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VIBRATIONAL ENERGY TRANSFER KINETICS IN MOLECULAR DISEQUILIBRIUM

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1. INTRODUCTION

The present program is an experimental study of the chemical kinetics of gaseous molecular systems under conditions of extreme disequilibrium of the vibrational energy modes. A continuous wave carbon monoxide laser is used to excite the vibrational mode of carbon monoxide in mixtures of CO and various additive gases flowing through an absorption cell. High steady-state excitation of the CO vibrational mode (0.3 eV/molecule) is achieved, while a translational-rotational temperature near 300°K is maintained by the steady flow of cold gas into the cell.

The nonequilibrium conditions created in the cell result in the substantial population of very high lying vibrational quantum states (to $V = 42$) of CO; these states have energies up to 8 eV, which is 75% of the CO dissociation energy. This pumping of high vibrational quantum states is the result of rapid redistribution of vibrational energy during molecular collisions (the so-called vibration-vibration, or "V-V" pumping mechanism). Recent research has shown that this V-V pumping mechanism can be a rate-determining influence in a variety of important kinetic situations. Examples are the high power laser excitation of CH_3F , and possibly other polyatomics; separation of light isotopes such as N^{15} and C^{13} in glow discharges and by laser pumping; the $\text{H}_2\text{-D}_2$ metathesis reactions leading to HD formation; and the production of population inversions in the CO infrared laser and in certain vibrational energy transfer lasers involving the asymmetric stretch mode and combination bands of triatomic molecules. The present experimental approach affords a unique opportunity to examine this mechanism over a large range of gas pressures and mixtures, in a steady-state environment free from electric discharge effects.

Initial experiments with this approach have demonstrated excitation of CO resulting in formation of C_2 vapor enriched in ^{13}C ; in a separate series of experiments, excitation of CO/ N_2 mixtures has resulted in cyanogen, $(\text{CN})_2$, synthesis. These results are true laser-induced chemistry; vibrational excitation and subsequent reaction proceeds in an environment very near room kinetic temperature. This work has recently been published, and will not be reviewed in detail here.

The present D.O.E. program has been underway for six months. The first year's effort is concentrating on the details of the kinetics of the observed C_2 formation and C^{13} isotope enrichment resulting from the extreme V-V pumping of CO. A summary report of the work-to-date is given in the following sections.

2. EXPERIMENTAL SETUP

In the present experiments, a cw supersonic-flow carbon monoxide laser is used to pump optically a flowing mixture of CO and other gases. The experimental apparatus is shown schematically in Fig. 1. Test gases are flowing through the 25-cm-long absorption cell. Radiation from an electrically excited supersonic flow cw carbon monoxide laser is admitted along the axis of the cell through a calcium fluoride window; the beam diameter nearly fills the 0.95-cm cell diameter. The degree of absorption of the laser beam by the gases is determined by measuring the power incident upon and transmitted through the cell using thermopiles. The cell is equipped with calcium fluoride windows along its length to permit spectroscopic monitoring of carbon monoxide vibrational excitation and other fluorescence from excited species.

The pump laser radiation is absorbed by the lower vibrational states of the carbon monoxide in the cell. Vibration-to-vibration (V-V) energy exchange quickly populates the upper vibrational states of the CO. The temperature of the translational and rotational modes of the pumped gases is maintained at a low value in steady state by the flow through the cell. By this means, a higher vibrational energy per CO molecule is achieved in the cell than is typical of the pumping achieved directly in electrically or chemically excited CO lasers. In addition, kinetic processes involving such strongly V-V pumped molecules can be studied in an environment free of electric discharge effects, and over ranges of gas concentrations incompatible with glow discharge operation.

The first experiments with this technique were performed in mixtures of CO and Ar, at relatively high gas pressures in the cell, specifically a CO partial pressure of 0.018 atm and an argon diluent pressure of 28.2 atm.

