

## ELECTRONIC-TO-VIBRATIONAL ENERGY TRANSFER BETWEEN MOLECULES

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(Received April 22, 1975)

### Summary

The overall efficiency of electronic-to-vibrational energy transfer has been studied in three systems,  $\text{CO}(d^3\Delta)_{v=7} + \text{CO}$ ,  $\text{CO}(d^3\Delta)_{v=7} + \text{N}_2$ , and  $\text{CO}(a^3\Pi)_{v=0} + \text{CO}$ . Relative to a previously measured efficiency for the  $\text{O}(^1\text{D}) + \text{CO}$  system of 40%, the new values are, respectively,  $(62 \pm 12)\%$ ,  $(96 \pm 27)\%$ , and  $(89 \pm 24)\%$ . Such high efficiencies probably preclude participation of a long-lived collision complex.

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### Introduction

The literature data on electronic-to-vibrational energy transfer processes are very sparse. The greatest amount of information concerns spin orbit relaxation of alkali metals, where the energy transferred is  $< 1$  eV [1]. A venerable body of literature also exists on quenching of  $\text{Hg}(^3\text{P}_{0,1,2})$ , where, in a few isolated instances, experiments were performed to evaluate the efficiency of the  $E \rightarrow V$  transfer processes with CO [2, 3] and NO [4]. Our own recent work [5] has extended the sphere of knowledge to some  $E-V$  processes involving  $\text{O}(^1\text{D})$ , to which Shortridge and Lin [6] have recently contributed.

The systems studied have, practically without exception, involved only atom-diatom collisions. This is to be expected, since one wishes to understand the simplest examples of a class of collisions before facing the complexities of larger systems. However, the work we have previously done [5] on the  $\text{O}(^1\text{D})-\text{CO}$  and  $\text{O}(^1\text{D})-\text{N}_2$  cases has been easy to extend to diatom-diatom systems, and we felt that a useful contribution can be made by measuring  $E-V$  transfer efficiencies arising in such interactions.

Recent calculations by Tully [7] on the  $\text{O}(^1\text{D})-\text{N}_2$  system have shown that excellent agreement with our results is obtained if it is hypothesized that the interaction takes place through an  $\text{N}_2\text{O}$  complex with a lifetime long enough that energy migration can occur. Application of RRKM theory

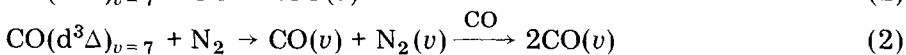
then leads to an absolute transfer efficiency in the neighborhood of 30%, whereas our experimental value is 33%. Attempts to model the interaction by a simple curve crossing picture have failed, giving reaction rates and  $E-V$  transfer efficiencies that are much too small [8, 9].

The study of  $E-V$  transfer reactions in systems of four or more atoms can be of considerable practical significance. For example, for all molecular laser transitions operating between electronic levels, it is important to know the consequences of quenching the radiating state. Lasing action will not be favored to lower levels that are being filled up through  $E-V$  transfer processes from the upper state. For such reasons, it is important to make a start in evaluating these processes.

## Experimental

The essence of the technique that we have previously employed to evaluate the  $O(^1D)-CO$  and  $O(^1D)-N_2$   $E-V$  transfer efficiencies is to measure the production rate of  $CO$  in the  $v = 1$  level. In the systems studied all vibrational energy, whether from higher levels of  $CO$  or from  $N_2$  vibrational levels, eventually funnels into the  $v = 1$  level of ground state  $CO$ . The  $v = 1$  concentration thus produced is measured by observing resonance fluorescence following the absorption of the  $CO A^1\Pi-X^1\Sigma^+$  (0-1) band, at 1597 Å, and signal calibration is accomplished by observing the signal from the  $v = 1$  population in room temperature  $CO$ .

In this work, we have investigated three reactions:



In reactions (1) and (2), the  $CO(d^3\Delta)$  state is generated with the same light source that was previously used to produce  $O(^1D)$  by  $O_2$  photodissociation, the Xe(1470 Å) resonance lamp [5]. The  $CO(a^3\Pi)$  state is produced in a manner pioneered by Harteck and coworkers [10], the absorption of radiation at 2062 Å from a microwave-powered iodine lamp.

