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APPENDIX D

ENERGY TRANSFER AND ISOTOPIC ENRICHMENT IN VIBRATIONALLY PUMPED DIATOMIC MOLECULES

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ENERGY TRANSFER AND ISOTOPIC ENRICHMENT IN VIBRATIONALLY PUMPED DIATOMIC MOLECULES

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Abstract

The preliminary results from two experiments on vibration-vibration pumped CO are reported. The first experiment is a demonstration of isotopic enrichment by vibration-vibration pumping. An ~300°K translational temperature flowing mixture of CO, Ar and He is excited by a CO laser and the resulting non-equilibrium vibrational distribution is probed by laser induced fluorescence. In CO plus Ar mixtures, ^{13}CO enrichments of a factor of three times the natural ^{12}CO abundance are observed for high, v ≈ 30, vibrational states. In CO plus Ar and He mixtures the ^{13}CO enrichment is reduced to approximately its natural abundance. Calculations indicate that larger He mole fractions could result in relative enrichment of the ^{12}CO isotope. The second experiment is a time and state resolved kinetics study of vibration-vibration pumped CO. A pulsed CO laser is used to produce a highly excited vibrational distribution. The vibrationally resolved overtone emission from the ground electronic state is monitored as a function of time for states v = 2 to 40. Electronic emission from the A-X band is also observed. In order to derive the kinetic rates for the various vibrational exchange processes, the data are compared with a kinetic model including all of the energy exchange terms. Preliminary calculations show reasonable agreement with the observed ground electronic state emission.

Introduction

Two experiments on vibration-vibration (V-V) pumped CO are described and compared with model calculations. The first experiment shows the effect of helium addition to control vibrational population distributions in V-V pumped CO. These data are useful in isotope separation schemes. The second experiment is a kinetics study of vibrational exchange in V-V pumped CO. Understanding of the detailed rates of energy exchange between vibrational, translational and electronic modes is important in designing isotope enrichment models and energy transfer lasers.

Isotope Enrichment

Experimental

A flowing mixture of CO + Ar + He is excited by a CW supersonic CO laser which oscillates on a number of $\Delta v = 1$ transitions[1]. The flow rate is such that the gas translational temperature remains approximately at room temperature[2]. The CO laser energy is absorbed by the CO molecules which subsequently vibration-vibration pump[3] into a highly excited non-equilibrium distribution. Vibrational populations in such distributions have been previously characterized by IR emission spectra fit to computer generated synthetic spectra[4].

In the present investigation only the relative populations of ^{13}CO and ^{12}CO vibrational states are desired. These were obtained by careful comparison of ^{13}CO and ^{12}CO laser induced fluorescence (LIF) signal intensities[2]. Two different LIF signals were used. The $A^1\Pi - X^1\Sigma^+, v' = 14 \rightarrow v'' = 25$ transition was excited by a frequency doubled Molectron dye laser and the LIF spectrum was observed. This measurement provided a probe of the population of the X state v" = 25 level. Similar LIF on the newly discovered $D'\ ^1\Sigma^+ - X^1\Sigma^+, v' = 1 \rightarrow v'' = 30$ spectrum[5] was used to probe the population of the v" = 30 level. In the mixtures containing He the v" = 30 LIF signal intensity was very low; therefore a 10% enriched ^{13}CO mixture was used for this data point.

Calculations

The analytical theory of Gordiets and Mamedov[6], which models the vibrational populations, has been extended to include the effects of an inert gas diluent[2]. Calculations using this model have been made and are shown by the solid curves in figures 1 and 2. Note the general features of each distribution: the rapidly falling low vibrational region, the plateau region and the rapidly falling region at extremely high vibrational levels.

The theoretical curves show the distribution of each isotope for the current experimental conditions. Since each curve is normalized to the total number density of a particular isotopic species, the curves for ^{12}CO and ^{13}CO would be identical if the ^{13}CO vibrational distribution was equal to that of ^{12}CO. We define an isotopic enrichment factor for the vibrational state v:

$$\beta_v = \frac{\text{Population } v^{th} \text{ state in } ^{13}CO}{\text{Population } v^{th} \text{ state in } ^{12}CO \times \text{natural } ^{13}CO \text{ abundance}}$$

$\beta_v = 1$ at the natural abundance ratio. For $\beta_v > 1$ the ^{13}CO curve lies above that of ^{12}CO.