The large preponderance of argon diluent was used to provide a high degree of convective cooling of the test gases and to pressure-broaden the CO absorption lines, in an effort to maximize the fraction of pump laser energy absorbed. It was found that a V-V pumped distribution could be created and maintained in the steady-state over the first thirty vibrational levels of CO, with this technique. More recent work has centered on pumping at somewhat higher pump-laser intensities and at lower cell pressures in the range of 40 to 800 torr. It has been found that, under certain conditions of flow velocity and gas concentrations, as much as 70% of the pump laser beam can be absorbed, and CO vibrational level populations can be measured at energies within 75% of the dissociation energy.

3. MASS SPECTROMETRY

In order to monitor reactant and product concentrations along the length of the reaction cell, a small monopole mass spectrometer (Veeco Instruments Model SP1-10 Residual Gas Analyzer) has been installed for on-line use with the experiment. The instrument has a one amu resolution in the 1-50 amu range; mass ranges from 1-200 amu can also be scanned with reduced resolution.

Samples can be taken at stations along the length of the cell, and also from a station in the discharge port downstream of the cell, out of the laser beam. The sampling line leading to the mass spectrometer is fitted with an automatically controlled valve, which maintains a preset constant pressure in the monopole tube during changes in the operating pressure of the reaction cell. Response to changes in operating conditions of the reaction cell is ~ 1 sec, thereby permitting real-time investigation of the influence of operating parameters such as laser power, reactant concentrations, flow velocity, etc.

Mass spectra are presently being obtained for laser excitation of both CO/Ar and CO/NO/Ar mixtures. Table 1 summarizes some of the recent CO/Ar results. It has been previously observed that the optically-pumped CO in the

CO/Ar mixture reacts to form vapor-phase C_2 molecules. Substantial carbon is precipitated on the cell walls during this process. To determine the details of the kinetic mechanism of the C_2 formation, the mass spectrometer was used to investigate the O-atom containing species produced in the reaction. It was found that CO_2 was the principal oxygen-containing compound formed in the reaction; in addition, a slight amount of O_2 production was observed in some runs. No other stable oxygen-containing product was observed. Data for two runs, at different cell pressures, are shown in the table. It will be observed that, at these pressures, two to four percent of the CO is consumed; as cell pressure decreases, a larger fraction of CO reacts. The use of these results in developing a kinetic model for the laser-induced reaction is discussed in Section 5 of this summary report.

Figure 2 and Table 2 show some preliminary results for the optical pumping of CO/NO/Ar mixtures to produce cyanogen, $(CN)_2$. The figure shows a section of the mass spectrum of a sample taken from the discharge of the reaction cell. The large peak on the left is CO_2 , 44 amu. The circled peak is $(CN)_2$ at 52 amu; its intensity depends on laser power, and the peak vanishes entirely when the pump laser is off. Table 2 gives the cell/laser operating conditions for the spectrum of Fig. 2.

4. VISIBLE AND U.V. CELL SIDELIGHT EMISSION

To obtain quantitative measurements of the cell sidelight emission, during optical pumping of CO/Ar mixtures, the experiment is set up as sketched in Fig. 1. A 3/4 meter focal length spectrometer equipped with a 500 nm blaze grating and photomultiplier is used to record the visible and UV emission. An absolute calibration of this instrument is obtained by scanning a calibrated tungsten filament lamp. Using this calibration and the sidelight emission, populations of the emitting states can be calculated. In addition, the infrared first overtone emission from the CO vibrational states is monitored by a 1/4 meter focal length instrument. Through the appropriate choice of mirrors the infrared instrument is calibrated relatively by a blackbody source.

In cell gas mixtures of CO and Ar, the strongest visible emission typically observed is from the C₂ Swan System $A^3\Pi_g - X^3\Pi_u$. Of these bands the transitions with the least amount of overlap occur in the $\Delta v = 0, +1$, and $+2$ sequences. One such sequence, the $\Delta v = 0$, is shown in Fig. 3. The transitions chosen for analysis and their calculated number densities are listed in Table 3 along with the cell conditions. The average populations listed would suggest that a vibrational population inversion exists in the $A^3\Pi_g$ electronic state. However, it is thought that with greater care exercised, such as the use of an optical filter to remove second order radiation effects, the state populations will decrease at higher vibrational levels.