The apparatus has been described in a previous paper [5], and consists of a 1 liter Pyrex reaction vessel through which gases flow at about 1 l/s. Orthogonally mounted on this cell, and viewing it through LiF windows, are the excitation source (the Xe or I lamp), the  $CO$  discharge lamp, and an EMR 542G-08-18 solar-blind photomultiplier. Opposite the Xe or I lamp is a photodiode, used to determine the relative lamp intensities. This was used principally to compare the Xe and I lamp fluxes, but also to measure  $CO$  absorption cross-sections at 1470 Å and 2062 Å. The photodiode wavelength response was known absolutely.

The 1470 Å and 2062 Å lamps were operated in a pulsed mode, at frequencies of 0.25 - 1 Hz, with equal on and off times. The time-dependent signal detected by the photomultiplier was the undispersed u.v. radiation

from the  $v = 0$  level of the CO  $A^1\Pi$  state, at wavelengths  $\geq 1544$  Å, following absorption of the  $A^1\Pi-X^1\Sigma^+$  (0-1) band from the CO lamp. Although the radiation itself has a lifetime of  $10^{-8}$  s, it follows the population of the  $v = 1$  level in the ground state. This level decays with a lifetime of 100 - 300 ms, much longer than the 33 ms radiative lifetime of the  $1 \rightarrow 0$  i.r. transition, as a consequence of i.r. resonance trapping at the CO pressures employed.

The photomultiplier signal is fed through an a.c. amplifier to a 100 channel PAR waveform eductor, and thence to a scope. Synchronization of the lamp cycle and the eductor sweep is accomplished through a pulse generator. Measurements are made immediately following the extinction of the lamp, *i.e.*, a decay curve is generated. Integration times of 2 - 5 min were used in these experiments. A typical decay curve is shown in Fig. 1.

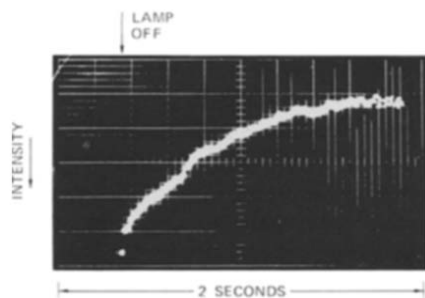


Fig. 1. CO( $v = 1$ ) decay curve, 2062 Å excitation [CO] = 9 Torr.

As we have discussed in previous papers [5, 11], the purity of the CO is critical to the experiment. An as-yet-unidentified material is present in most CO cylinders that both quenches vibrationally excited CO with very high efficiency, as first described by Millikan [12], and also destroys O( $^3P$ ) atoms. We have followed Millikan's solution to this problem, passing the Matheson UHP grade CO that we used through two copper traps at  $-78$  °C, one containing alumina chips, and the other copper wool. It was found that with the flow rates of CO that were employed, regeneration was needed at least once a week. This involved heating the traps with a torch while pumping on them. It was evident when regeneration was required, as the u.v. signal would vanish.

The Xe lamp was made in the standard manner, using 1 Torr pressure in a sealed tube equipped with a sapphire window, and containing a Ba-Al-Ni getter. The iodine lamp was also sealed, had a commercial quartz window, and contained a few crystals of  $I_2$  and 1 Torr of He. Heating or cooling the  $I_2$  reservoir or flowing the gas did not make a substantial difference to the output. This lamp is very intense compared with the rare gas resonance lamps, giving an output flux through the 1 in. quartz window of  $\sim 5 \times 10^{16}$  quanta/s at 2062 Å.

The CO lamp was a flowing lamp, equipped with a sapphire window, through which a 1% CO<sub>2</sub>-Ar mixture was pumped. In previous work, we suppressed the radiation terminating on the  $v'' = 0$  level because we wished to sample only the newly created  $v'' = 1$  molecules, not the  $v'' = 0$  molecules, which are  $3 \times 10^4$  times more numerous. However, this was found not to be a problem, for two reasons. At the relatively high CO pressures used, A-X( $v'' = 0$ ) bands are very strongly absorbed right at the CO lamp entrance window, and re-emission takes place out of view of the detector. Secondly, the  $v'' = 0$  population does not vary significantly with time, so that any scattering from  $v'' = 0$  molecules only adds to the d.c. background.

