3\Pi$ population may be modulated by at least an order of magnitude. By contrast, the modulation of the $X \ ^1\Sigma^+ (\nu = 20)$ level is only about 3 at a translational temperature of 850 K. Such a time variation of the $A \ ^3\Pi$ population with fourth positive emission from $A \ ^3\Pi \rightarrow X \ ^1\Sigma^+$ accounts for the photomultiplier signal observed in the experiment. With the second laser on, however, some of the fluorescence may be due to emission from C$_2$ Swan bands resulting from chemical reactions [2]. The $C_2$ emission, which is expected to be related to the production of CO($a \ ^3\Pi$) (resonant with $X \ ^1\Sigma^+ (\nu = 27)$) cannot by itself explain the large modulation of the observed fluorescence. The modulation of the $X \ ^1\Sigma^+ (\nu = 27)$ population is not very different from the modulation of the $X \ ^1\Sigma^+ (\nu = 20)$ population. The $X \ ^1\Sigma^+ (\nu = 20)$ populations are displayed in figs. 11–13, for the three cases described in section 4. Since the chemistry was not accounted for in our model, no estimate could be made of the fraction of the fluorescence signal emanating from the C$_2$ Swan bands.

Several conclusions may be drawn from the modelling calculations of the experiment:

(1) From the results of case 1, the translational temperature in the irradiated volume of the absorption cell had to be at least 750 K. This conclusion is also consistent with the work of Rich and Bergman [4], who measured the translational temperature in their experiment to be 370 K. Their measured $A \ ^3\Pi$ signal had a rise time of the order of 1 ms, in contrast to the less than 0.1 ms rise time in our experiment. This is due to the lower translational temperature and hence slower VV rates in the experiment of Rich and Bergman [4].

(2) The fluorescence signal cannot be explained by chemistry alone. C$_2$ Swan band emission alone can-
not account for the large amplitude modulation of the signal in case 1, since chemistry producing C$_2$ would require the X $^1\Sigma^+ (v=27)$ level to be highly modulated, which it is not. This signal must then be mainly from the 4th positive A $^1\Pi \rightarrow X$ $^1\Sigma^+$ emission for case 1. This 4th positive A $^1\Pi \rightarrow X$ $^1\Sigma^+$ emission must also be partially responsible for the observed signals when laser II is on (i.e. cases 2 and 3).

(3) As can be seen from the three cases considered in this paper, the peak value of the total A $^1\Pi$ population increases when laser II is turned on. This is consistent with the results of our experiment, which show increasing magnitude of the fluorescence signal with increasing average power on laser II.

(4) From the results of case 2 and case 3, the modulation is seen to decrease when laser II is turned on. However, the experimental results show that when laser II is on at 2 W, the photomultiplier signal is still well modulated. This discrepancy may be explained by the fact that the translational temperature may be higher than 850 K when the second laser is turned on. This decreasing modulation with increasing power from laser II seen in the simulation may, however, partially explain the experimental result when the power on laser II is increased to 5 W. There are three principal effects as the power from laser II is increased from 0. First, the translational temperature increase so that both VV and VT rates increase. This would tend to increase the modulation of the total A $^1\Pi$ population. Second, chemistry leading to production of C$_2$ would be enhanced. Consequently, the total emission would consist of both A $^1\Pi \rightarrow X$ $^1\Sigma^+$ 4th positive emission as well as C$_2$ Swan emission. Since the C$_2$ Swan emission would have a longer decay time compared to the 4th positive emission, the total photomultiplier signal would appear less modulated and more intense. Without accounting for chemistry, it is difficult to resolve this simulation with experiment for the cases when the second laser is on at 2 and 5 W. Third, as was mentioned in section 4, increasing the average power on laser II causes the resulting A $^1\Pi$ populations as well as the higher vibrational X $^1\Sigma^+$ levels to have wider pulse shapes. In other words, the upper populations start to assume the temporal shapes of the $v=3 \rightarrow 2$ and higher band components.

This paper cannot be concluded without some mention of the rate expressions (VV, VT, and VE) used in the modelling calculations, as well as the sensitivity of the final results to these rate expressions. At pressures of interest here, the CO–Ar VT rates are not as relevant as the VE coupling between the X $^1\Sigma^+$ and A $^1\Pi$ states in limiting the extent of VV up-pumping. The VE and VV rates are most important for the situation under consideration here. We will discuss each separately.

The VE rate used in our modeling calculations contains one adjustable parameter [11]. The value of this parameter has been chosen to be such as to give a VE rate that is $10^{-4}$ of the gas kinetic collision frequency. This value was found to give satisfactory agreement between simulation and experiment in parametric variation studies conducted by DeLeon and Rich [12]. It must be pointed out here that while the low-lying vibrational levels of the X $^1\Sigma^+$ state are not very sensitive to this parameter, the higher vibrational levels near the overlap region of the X $^1\Sigma^+$ and A $^1\Pi$ are. Consequently, the relative populations of individual A $^1\Pi$ vibrational levels are sensitive to this parameter in the VE rate expression.

The VV rate used in the calculations of section 3 consist of long-range and short-range contributions. Each of these contains one adjustable parameter. These parameters have been selected to give rates in agreement with measured VV data over the range of vibrational levels $1 \leq v \leq 35$ [11,12]. The VV up-pumping is clearly influenced by these parameters,
which can therefore influence the characteristic time for the ultimate transfer of the irradiating laser energy to the A \(^1\Pi\) state.

The approach taken in the modelling calculations in this paper has been to fix the adjustable parameters in the rate expressions used (based of course on agreement with existing experimental state-resolved information), and to investigate instead the strong dependence of the VV rate on the translational temperature. This arises from the fact that the low-lying vibrational levels have larger resonance defects so that the short-range part of the VV rate is dominant. This short-range part resembles the VT rate, and is hence strongly temperature dependent. Thus, although our calculations may not predict the correct relative populations of the individual A \(^1\Pi\) vibrational levels, they are capable of modelling the modulation of the A \(^1\Pi\) populations with the correct response times as observed in the experiment.

Summarizing, it has been shown in the experiment and in the simulation results presented in this paper, that it is possible to excite CO up to high vibrational quantum numbers (\(v \geq 40\)) by CO laser irradiation at the fundamental \(v = 1 \rightarrow 0\) band component. An argument for the fluorescence being due to the 4th positive A \(^1\Pi\) \(\rightarrow X \, ^1\Sigma^+\) emission, has been given. This argument is based on a comparison of signal rise and decay times with characteristic times for chemical reaction, and the amplitude modulation of the observed signal. Finally, while it has been demonstrated that the 4th positive emission can explain the experimental results, we note that when the cw laser (laser II) is turned on, emission from the \(C_2\) Swan bands may also contribute to the observed fluorescence signal.

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