Results

Figure 1 shows that, for a dilute mixture of CO in Ar, the ^{13}CO curve lies above the ^{12}CO curve for all but the few lowest vibrational states. The predicted enrichment is about $\beta \sim 3$ in the plateau region. The experimental observations, both in figures 1 and 2, are all relative to the ^{12}CO in Ar v = 25 and v = 30 points. These points were placed on the ^{12}CO curve and the ^{13}CO results can be compared to the $\beta \sim 3$ predicted by the theory. The results of the present investigation, in figure 1, fit very well, in confirmation of reference 2. An additional study has been made at the Laboratoire d'Infrarouge University de Paris-Sud[7] in which β_n values similar to the present results are observed.

In figure 2 a profound change in the distributions is observed upon the addition of He to the CO and Ar mixture. Since helium is a much faster vibration-translation relaxer, the vibrational distributions decrease rapidly at much lower values of v. The ^{12}CO and ^{13}CO curves are predicted to cross in the vicinity of v~30. The v = 25 data for both ^{12}CO and ^{13}CO fall reasonably on the theoretical curves. The v = 30 data show the expected large decrease in LIF signal intensity with the ^{13}CO enrichment reduced to $\beta_{30} \sim 1$. The experimental error is such that is is not possible to state with confidence whether the curves have crossed or not.

The basic concept of isotope enrichment by vibration-vibration pumping has been demonstrated. The addition of He to control the vibrational distribution and the isotopic enrichment factors has been shown. If the He addition can be used to preferentially enrich the lighter isotope, this could allow for the separation of the middle isotope, $C^{17}O$, from a mixture of $C^{16}O$, $C^{17}O$ and $C^{18}O$. The idea is to add just enough helium to reduce the distribution of the heaviest isotope, $C^{18}O$, while maintaining the enrichment for the middle isotope, $C^{17}O$, above that of the light isotope, $C^{16}O$.

Time and State Resolved Kinetics

Experimental

The experimental procedure was similar to that described in the preceding section. However, the supersonic CO laser was 100% amplitude modulated by a triode device. Rise and fall times of ~100 μseconds were obtained with a variable pulse length. The CO laser vibrationally excited a flowing mixture of CO and Ar maintained at room translational temperature. The resulting V-V pumped distribution produced when the laser is on is similar to those previously described but the time dependence of the rise and decay of the vibrational populations can be studied. The populations are monitored by the IR overtone emission. The IR emission was partially resolved by a monochromator[4], detected and computer signal averaged. Due to the overlap of adjacent P and R branches, the observed signal from the state v contains contributions from adjacent states v ± 1 as well.

UV emission from the $A^1\Pi - X^1\Sigma^+$ band system was observed in an analogous manner. Emission from the C_2 Swan bands produced by the dissociation of a small fraction of the CO was also observed[8]. Analysis of the electronic and C_2 data is preliminary and will not be discussed here.

Results

Figure 3 shows a typical experimental IR emission curve for v = 11. Data ranging from v = 2 to v = 40 were obtained. At t = 0 the laser was turned on and after a short delay the v = 11 population increased up to its steady state value. At the time indicated, the laser was turned off and the decay of the v = 11 population was monitored.

Also shown in figure 3 is a curve calculated from a kinetic rate model[9]. The model expresses the time dependent population in terms of the rates: vibration-vibration, vibration-translation, vibration-electronic, stimulated emission and absorption. Model rate parameters are obtained from the low, v $\leq$ 16, vibration-vibration exchange data of Hancock and Smith[10]. Vibration-translation data for Ar + CO are from reference 4. No adjustment of these rates was made to produce the calculated curve in figure 3. The steady state value of the calculation was normalized to the observed intensity. The v = 11 calculation agrees reasonably well with the experimental results.

It is expected that the low v rates should fit well since the V-V rate data are taken from low vibrational states. Figure 4 shows the time for the population to decay to 1/e of its steady state value for a series of vibrational levels. The lower levels are fit better than the v $>$ 20 levels, where the calculated rates are too slow. The vibration-vibration exchange rates are faster than gas kinetic for the high vibrational states. A similar trend is seen in the delay times. The v = 11 calculation is close but the high v delay times are too slow.

These time resolved data should provide enough information to obtain V-V, V-T and possibly V-E rates among the very high CO states up to v ~ 40. Further experiments and calculations are in progress.