As before, pressures in the system were measured with Pace pressure transducers and with a 0 - 20 Torr Wallace and Tiernan gauge.

Both of the lamps and the photodiode were equipped with attenuation chambers in front of them through which various absorbing gases could be flowed, either to analyze the radiation or to eliminate unwanted radiation.

## Results

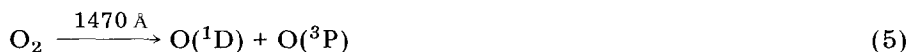
To be certain that the signal associated with the CO( $X^1\Sigma^+$ ) <sub>$v=1$</sub>  concentration is indeed a linear function of [CO( $v = 1$ )], it was necessary to determine the permissible working range of CO pressures. The resonance absorption cross-sections for the CO(A<sup>1</sup>Π ← X<sup>1</sup>Σ<sup>+</sup>) bands are so high that it is possible for the system to become optically thick even on the  $v'' = 1$  level. Figure 2 shows the behaviour of the CO( $v = 1$ )-associated signal as a function of [CO]. It peaks at 20 Torr, and it is clearly satisfactory to work at pressures as high as 10 Torr. The peak in the signal will occur at approximately the condition that  $\sigma_{CO} [CO]l = 1$ ,  $\sigma_{CO}$  being the absorption coefficient. The distance,  $l$ , from the CO lamp entrance window to the center of the viewing region was 7 cm, so that  $\sigma_{CO}$  is roughly  $2 \times 10^5 \text{ cm}^{-1} \text{ atm}^{-1}$  {bearing in mind that [CO( $v'' = 1$ )]/[CO( $v'' = 0$ )] =  $3.4 \times 10^{-5}$  at 300 K} for the A ← X (0-1) band. This is a very reasonable figure and indicates that the transient signal is entirely associated with the  $v'' = 1$  level, and not  $v'' = 0$ .

### CO( $d^3\Delta$ ) quenching by CO

For reaction (1), determination of the  $E-V$  transfer efficiency is made by comparison with the reaction:



for which we have measured an efficiency [5] of  $(40 \pm 8)\%$ . The experiment is carried out by determining the steady state intensity (from a transient decay experiment) associated with the newly produced CO( $v = 1$ ) made in reaction (1), then adding O<sub>2</sub>, which results in O(<sup>1</sup>D) production by reaction (5):



The increase in CO( $v = 1$ ) concentration, caused by participation of reaction

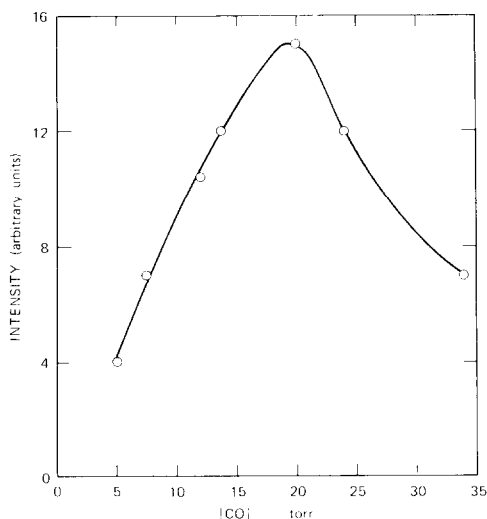


Fig. 2. Steady state intensity of signal from  $\text{CO}(v=1)$  as a function of  $[\text{CO}]$ , 1470 Å excitation.

(4), is then a measure of the efficiency of reaction (1) compared with reaction (4). Radiative losses of  $\text{CO}(d^3\Delta)$  are negligible compared with collisional losses at the CO pressures used. The  $\text{CO}(v=1)$  concentration generated by reaction (1) is given by:

$$[\text{CO}(v=1)]_{\text{CO}} \propto [\text{CO}] \cdot E_1 \cdot \epsilon_{\text{CO}} \cdot \sigma_{\text{CO}} \quad (\text{a})$$

where  $E_1$  is the desired  $E-V$  transfer efficiency,  $\epsilon_{\text{CO}}$  is the electronic energy of  $\text{CO}(d^3\Delta)_{v=7}$ , 8.43 eV, and  $\sigma_{\text{CO}}$  is the CO absorption cross-section at the Xe resonance line [13] at 300 K,  $0.18 \text{ cm}^{-1} \text{ atm}^{-1}$ . The additional  $\text{CO}(v=1)$  generated through reaction (4) is given by:

$$[\text{CO}(v=1)]_{\text{O}(^1\text{D})} \propto [\text{O}_2] \cdot E_4 \cdot \epsilon_{\text{O}(^1\text{D})} \cdot \sigma_{\text{O}_2} \quad (\text{b})$$

where  $E_4$  is the  $E-V$  transfer efficiency for reaction (4),  $\epsilon_{\text{O}(^1\text{D})}$  is the  $\text{O}(^1\text{D})$  electronic energy, 1.96 eV, and  $\sigma_{\text{O}_2}$  is the  $\text{O}_2$  absorption cross-section at 1470 Å and 300 K [14],  $320 \text{ cm}^{-1} \text{ atm}^{-1}$  (for the optically thin conditions of all the experiments).

The increase in ground state  $[\text{CO}(v=1)]$  on addition of  $\text{O}_2$  is proportional to the increase in steady state intensity, given by:

$$\frac{I}{I_0} = 1 + \frac{[\text{O}_2]}{[\text{CO}]} \cdot \frac{E_4}{E_1} \cdot \frac{\epsilon_{\text{O}(^1\text{D})}}{\epsilon_{\text{CO}}} \cdot \frac{\sigma_{\text{O}_2}}{\sigma_{\text{CO}}} \quad (\text{c})$$

In terms of the desired ratio,  $E_1/E_4$ , after substitution of the known quantities, the expression becomes:

$$\frac{E_1}{E_4} = \frac{[\text{O}_2]}{[\text{CO}]} \cdot \frac{410}{(I/I_0 - 1)} \quad (\text{d})$$

TABLE 1

Determination of  $E$ - $V$  transfer efficiency ratio for reaction (1)

[CO] (Torr)	[O <sub>2</sub> ](mTorr)	$I/I_0$	$E_1/E_4$
3	3.8	1.42	1.25
3	6	1.56	1.49
3	10	2.24	1.12
5	25	2.25	1.66
7	10	1.33	1.78
7	25	2.00	1.49
7	40	3.00	1.19
7	50	3.17	1.38
10	10	1.20	2.09
10	20	1.40	2.09
10	40	2.00	1.66
10	50	2.50	1.39
Average = $1.55 \pm 0.30$			

Table 1 gives a set of data taken at various [CO] and [O<sub>2</sub>], along with the observed  $I/I_0$ , and the derived quantity  $E_1/E_4$ . The signal decay time is invariant with [O<sub>2</sub>], for these small O<sub>2</sub> additions. The average transfer efficiency ratio, with the root-mean-square deviation, is  $1.55 \pm 0.30$ . The principal error source is the fact that the  $I_0$  signal (taken in the absence of O<sub>2</sub>) is not very large. In the previous work [5] on reaction (4) typical O<sub>2</sub> concentrations of 100 mTorr were used, leading to photon absorption rates higher by a factor of 12 than those obtained in the present experiment for [CO] = 10 Torr.

#### CO( $d^3\Delta$ ) quenching by N<sub>2</sub>

The study of reaction (2) is somewhat more difficult than reaction (1), because the addition of N<sub>2</sub> causes a decrease in the steady state CO( $v = 1$ ) concentration, as discussed in a previous paper [5]. In this case, we wished to add enough N<sub>2</sub> so that half of the CO( $d^3\Delta$ ) was deactivated by CO and half by N<sub>2</sub>. In earlier work [15] we determined a value of  $1.2 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for CO quenching of CO( $d^3\Delta_{v=7}$ ) and  $3.6 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for N<sub>2</sub> quenching. Thus, for equal quenching, it was necessary to use approximately three times more N<sub>2</sub> than CO. In this case, equation (c) is still valid, but instead of  $E_1$  we must substitute  $aE_1 + bE_2$ , while  $E_4$  becomes a weighted average for the  $E$ - $V$  transfer efficiency of reaction (4) compared with reaction (6):