Besides the C₂ Swan Band emission, there is weaker emission from the C₂ Deslandres-D'Azambuja system, $c^1\Pi_g - b^1\Pi_u$, and from the CO Fourth Positive system, $A^1\Pi - X^1\Sigma$. Detection of the CO Fourth Positive was achieved by having the mirrors of the optical system coated with a high reflectance UV coating into the VUV. The excited state populations for these systems are not yet reduced; this work is presently in progress.

5. KINETIC MECHANISM OF C₂ FORMATION

At the beginning of the present program, the mechanism by which V-V pumped CO reacted to produce the observed vapor phase C₂ was not known. During the first six months of the present program, this mechanism has been clarified. These results are summarized in the present section.

Preliminary study of the experiment suggested two possible reactions leading to C₂ formation. The first possibility is direct dissociation of CO by collisional-induced multiquantum V-V exchange, i.e.:

This mechanism requires a quite small but finite probability for a multi-quantum V-V exchange, with one CO molecule making a transition to the dissociation continuum. Preliminary estimates suggest that probabilities as small as 10^{-6} per collision could yield a CO dissociation rate consistent with the observed C_2 yields.

The second possible mechanism involves the production of electronically excited CO (most likely, the low-lying $a^3\Pi$ metastable) as a reaction intermediate:

While the rate of internal conversion from vibrationally-excited ground state CO molecules to the $a^3\Pi$ state, Reaction (2a), is not known, the CO_2 production step, (2b), has been observed and is an important process in CO gas discharges.

With the aid of mass spectroscopic data obtained during this year's program, it has been determined that reaction mechanism (2a-c) is the dominant path. Almost no free oxygen production can be measured; almost all the oxygen in the reacted CO goes to CO_2 (see Section 3). This result is consistent with (2a-c). In addition, the observed strong fluorescence of the C_2 Swan bands during the reaction appears due to energy transfer from the $CO(a^3\Pi)$ state:

Such molecular electronic-to-electronic mode transfers can occur with high probability on collision, and these results further support the conclusion that mechanism (2a-c) is responsible for the C_2 formation.

Figure 1

EXPERIMENTAL APPARATUS

Figure 2 CYANOGEN MASS SPECTRUM

Figure 3 $\Delta V = 0$ SEQUENCE OF C₂ SWAN BANDS,

Table 1

Mass Spectroscopic Monitoring of CO/Ar Excitation (Pressures in Torr)

Cell Pressure	P_{CO}	P_{CO_2}		
		Station 1 (3 cm)	Station 2 (12 cm)	Station 3 (Exhaust)
850	4.76	0.0016	0.0040	0.0043
133	2.07	0.0016	0.0031	0.0031

Table 2

Mass Spectroscopic Monitoring of CO/NO/Ar Excitation.

Summary of Run Conditions.

Pressures in Torr.

Cell Pressure - 44

P_{CO} - 10.4

P_{NO} - 0.3

P_{Ar} - 33.3

Table 3

 C_2 Swan Band Excited State Populations

Sequence	Vibrational Transition	Number Density of Upper State N_v, cm^{-3}	Average N_v cm^{-3}
0	0-0	3.4×10^8	3.2×10^8
+1	0-1	3.0×10^8	
0	1-1	7.4×10^8	6.5×10^8
+1	1-2	5.5×10^8	
+1	2-3	2.8×10^8	2.8×10^8
+1	3-4	6.5×10^8	6.6×10^8
+2	3-5	6.7×10^8	

Cell Conditions: $P_{\text{TOT}} = 130 \text{ torr}$

0.8% CO , 99.2% Ar