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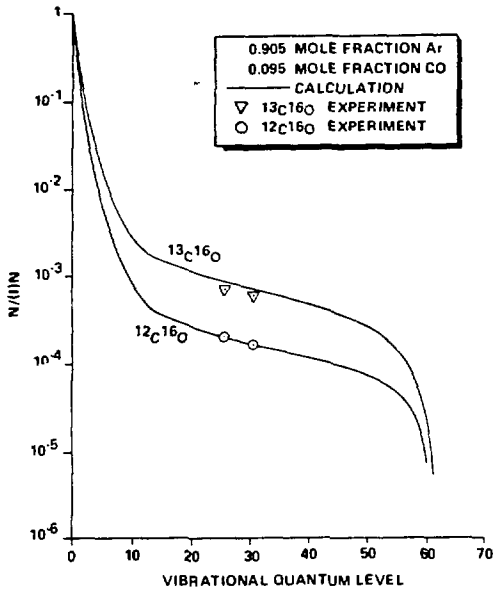

Figure 1 VIBRATIONAL DISTRIBUTION IN CO + ARGON

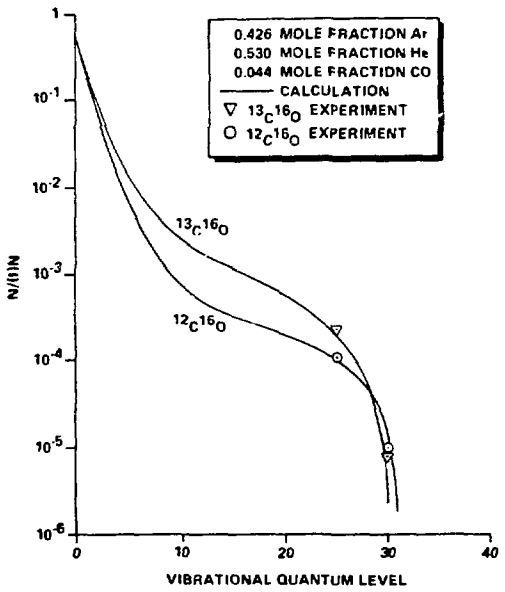

Figure 2 VIBRATIONAL DISTRIBUTION IN CO + ARGON + HELIUM

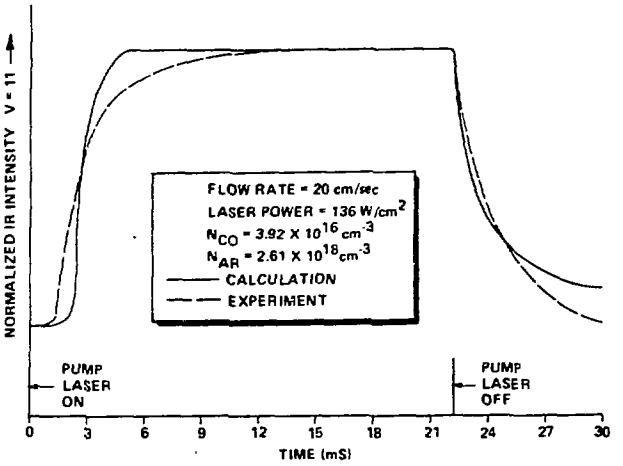

Figure 3 V=11 EXPERIMENTAL DATA AND CALCULATION

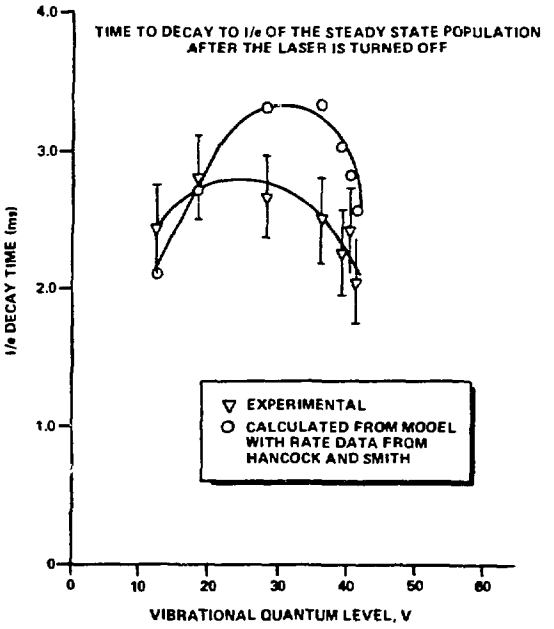

Figure 4 VIBRATIONAL STATE DECAY TIMES