The efficiency of reaction (6) has a value of  $(33 \pm 10)\%$ , while for reaction (4) it is  $(40 \pm 8)\%$ . Since three times as much N<sub>2</sub> as CO is used, the appropriate average value for  $E_4$  (av) is 35%. The factors  $a$  and  $b$  are equal to 0.53 and 0.47, respectively, since the [N<sub>2</sub>]/[CO] ratio used was slightly

different from the rate coefficient ratio for CO and N<sub>2</sub> quenching of CO(*d*<sup>3</sup>Δ<sub>*v*=7</sub>). We then find that the *E*-*V* transfer efficiency ratio for reaction (2) is given by:

$$\frac{E_2}{E_4(\text{av})} = \frac{[\text{O}_2]}{[\text{CO}]} \cdot \frac{880}{(I/I_0 - 1)} - 1.1 \frac{E_1}{E_4(\text{av})} \quad (\text{e})$$

Table 2 gives data for the case where *I*/*I*<sub>0</sub>, the increase in steady state concentration of CO(*v* = 1) on O<sub>2</sub> addition, is determined for N<sub>2</sub>-CO mixtures. For evaluation of equation (e), a value of 1.55 × (40/35) = 1.77 is used for *E*<sub>1</sub>/*E*<sub>4</sub>(av). Clearly, the additional reduction in signal is the cause of the large error limits. The data should probably only be used as an indication that the *E*-*V* transfer efficiency for reaction (2) is larger than for reaction (1).

TABLE 2

Determination of *E*-*V* transfer efficiency ratio for reaction (2)

[CO] (Torr)	[N <sub>2</sub> ] (Torr)	[O <sub>2</sub> ] (mTorr)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>E</i> <sub>2</sub> / <i>E</i> <sub>4</sub> (av)
3	9	7.5	1.37	3.91
3	9	10	1.55	3.29
3	9	12	1.78	2.49
5	15	20	1.67	3.23
5	15	22	2.00	1.86
7	21	30	2.00	1.77
Average: 2.75 ± 0.77				

### CO(*a*<sup>3</sup>Π) quenching by CO

Reaction (3) must be treated in a different manner, since generation of CO(*a*<sup>3</sup>Π) involves a different photon source, the 2062 Å I line. In this case, comparison of ground state CO(*v* = 1) production is made with reaction (1). The experiment consists of comparing the relative steady state intensities associated with the CO(*v* = 1) concentration (obtained in a transient experiment) produced by the Xe(1470 Å) and I(2062 Å) lamps, at equal CO pressures. In this instance the *E*-*V* transfer efficiency ratio for reaction (3), *E*<sub>3</sub>/*E*<sub>1</sub>, is given by:

$$\frac{E_3}{E_1} = \frac{I(2062)}{I(1470)} \cdot \frac{I_0(1470)}{I_0(2062)} \cdot \frac{\sigma(1470)}{\sigma(2062)} \cdot \frac{2062}{1470} \cdot \frac{T(2062)}{T(1470)} \quad (\text{f})$$

where *I*(2062)/*I*(1470) is the observed steady state intensity ratio associated with the newly produced CO(*v* = 1), *I*<sub>0</sub>(1470)/*I*<sub>0</sub>(2062) is the lamp intensity ratio, σ(1470)/σ(2062) is the CO absorption coefficient ratio, the ratio 2062/1470 is simply a measure of the different photon energies, and *T*(2062)/*T*(1470) refers to the ratio of window transmittances between the cell and the photodiode measuring the lamp intensities, found to be 1.5.

Figure 3 shows the CO(*v* = 1)-associated signal using the two lamps,

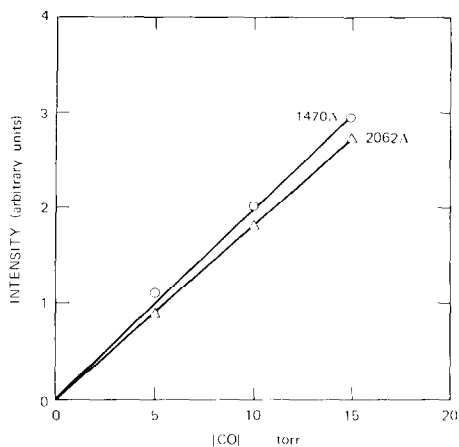


Fig. 3. Steady state intensities of signal from  $\text{CO}(v=1)$  with 1470 Å and 2062 Å lamps as a function of  $[\text{CO}]$ .

demonstrating that  $I(2062)/I(1470)$  has a value of 0.9. The ratio  $I_0(1470)/I_0(2062)$  has a value of 0.05, which includes a correction for the wavelength response of the photodiode, and also takes into account the fact that only a fraction of the light from the I lamp is 2062 Å radiation (however, only the 2062 Å radiation is absorbed by CO). The fraction was obtained by observing the attenuation of the lamp radiation as  $\text{NH}_3$  and  $\text{N}_2\text{O}$  were passed through the chamber between cell and photodiode. Knowing the 2062 Å absorption cross-section for these two gases [14], it was simple to demonstrate that  $40 \pm 4\%$  of the observed radiation was at 2062 Å (the photodiode was sensitive out to 3000 Å). The Xe(1470 Å) lamp was clean, showing  $> 95\%$  of the observed radiation at the resonance line.

Perhaps the biggest problem is to evaluate the ratio  $\sigma(1470)/\sigma(2062)$  in equation (f). The value of  $\sigma(1470)$  is well established as  $0.18 \text{ cm}^{-1} \text{ atm}^{-1}$ , but the value of  $\sigma(2062)$  is very small. A previous determination by Dunn *et al.* [16], carried out at the single CO pressure of 400 Torr, resulted in a coefficient of  $2.4 \times 10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$ . Since our work was done at much lower pressures, and Beer's absorption law certainly does not hold for absorption of the 2062 Å line by a  $\text{CO}(a^3\Pi \leftarrow X^1\Sigma^+)$  line, it was necessary to measure the coefficient. This was done by absorbing the 2062 Å line with CO added to the body of a 0.5 m monochromator ( $l = 101 \text{ cm}$ ). The data are shown in Fig. 4, and it may be seen that the initial slope corresponds to a coefficient of  $1.2 \times 10^{-2} \text{ cm}^{-1} \text{ atm}^{-1}$ , five times higher than the value obtained by Dunn *et al.* [16]. At higher pressures, the absorption strength decreases because of the decreasing overlap between the  $\text{CO}(a^3\Pi \leftarrow X^1\Sigma)$  lines and the residual 2062 Å line, so that at the highest pressures used, the apparent coefficient, based on a line drawn through the origin, is down to  $4 \times 10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$ .

Using the value of  $1.2 \times 10^{-2} \text{ cm}^{-1} \text{ atm}^{-1}$  for  $\sigma(2062)$ , we can evaluate equation (f), and thus  $E_3/E_1$  is found to have a value of 1.43.



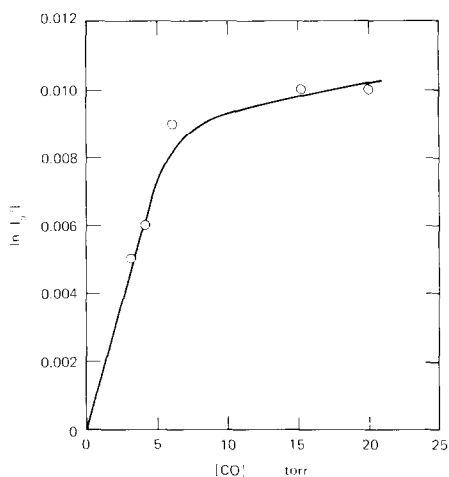


Fig. 4. 2062 Å attenuation by CO,  $l = 101$  cm.

Subjective error limits result in a value of  $1.43 \pm 0.30$ , but the overall error limits will be larger, since this reaction is only linked to reaction (4) through reaction (1).

## Discussion and Conclusions

Table 3 gives the  $E-V$  transfer efficiency ratios for the reactions studied, relative to the efficiency for reaction (4). The Table also includes absolute efficiencies, based on a value of 40% for reaction (4). The good agreement between theory and experiment for the  $E-V$  transfer efficiency for reaction (6), which is also evaluated experimentally relative to reaction (4), lends a degree of confidence to the very high absolute efficiencies given in Table 3. It should be kept in mind, however, that there are two other values for  $E_4$ . Shortridge and Lin [6] have recently published a value of 16%, based on laser absorption experiments, and Collins and Husain [17] have a value of approximately 12 - 15%, which can be extracted from their data when appropriate corrections are made. Donovan and Husain [18] made a measurement several years ago of  $E_3$ , finding a value of 20%, which is lower than our determination by a factor similar to that by which Collins and Husain's corrected value of  $E_4$  is lower than ours.

The complex formation model of Tully [1] seems to be quite successful in explaining the results of the  $O(^1D)-N_2$  interaction, and the same is probably true for  $O(^1D)-CO$  as well. However, if the complex lives long enough to equilibrate its internal energy, then the partitioning of the energy between the  $3N$  degrees of freedom will not permit as high a fraction of the energy as 0.62 - 0.96 to go into vibrational modes. It appears more likely that, if our numbers are correct, the interaction and transfer take place within no more than a few vibrations of a  $C_2O_2$  or  $CON_2$  intermediate, although it is admittedly surprising to find such efficient conversion of electronic to vibrational energy.

TABLE 3

*E*-*V* transfer efficiencies

	Ratio	Absolute efficiency (%)
$E_1/E_4$	$1.55 \pm 0.30$	Reaction (1) $62 \pm 12$
$E_2/E_4$	$2.41 \pm 0.67$	Reaction (2) $96 \pm 27$
$E_3/E_4$	$2.23 \pm 0.6$	Reaction (3) $89 \pm 24$

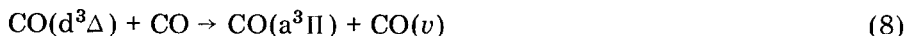
Ogryzlo and Thrush [19] have studied the *E*-*V* transfer reaction:



by NO i.r. emission, and although they did not make an absolute measure of transfer efficiencies, they did conclude that all NO(*v*) observed cascaded down from the *v* = 4 level (the level in closest resonance with the  $^1\Delta_g$  quantum). This may be taken as evidence that close to 100% of the electronic energy goes into NO vibration, although a bimodal distribution with a second peak at *v* = 0 is not excluded. Furthermore, the possibility of O<sub>2</sub> vibrational excitation also exists.

In the present study, one can probably conclude that the vibrational energy is shared roughly equally between the colliding molecules in each case. For example, if 89% of the CO( $\text{a}^3\Pi$ ) electronic energy is converted into vibrations in only one CO molecule, the average vibrational level excited is *v* = 23. The energy deficit for the process CO(*v* = 23) + CO(*v* = 0) → CO(*v* = 22) + CO(*v* = 1) is 575 cm<sup>-1</sup>. Although *V*-*V* exchanges for such high *V* have never been measured, an extrapolation of the data of Hancock and Smith [20], which go up to *v* = 12 ( $\Delta E = 287 \text{ cm}^{-1}$ ), indicates a rate coefficient of  $2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the 23 → 22 process. For a typical CO pressure of 5 Torr, this corresponds to a time constant of 30 ms. However, the radiative lifetime for the *v* = 23 → *v* = 22 + *hν* process is ~ 4 ms (extrapolated from *v* = 14 [20]), and energy lost by the system by radiation is not available to populate the *v* = 1 level. Only at *v* ~ 18 do the *V*-*V* exchange and the radiative loss become equal. It seems probable that most of the excitation is to levels below *v* = 18; if the energy transferred from CO( $\text{a}^3\Pi$ ) is equally shared by the two CO molecules, *v* = 11 is the mean level excited, which has a collisional relaxation time at 5 Torr CO of 0.15 ms.

One might consider the question of whether reaction (1) takes place in one step, or is in fact a combination of two processes:



Since the energy transferred into vibrations is very similar in reactions (1) and (3), ~ 5.3 eV, one would be led to conclude that the *E*-*V* transfer efficiency in reaction (8) was zero. This is unlikely, so that to the extent

that the ratio  $E_3/E_1$  that we have obtained is valid, there is support for saying that reaction (8) does not take place.

The present results indicate that in these molecule-molecule collisions, the fraction of energy transferred from electronic energy into vibrations is high, so that the initial vibrational distribution in the products will be peaked at high  $v$ . Thus, a population inversion will exist, which may be useful for i.r. lasing transitions, as well as for electronic transitions to low  $v$  (which maximizes the photon energy).

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